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PROCESS ANALYSIS AND MATERIAL BEHAVIOUR OF
THERMOPLASTIC ELASTOMERS THROUGHOUT THE
LASER SINTERING PROCESSING CHAIN

by

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Abstract

Laser sintering (LS), an additive manufacturing (AM) technology, allows for the production of 3-dimensional parts by fusing together successive layers of polymer powder without the need for tooling. Its potential and applicability, however, is still constrained due to the limited repertoire of materials available and the lack of detail in understanding both the important process-material interactions and consequently the requirements for the development of new materials. Past research has mainly focused on polyamide 12 (PA12) as the standard material, hence most of the empirically grown or theoretical, often idealized, process models are based on this polymer. As a result, it was shown that there are strong interactions between the material and the process leading to an undesired deviation of part properties. Thermoplastic elastomers (TPEs) for LS have gained more and more popularity for the production of, for example flexible parts in the recent past but they are a group of polymers that is neither well studied nor understood regarding their use in LS. Therefore, this PhD investigation has focused on TPEs in order to reveal their process specifics throughout the processing chain in LS.

As the properties of parts manufactured by LS are, amongst others, influenced by the packing and flow efficiencies of the powders, the bulk (static) and flow (dynamic) characteristics of the observed TPEs were examined on the powder scale as well as their effects on the process and parts. The resulting part properties were evaluated in terms of their tensile properties, surface roughness and density. In contrast to previous studies which have rarely taken into account the characteristics of the un-sintered particles, this work provided a novel approach quantifying and describing the interconnection between the powder characteristics as well as its performance and the part properties, thus providing valuable input on future material design.

As mentioned before, for typical semi-crystalline thermoplastics such as PA12, different idealized process models describing the Pre-Process specifics exist, but

they might not necessarily be applicable for thermoplastic elastomers with significantly different thermal characteristics. Consequently, the important interactions during processing of TPEs have been studied by high speed and high resolution thermography helping to indicate the most important material properties in combination with calorimetric analysis. The resulting understanding of crystallization and melting behaviour helped to derive a design of experiments revealing the possible range for the process management in terms of temperature control as well as energy input and the resulting part properties. Moreover, it is known that polymers used in LS change their intrinsic properties due to processing conditions that are close to the crystalline melting temperature. As a result, within this PhD investigation the ageing behaviour of TPEs was studied. Both the powder and the sintered parts were examined for chemical and physical ageing effects. The results showed that the materials observed could be used without refreshing throughout the applied ageing cycles, however, changes in the processing behaviour as well as in the parts' mechanical properties were evident. These changes were due to the differing ageing states of the LS-powder showing an increase in the particle size affecting the bulk materials packing density. In the literature, modifications in the rheological properties due to thermal loads during LS are already known on basis of PA12. It was shown that they tend to experience an increase in molecular weight with increasing processing cycles. In this work it was found that TPEs exhibit the exact opposite trend in a slight decrease of molecular weight likely to reduce the mechanical strength of tensile specimens.

By using novel process adapted methods in order to reveal vital interactions of TPE powders for LS, this thesis makes a significant contribution to an AM database. In addition, the comprehensive observation and applications of these methods over the whole processing chain helped expanding the understanding of important requirements for the development of new polymers for LS and builds a substantial basis for future work and quality assurance.

In loving memory of my father-in-law Romano Gaiera –
Without intending you showed me what strength and patience really mean.
We miss you!

***“Endurance is nobler than strength,
and patience than beauty”***

John Ruskin

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Presentations:

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10/2012	BMW “Doktorandenkolloquium” BMW “PhD-Colloquium”, Presentation of PhD Project	Requirements regarding new Laser Sintering Polymers and their potential Application within Automotive Manufacturing
07/2012	“ProMotion Dialogtag” Dialog Day between Universities and BMW PhD Students, Poster Presentation of PhD Project	Requirements regarding new Laser Sintering Polymers and their potential Application within Automotive Manufacturing

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List of Abbreviations

3D	Three Dimensional
AM	Additive Manufacturing
ASTM	American Society for Testing and Materials
b/l	Breadth to Length Ratio
C	Carbon
CAD	Computer Aided Design
CAGR	Compound Annual Growth Rate
CL	Chlorine
CONV	Convexity
CO ₂	Carbon Dioxide
DF	DuraForm [®] Flex
DIN	German Institute for Standardisation
DSC	Differential Scanning Calorimetry
E _A	Area Related Energy Density
EaB	Elongation at Break
EMR	Energy Melt Ratio
Eq	Equation
E _V	Volume Related Energy Density
F	Fluorine
FT-4	Freeman Powder Rheometer
FSC	Fast Scanning Calorimetry
GPC	Gel Permeation Chromatography
HT-GPC	High Temperature Gel Permeation Chromatography
H	Hydrogen
HR	Hausner Ratio
LS	Laser Sintering
MC	Moisture Content
MVR	Melt Volume Rate
N	Nitrogen
O	Oxygen
P	Power (Laser Power)
PA	Polyamide

PBF	Powder Bed Fusion
PE	Polyethylene
PP	Polypropylene
PSD	Particle Size Distribution
PU	Polyurethane
RPA	Revolution Powder Analyzer
S	Sulphur
SPHT	Sphericity
SYMM	Symmetry
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TGA-MS	Thermogravimetric Analysis coupled with a Mass Spectrometer
T _g	Glass Transition Temperature
T _m	Melting Point
TPE	Thermoplastic Elastomer
TPE-E	Thermoplastic Elastomer based on (Co-) Polyester
UTS	Ultimate Tensile Strength
V _c	Scan Count
V _s	Scan Spacing

List of Symbols and Units

°C	Degree Celsius
°	Degree
λ	Wavelength
%	Percent
μm	Micrometre
μs	Microseconds
cm	Centimetre
cm^2	Square centimetre
cm^3	Cubic centimetre
g	Gram
kg	Kilogram
Hz	Hertz
J	Joule
K	Kelvin
min	Minute
mm	Millimetre
mm^2	Square millimetre
mm^3	Cubic millimetre
nm	Nanometre
mm^2	Square millimetre
μm	Micrometre
N	Newton

Pa	Pascal
s	Second
W	Watts
®	Registered

1 Introduction

1.1 Context

The term Additive Manufacturing (AM) covers a variety of technologies used to build parts directly from a three-dimensional digital file. Powder Bed Fusion (PBF) is a category of AM using powders as the starting material that includes the specific technology known as laser sintering (LS) [1]. LS is currently one of the main additive processes for producing functional parts by fusing together successive layers of polymer powder [2]. The advantage of LS over other additive processes is that it doesn't require support material which allows for reduced efforts in unpacking of the parts and for a higher geometrical freedom [3]. It is of interest to industry as it does not require tooling and therefore enables manufacturers to offer parts with a high degree of design freedom compared to conventional manufacturing technologies such as injection moulding. This opens new opportunities towards an increased level of flexibility in adjusting the design of parts at an early stage of the product development cycle as well as the degree in personalization or individualization and reduces the high investments for tooling within luxury or one-off products. Furthermore, it is possible to combine many individual parts of an assembly into a single component helping to eliminate part numbers, inventory, assembly steps, labour and inspection [4]. However, since there are many different requirements for polymer consumer products, it is clear that the current repertoire of available polymers in LS is not sufficient. The most common polymers used in LS are semi-crystalline polymers typically polyamides (PA12 or PA11), polyamide-based compounds as well as some filled varieties and a small number of thermoplastic elastomers [5, 6]. Within industrial use, the performance of components, mainly built from PA12, is still limited concerning their near series properties. Thus the general aim of the investigation in this PhD research was to gain a deeper understanding of the requirements for new laser sintering polymers with the focus on thermoplastic elastomers (TPEs).

The work has been carried out collaboratively between BMW AG, Germany and the University of Nottingham, UK. Therefore, one aspect of the investigation

was on the applicability within industry when it came to the choice of materials and the specific outcome of the research findings. In particular the aim was to understand the complex nature of powders used in LS, strongly dependent on its manufacturing method, the interactions of the polymer during all relevant processing stages as well as the resulting part properties and efficiency of the materials observed in terms of reuse. These processing stages can be divided into the following sub-processes: *Pre-Process*, taking into account the important powder interactions and its analysis; *In-Process*, observing the interactions between process and polymer (packing, exposure, melting etc.) and the *Post-Process* in which the mechanical properties and effects of thermal loads on the polymer's potential degradation are determined. In carrying out systematic experiments that aligned to this LS processing chain, the qualification of suitable process adapted analysis methods and their values allowing for quantification of material properties was targeted. An additional outcome was given by proving the scientific validity and transfer of practical analysis methods essential for industry in terms of quality assurance.

Processing of TPEs by LS, in particular, the effects of powder bulk and flow behaviour of LS polymers on resulting part properties is not widely reported and no empirical database exists. Therefore, this PhD aims to reveal and elucidate some of the complex relations between polymer properties, processing conditions and the resulting part properties as well as the reuse of the TPEs throughout the single processing steps. Thus it is helping to indicate the scientific challenges and the important interactions for a material that is not well studied, ultimately contributing to a substantial LS database and potentially serving as input for simulations.

1.2 Methodology and Thesis Structure

In order to generate substantial knowledge and allow for holistic understanding of a group of polymers that has been subject to very little research to date, the approach applied in this thesis aligns to the logic of the LS processing chain. As introduced in section 1.1 it starts with powder handling and the raw materials' most influential properties on packing and flowability (*Pre-Process*), to then investigate the interactions during processing (*In-Process*) to finally examine the outcome of the process (*Post-Process*) in terms of mechanical properties

used for validation of pre and in-process interactions and reuse or ageing of the materials observed (see Figure 1).

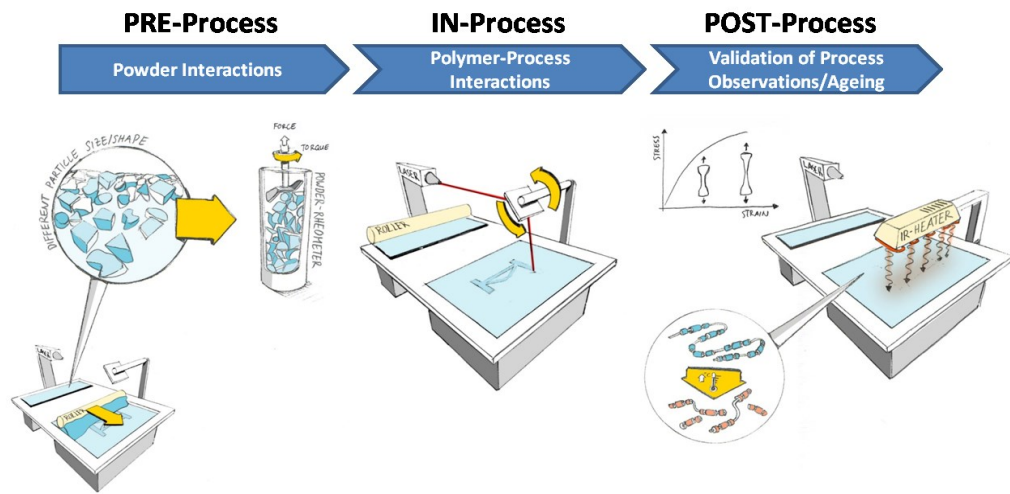


Figure 1: Approach aligning to additive processing chain

Applying the idea of the LS process pattern, the principle stages of this PhD thesis are structured into three stages. In the first stage a substantial literature review was carried out in order to identify the major gaps in the current state of research and is presented throughout chapter 2. The second stage, the research hypothesis and novelty (Chapter 3), were derived from the understanding of stage one. The hypothesis built the basis for the third stage, the research objectives and its investigations that are were concluded within chapter 9 and chapter 9.2 as recommendations for future work.

2 Literature Review

2.1 Polymer Laser Sintering

The LS process has great potential for the production of small series components as it allows the manufacture of mechanically resilient objects directly from three-dimensional (3D) digital data by selectively exposing successive layers of thermoplastic powder without the need for tooling. This section gives an overview of the polymers available in LS, the single processing steps as well as the essential interactions between machine parameters and material properties. As this process is well described in literature today [6, 7], within the subsequent sections (2.1.1 - 2.1.5), only the relevant information in connection with the thesis topic is presented.

2.1.1 Polymers for Laser Sintering

The benefits that result from the layer-wise production of parts are frustrated, to some extent, by the scarce availability of new materials with properties sufficient to meet the requirements of series applications. The most common polymers in LS are semi-crystalline thermoplastics. With regard to LS, they can be partially recycled, meaning they can be reheated, reshaped and solidified repeatedly due to their secondary binding forces, and therefore help to save material use. In addition to semi-crystalline polymers, amorphous polymers such as polystyrene can also be processed in LS [8]. These polymers differ in the way their chains are arranged and therefore show significantly different thermal properties [6, 9]. The manufacturers of the LS systems supply a range of polymer materials designed for their machines such as Polyamide 12 (PA12, e.g. PA2200, EOS GmbH), Polyamide 11 (PA11, e.g. Primepart DC, EOS GmbH), polystyrene (PS, e.g. Primecast, EOS GmbH), and in few cases thermoplastic elastomers (TPE) [10-12]. As the currently available TPEs are not made from precipitation crystallization they long for additional processing steps such as grinding to reach the powdered state [13].

Trade name	Distributor	Type of polymer
DuraForm [®] Flex	3D Systems	TPE-E (no official information available)
Desmosint	Lehmann & Voss & Co.	TPU
ALM TPE 210-S	Advanced Laser Materials, LLC	TPU

Table 1: Commercially available TPEs for LS

EOS released a PEEK material and Advanced Laser Materials (ALM) has Polyamide 11, Polyamide 12 based products which are customized to certain applications by the use of additives [6]. Rhodia announced an intention to challenge the limits of plastic part manufacturing by offering a PA6 and PA66 to the market, but the materials are still in the development phase [14]. As mentioned before, thermoplastic polymers can be classified into semi-crystalline and amorphous. In principle, both polymers can be processed in LS, however, due to the better mechanical properties semi-crystalline polymers are the most frequently used [6, 15]. Because of their wide softening range amorphous thermoplastics lead to less dense parts and are therefore less preferable for use in LS [16]. Currently, however, more and more applications occur that demand a wide range of diversity in parts with favourable mechanical properties and a high density [17]. For that reason the currently available repertoire of materials is not sufficient to conform to the requirements of series production. Industry as well as academia has been trying to enable more polymers for the LS process.

2.1.2 Processing Steps

Laser Sintering is one of the most common and widely accepted AM processes [18, 19]. During the LS process, a layer of pre-heated powder is deposited across the build platform. After being pre-heated close to the crystallite melting point (for amorphous polymers close to T_g), the powder layer is exposed selectively by the CO₂-laser corresponding to the cross-section of the CAD-part fusing together particles and the underlying layer.

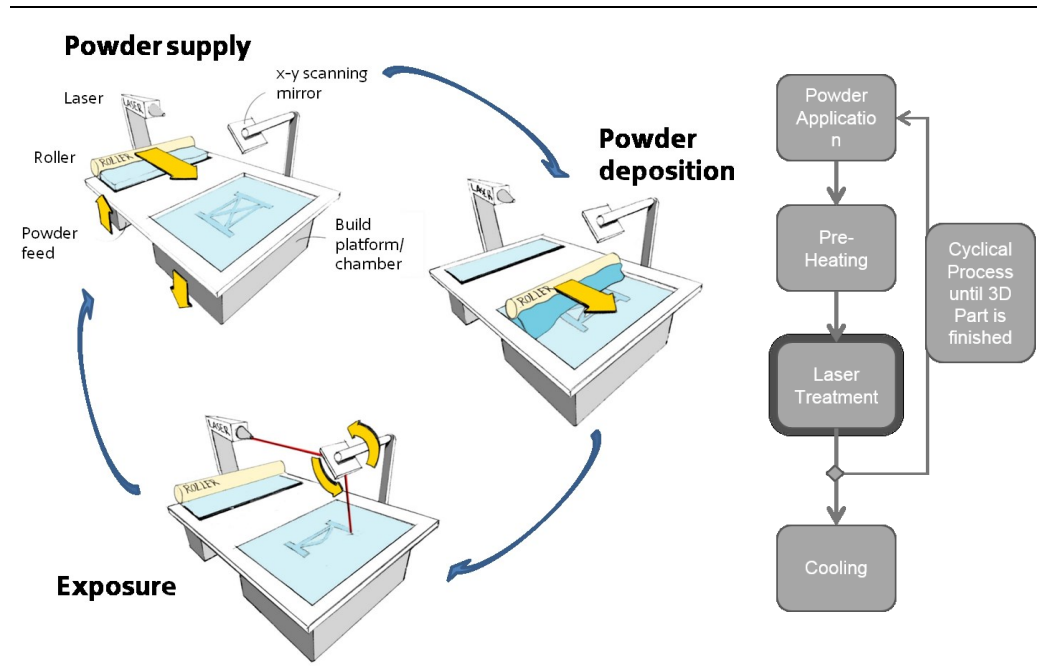


Figure 2: Schematic representation of processing steps during Laser Sintering

During part production, LS does not require structures to support overhangs as the un-melted powder supports the melted polymer. These processing steps are repeated until the three-dimensional part is completed so that the part cake and the contained parts cool down and solidify. After the build is completed the un-sintered powder can be re-used to a certain extent depending on the type of polymer [20-24]. The manufactured parts can now be used or refined conforming to their later application.

2.1.3 Effect of Powder Properties during Laser Sintering

Research carried out on LS powders has shown that non-intrinsic properties such as particle size, shape, surface topology, powder bed density and flowability have a great influence on the process and the quality of the manufactured parts. For example Lim *et al.* [25] employed an alternative way of manufacturing PA12 powders with a comparable chemical structure by a high pressure wet process. The powders, though, differed in particle size and distribution as well as particle shape. Particles with a shape closer to a sphere thereby showed enhanced processability during LS and the powders' size distribution was found to have a strong influence on the precision of the fabrication [25]. The influence of the powder particles' morphology and the LS process parameters on the characteristics of the laser sintered parts has been observed by Hao *et al.* [26].

The sintered density and porosity of the specimens were influenced by the particle size and the processing parameters. The inter-particle connectivity and the pore size range of the specimens were found to be predominantly determined by the particle size and to a lesser extent by the applied parameters. However, as they applied higher energy densities with increasing average particle sizes the effects on the properties of the specimens observed could not directly be linked to the particle characteristics. According to Alscher [27] the sintered density of parts manufactured in LS can be calculated as follows.

$$\rho_{Sinter} = \frac{\rho_{Bulk}}{\rho_S} = 1 - \frac{\rho_S - \rho_{Bulk}}{\rho_S} \quad \text{Eq. 1}$$

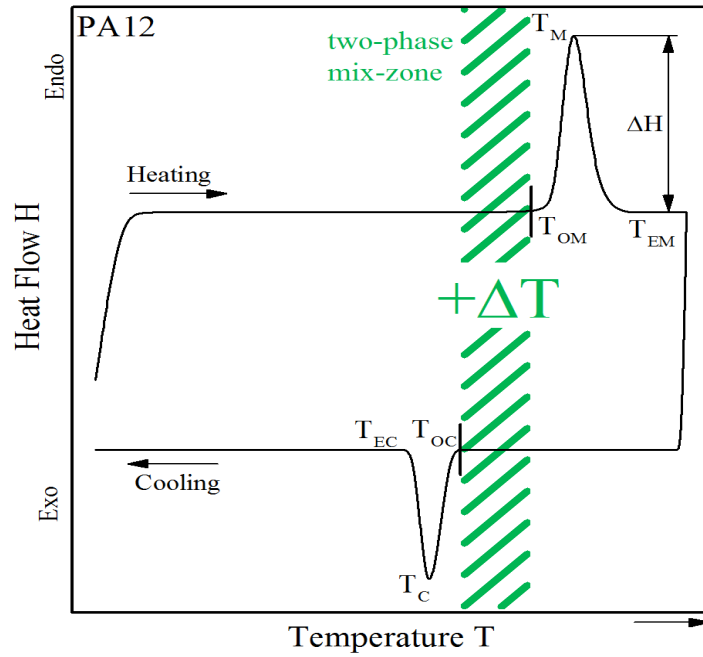
ρ_{Sinter}	Density of sintered Part
ρ_{Bulk}	Density of Powder Bulk inside the LS Process
ρ_S	Solid Density of Raw Material

Amado *et al.* [28] presented an extensive study examining the properties of a selection of various commercially available powders for LS as well as some experimental polymer materials. They emphasised that current research is mainly concentrating on intrinsic material properties but is lacking in the correlation of the materials bulk and flow behaviour with properties of the sintered parts. As a result of their research they proposed a characterization indicator that could help to differentiate more precisely between varying powders and their dynamic as well as their packing properties. The packing properties are, besides others, highly dependent on particle size (see section 2.3) and therefore have to be taken into account when the behaviour of the materials and their suitability for the LS process is being investigated. Higher packing densities have been found to contribute to higher part densities and in addition influence the size deviation and mechanical properties of a specimen [29, 30]. In the case of continuous particle size distribution such as LS powders, there is a theoretical packing density of around 66.3% [31]. However, real packing densities of commercially available LS powders are in the range between 41 to 45.3% [29, 32]. A previous study published by Shi *et.al* [33] describes the effect of the properties of the polymer materials, such as molecular weight, melt viscosity, crystallization rate and the particle size of the powder, on the quality

of laser sintered parts, proposing an optimal particle size distribution (PSD) for the powders between 75 – 100 μm in order to ensure improved processability, but commercial powders currently used in LS don't fall in this range. Moreover, Goodridge *et al.* [6] reported that the desired PSD for processing a material in LS is between 45 – 90 μm , based on results for polyamide 12 and their specific PSDs. Studies on the influence of material ageing have shown a shift in PSDs as well as in the shape of the powders observed. As a result flowability of the powders decreased and consequently affected processability and the parts manufactured [32, 34]. The effect of poor flowability on process stability and part quality was also reported by Koo *et al.* [35] but they did not quantify the relationship between the powder properties and their processing behaviour.

2.1.4 Quasi-Isothermal Laser Sintering – Energy Input and Thermal Boundary Conditions

Quasi-isothermal laser sintering describes the idealized model for the processing of semi-crystalline thermoplastics in a two-phase (liquid/solid) mixed-zone meaning powder and melt coexist simultaneously during manufacturing. To ensure this, the build chamber temperature has to be close to the crystalline melting point of the processed polymer so that the laser only introduces the remaining amount of energy to exceed the phase transition and therefore selectively melt the material. In addition, the crystallization temperature of the material used has to range at a lower temperature than its melting temperature and the delta between crystallization and melting has to be higher than potential temperature gradients on the powder bed and the build chamber. Thus, a build temperature higher than the materials' crystalline melting point would cause uncontrolled melting of the powder bed, whereas a temperature very close to or lower than the crystallization temperature leads to shrinkage effects of the previously melted layer during the process, an effect also known as curling [36]. After the build process is completed the crystallization process begins as the powder bed slowly cools. This idealized model, though, has not yet fully been proven on existing systems, it was instead derived from differential scanning calorimetry (DSC) data. Figure 3 provides a schematic representation of the model based on PA12 [3, 27, 32, 37].



T_{OM}	Onset of Melting	[°C]
T_M	Peak Temperature of Melting (Melting Point)	[°C]
T_{EM}	End of Melting	[°C]
ΔH	Enthalpy of Fusion	[J/g]
T_{OC}	Onset of Crystallization	[°C]
T_{EC}	End of Crystallization	[°C]

Figure 3: Model of the quasi-isothermal laser sintering in the two-phase mix-zone on basis of a schematic display of a PA12 DSC-curve, adapted from [32]

It qualitatively shows the curve shape during heating and cooling and indicates the two-phase mix-zone between melting and crystallization, a property that is not necessarily inherent in many polymers.

If the polymer can be processed by LS the way the energy is being introduced can be divided into two paths. On the one hand there is the heating of the build chamber with the IR-heater, on the other hand there is the energy introduced into the powder bed by the laser in order to selectively melt the powder particles [38]. An overview of the different heating methods in various LS systems is given by Goodridge *et al.* [6]. In a 3D Systems Sinterstation® HiQ™ the powder in the machine is heated from above (Part Bed Heater), from the bottom within the build platform (Piston Heater) and with band heaters surrounding the corresponding chamber (Cylinder Heater). Within the feed chambers the powder is preheated in order to keep the temperature difference between the

powder/molten layers within the build chamber and the new powder supplied at a defined and low level as it can affect the build process [39, 40]. For example, newly applied powder from the feed that has a significantly lower temperature than the material within the build chamber rapidly cools down the underlying layer and consequently can lead to crystallization and curling [41]. Similarly, the previously described temperature delta can result in an overshoot of the heating impulse as the temperature regulation unit aims to quickly reach the heater set point possibly leading to uncontrolled melting. [36].

The energy locally introduced to melt the material takes place with a CO₂-laser at a wavelength of $\lambda=10.6\text{ }\mu\text{m}$. The energy introduced onto the surface of the powder bed is divided into reflection, absorption and transmission [42]. The reflection results in a deflection of the laser beam which in turn leads to a direct deflection into the build chamber or a reflection towards surrounding particles. A simplified representation of this process is given in Figure 4.

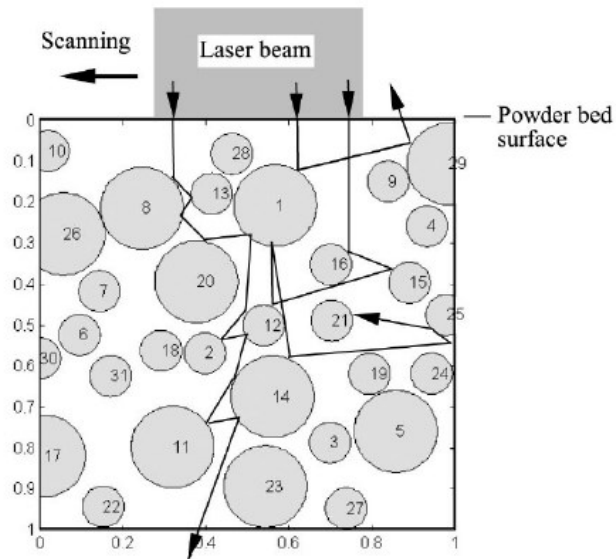


Figure 4: 2-dimensional Ray Tracking Simulation of the penetration characteristics of a laser beam in a powder bed [43]

A closer examination of the reflection behaviour of bulk powders, also taking into account transmission effects, shows that this leads to a residual radiation that in turn results in an indirect reflection. This substantially more complex consideration of the penetration characteristics is schematically represented for the case of polyethylene (PE) particles in Figure 5.

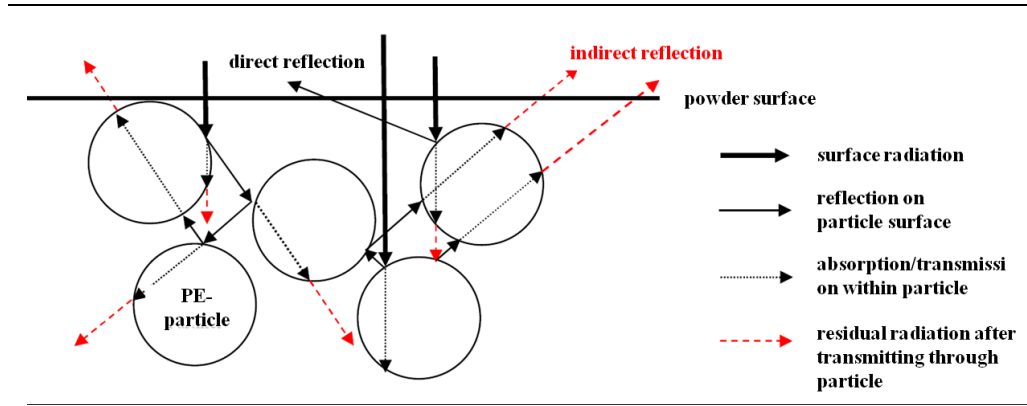


Figure 5: Schematic representation of the penetration characteristics of a laser beam into a PE powder bulk under consideration of transmission within the particles [42]

In the case of disperse systems such as LS powders a higher amount of the inserted radiation is being absorbed so that the indirect reflection is significantly lower. As shown in Figure 6, it comes to an increased ratio of absorption of the injected radiation in the PA12 bulk due to the higher amount of fine particles and the accompanying higher bulk density. As a result, less radiation is reflected back to the surface compared to the more porous PE-bulk [42].

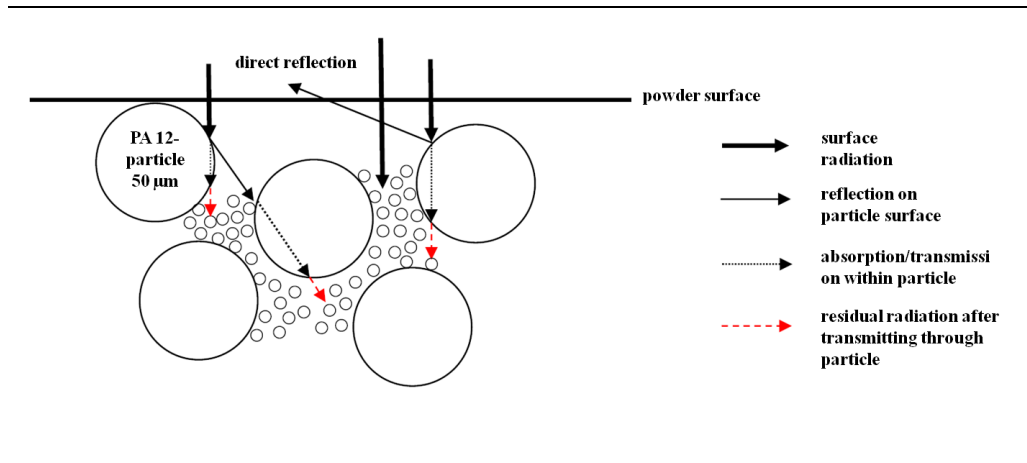


Figure 6: Schematic representation of the penetration characteristics of a laser beam into a disperse PA12 powder bulk under consideration of transmission within the particles [42]

Similar to the optical interactions between a bulk system and a heat source such as absorption, the effects of thermal conductivity are changing with respect to particle size and packing density that in turn lead to various forms of contact areas between the particles [44, 45]. Gusarov *et al.* [46] found that heat transfer

is strongly affected by formation and growth of necks between particles due to sintering when the contact conductivity becomes the main influencing factor on the powder bed's effective thermal conductivity. The contact size between adjacent particles, which in turn depends on packing efficiency of powder beds, was found to be of major importance for the overall conductivity and neck growth in LS. Their model describing the effective thermal conductivity approximately agrees with analytical models, though, is dependent on the assumption of mono-disperse particles, a property profile that does not apply to the current LS powders. In general thermal conduction arises from temperature differences in a material causing a heat energy transport towards the lower energy level. In the case of electrically conductive materials, such as metals, the energy can be transported by free electrons, hence they have a high thermal conductivity [44]. In contrast, materials with bound electrons have a low thermal conductivity as the energy has to be transported by means of atom or molecular vibrations, as is the case for polymers [47]. Hence, polymers typically have a thermal conductivity between 0.15 to 0.5 W/mk [47, 48]. Alscher [27] presents the effects of thermal conduction in the context of laser sintering. At higher thermal conductivity a broader so called "mixing-zone" consisting of agglutinated powder was observed, while the depth of the molten layer was reduced. The benefits or disadvantages in the context of thermal conduction can be concluded as follows:

- *Benefits of high thermal conductivity:*
 - increased geometrical accuracy due to decreased heat accumulation at the phase boundary (melt/powder)
 - enhanced heat transfer between molten layers
- *Drawbacks of high thermal conductivity:*
 - increased thermal loads of surrounding powder, probably affecting material reuse of material
 - reduced depth of melted layer
 - overall hindered melt pool formation

- *Benefits of low thermal conductivity:*
 - increased depth of melted layer
 - decreased thermal loads of surrounding powder
 - more homogenous melt pool formation
 - shorter exposure time (increased scan speed), probably increasing processing speed
- *Drawbacks of low thermal conductivity:*
 - decreased geometrical accuracy due to increased heat accumulation at the phase boundary (melt/powder)
 - higher probability of material degradation in melt pool due to heat accumulation

Ultimately for a comprehensive declaration of the LS process not only the approach of multiple reflections has to be considered but also the single particle and its absorption behaviour within the bulk system. However, within the literature generally the more simplified relationship between the different parameters during energy introduction is used which is described by the so called Andrew Number or also referred to as area related energy density (EA) shown in Eq. 2 [49, 50].

$$E_A = \frac{P_L}{v_s \times H} \quad \text{Eq. 2}$$

E_A	Area related Energy Density	[J/mm ²]
P_L	Laser Power	[W]
v_s	Scan Speed	[mm/s]
H	Hatch Distance	[mm]

The E_A thereby describes the nominal power introduced on the surface by the laser independent of the material processed. In order to take into account the influence of the layer thickness the E_A can be extended to a volume related energy density considering the variable for layer thickness shown in Eq. 3.

$$E_V = \frac{P_L}{v_s \times H \times d_{layer}} \quad \text{Eq. 3}$$

E_V	Energy Density based on Volume	[J/mm ³]
P_L	Laser Power	[W]
v_s	Scan Speed	[mm/s]
H	Hatch Distance	[mm]
d_{layer}	Layer Thickness	[mm]

The approach is often criticised as amongst other parameters the absorbance of the laser energy throughout the 100 µm layer is dependent on various parameters such as the above mentioned packing density of the material and it assumes the penetration depth of the laser complies with the thickness of the produced layer, which is generally not the case [51, 52].

Moreover, due to the Gaussian temperature distribution of the laser beam the heat introduced into the powder bed is not homogenous throughout the laser diameter as the highest temperature would occur at the innermost region (Figure 7 (a)). Thus, the particles being hit by the centre (targeted area) of the laser beam are exposed to higher temperatures than the ones at the edges [53].

Considering Eq. 2 in combination with Figure 7 (b) it can be observed that in dependence of the diameter of the laser beam and the hatch distance there is an overlap of the single scan paths of the moving heat source (laser spot), thereby some points get exposed multiple times. This overlap is represented by the area shown between the curves at $t=0$ and $t=1$ for constant scan speed a . If the beam is moving with an increased scan speed ($a + x$; where x is positive) the overlapping area decreases due to the reduced time the powder is exposed by the laser [53]. As a result of these effects, it becomes clear that the equations are simplified and limit the direct correlation to the real process as the build temperature was treated as a constant parameter and the time of exposure was only described in the E_V -approach in dependence of laser power, hatch space, scan speed and layer thickness.

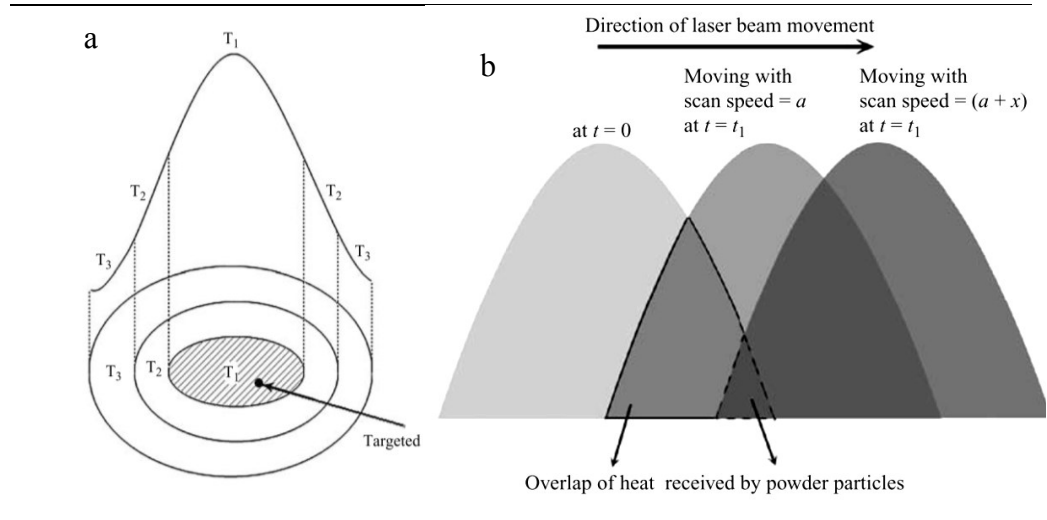


Figure 7: Temperature distribution of a CO₂-Laser beam (a) and sintering model of a moving laser beam (b) [53]

Another important influential factor is the size of the exposed area, as the heat conduction within large melt pools is slower compared to smaller sized melt spots. As a result, the polymer melt in the larger pool is capable of flowing for a longer period of time, thus, building a more homogenous film and connection to the underlying layer [54]. Consequently, the heating and cooling rates of the exposed areas are dependent on the size of the corresponding cross-section. According to Scholten *et al.* [55] the specific amount of heat loss resulting from convection and radiation as well as the incoming rate of heat flux of the part bed heater, the cylinder heater and the piston heater are negligible compared to the high-intensity laser radiation during exposure of the material. During pre-heating and applying a new layer but also the time between the exposure phases, though, the rate of heat loss from convection and radiation as well as the incoming rate of heat flux do play a dominant role [32]. Therefore, a temperature gradient should only be present during exposure with the laser in any other case an even energy balance is desired. The balancing of the heat flows can be represented simplified as follows in Eq. 4.

$$\underbrace{\dot{q}_a + \dot{q}_{Part\ Bed\ Heater} + \dot{q}_{Cylinder\ Heater} + \dot{q}_{Piston\ Heater}}_{\text{Incoming Heat Flux}} = \underbrace{\dot{q}_{HC} + \dot{q}_{con} + \dot{q}_{rad}}_{\text{Amount of Heat Loss}} \quad \text{Eq. 4}$$

$\dot{q}_a$	absorbed Laser Radiation
$\dot{q}_{Part\ Bed\ Heater}$	absorbed Radiation of Part Bed Heater
$\dot{q}_{Cylinder\ Heater}$	absorbed Radiation of Cylinder Heater
$\dot{q}_{Piston\ Heater}$	absorbed Radiation of Piston Heater
$\dot{q}_{HC}$	Rate of conductive Heat Loss
$\dot{q}_{con}$	Rate of convective Heat Loss
$\dot{q}_{rad}$	Rate of radiation Heat Loss

Although, the effects of varying build chamber temperature on the mechanical properties of sintered parts have been indicated, they often haven't been quantified [56, 57]. Starr *et al.* [58] used a total energy approach for the first time in describing the effect of the build temperature in dependence of the material properties as shown in Eq. 5. The aim of the study was to measure not only the effect of energy introduction by the laser but also the energy introduced by the IR-Heater as well as the influence of material parameters on mechanical properties of laser sintered specimen and to determine the range of conditions that provide consistent mechanical performance. For that purpose he set up the energy melt ratio (EMR) that puts the volume-based energy density (Eq. 3) in relation to the energy needed to fuse a single layer (Energy to Melt Layer).

$$EMR = \frac{E_v}{EML} \quad \text{Eq. 5}$$

EMR	Energy Melt Ratio	[-]
E_v	Energy Density based on Volume	[J/mm ³]
EML	Energy to Melt Layer	[J/mm ³]

In the following the derivation of the EML is given, consisting of the specific heat capacity (Eq. 6) and the enthalpy of fusion (Eq. 7) [59, 60].

$$c_p = \frac{Q_p}{m \times \Delta T} \quad \text{Eq. 6}$$

c_p	Specific Heat Capacity	[J/gK]
Q_p	Amount of Heat needed to increase the Temperature of a certain Substance from T_1 to T_2	[J]
m	Mass of Substance	[g]
ΔT	Absolute Value of Temperature Increase	[K]

$$h_f = \frac{Q_f}{m} \quad \text{Eq. 7}$$

h_f	Enthalpy of Fusion	[J/g]
Q_f	Heat of Fusion	[J]
m	Mass of Substance	[g]

The total amount of heat needed to melt a certain mass of a certain substance at a defined starting temperature is described by summarizing the amounts of heat given in the specific heat capacity (Eq. 6) and the enthalpy of fusion (Eq. 7). By expressing Eq. 6 and Eq. 7 by Q one can insert them in the summation formula for the total heat quantity below.

$$Q_{total} = Q_p + Q_f \quad \text{Eq. 8}$$

Q_{total}	Total Amount of Energy needed to melt a Substance	[J]
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In order to describe the energy needed to melt one layer in LS, the mass m of the substance is described by the density which is dependent upon the packing density. On the basis of this simplified assumption Eq. 9 can be set up describing the EML, the energy that is needed to melt a layer of a specific volume in dependence of material properties.

$$EML = [c_p(T_m - T_b) + h_f] \times \rho_M \times \rho_P \quad \text{Eq. 9}$$

EML	Energy to Melt Layer	[J/mm ³]
T _m	Melting Temperature of Polymer	[°C]
T _b	Powder Bed Temperature	[°C]
h _f	Melt Enthalpy	[J/g]
ρ _s	Solid Density of Raw Material	[g/cm ³]
ρ _p	Packing Density of Powder Bed	[g/cm ³]

The EMR can now be described as shown in Eq. 10 depending on process and material properties by inserting Eq. 3 and Eq. 9. in Eq. 5.

$$EMR = \frac{\frac{P_L}{v_s \times H \times d_{Layer}}}{[c_p(T_m - T_b) + h_f] \times \rho_M \times \rho_P} \quad \text{Eq. 10}$$

EMR	Energy Melt Ratio in dependence of Process and Material Parameters	[-]
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In the research conducted by Starr *et al.* [58] they found that the volume energy density, which includes the effect of different layer thickness, is a more general approach to correlate processing conditions to mechanical properties and therefore introduced the new dimensionless parameter EMR. It was shown that it is a useful parameter to relate process conditions to the physics of powder melting and furthermore to use it to predict potential changes of part properties by changing the powder bed temperature. Vasquez [13] applied the EMR on the overall energy approach for TPEs and found that it is a useful mathematical model in order to derive suitable process parameters in dependence of material properties.

In critically reviewing the approach it can be noted that it includes the same simplifications as mentioned in context with the E_v in Eq. 3. In addition the specific heat capacity, besides the packing density that is varying due to different thermal expansion of the material, is not a constant parameter as it changes with temperature. The problem here is, that measuring c_p as a function of temperature is complex and to analyse the in-situ thermal expansion of the certain powder

bulk is not currently possible. In addition, due to thermal gradients over the powder bed it will also not be consistent.

As described before, the heating within the build chamber has a significant influence on the processability of the material and the properties of the parts manufactured. After the laser scans each layer the melt cools down to the build chamber temperature and there is a delay whilst a new layer of powder is brought to the build platform before the next layer is going to be exposed. Goodridge *et al.* [6] described the effect in their publication and describe that the length of delay time is system dependent and only partly controllable. Pham *et al.* [61] found that applying high laser powers at low bed temperatures can result in increased delay time potentially causing curling due to loss of thermal energy in the form of conduction into the powder bed or radiation and convection at the powder surface. Jain *et al.* [62] described the layer delay time as the time between scanning two adjacent points on successive scanning lines for PA12. They found that this delay time changes in dependence of part orientation as the length of scan paths change alongside with varying size of a part's cross-section. They found that part strength increased with an increase in delay time to a certain extent reaching to decrease again after reaching its optimum due to thermal degradation. On the other hand, short scan paths causing shorter delay times were found to lead to poor bonding between the particles that again reduced part strength. However, the proposed approach of aiming for a specific angular orientation of parts in the process is at most feasible for standardized and simple geometries. In a typical day to day manufacturing environment with higher production values of varying and complex geometries this approach will not be practical. The approach can rather be considered for optimum orientation of critical sections that have to take high loads within i.e. functional testing.

Besides the previously described effects, within multiple part builds the delay time can also increase due to increasing amount of cross-sections that have to be exposed. For that purpose Goodridge *et al.* [6] conducted an experimental build for PA12 (PA2200) and two elastomeric materials (DuraForm® Flex and an experimental elastomer) including single and multiple part sections to later detect and compare tensile strength of the specimen. Thereby, a part built in the

multiple part section experienced longer delay times compared to one placed in the single part build. They found that an increase in delay time had a minimal effect for PA2200 and DuraForm® Flex whereas for the experimental TPE they found a drop in tensile properties by over 30%. They suggested that increasing the delay time between each layer reduces interpenetration between successive layers. As the polymer cools down its viscosity increases, thus achieving acceptable cohesion between the layers gets more difficult in this unpressurized process. They state that different polymers have different melting characteristics which are responsible for the observed differences.

2.1.5 Geometry and Orientation of Parts

The resulting properties of parts manufactured in LS are not only influenced by the material properties and the process parameters applied, but also by the orientation of the parts in the build and its geometry [63]. As LS is an additive process the parts built consist of, depending on their size, many individual layers between which delamination (detachment of single layers) could occur as indicated by Figure 8 [21]. The probability of delamination thereby increases proportionally with the amount of layers. This effect, though, is superimposed by notch effects emerging at the borders of the parts caused by the layer-by-layer structure (step-effect) and the Gaussian intensity distribution of the laser shown in Figure 8. Analogous to the delamination effect, the notch effect and therefore a potential component failure increases proportionally to the amount of layers [64]. Moreover, the surface roughness which has a direct impact on mechanical strength of the parts is affected by the step effect that in turn is most significant at curved or angled areas [63, 65].

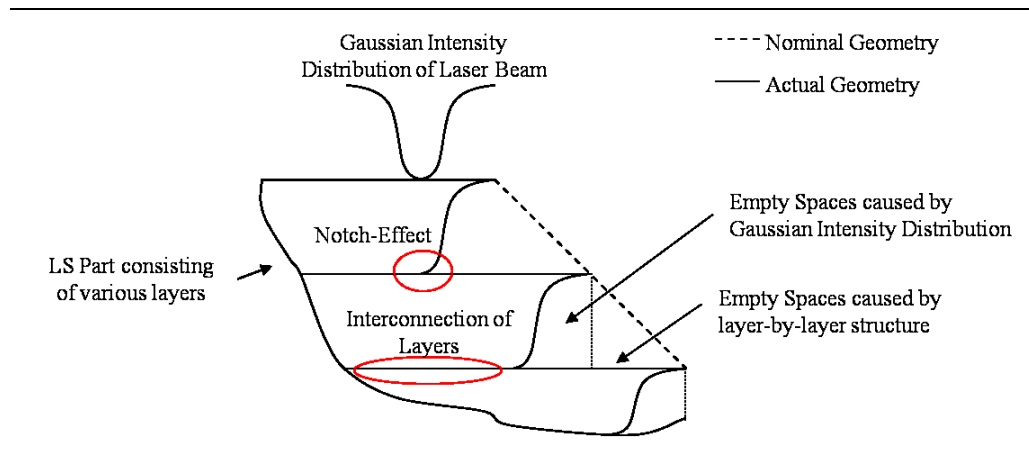


Figure 8: Layer-by-layer structure of a LS part indicating areas of notch effect and interconnection between the layers at which delamination could occur, adapted from [63]

The effects of orientation and anisotropic properties of LS parts are well described in literature and therefore are only briefly discussed here to indicate their importance [64, 66-70].

2.2 Polymers and Polymer Ageing

This section provides some general information on polymers and their classification. As within the Post-Process observations of this thesis the reuse of TPEs and in particular the newly developed TPU was examined, additional information on the principles of polymer ageing and a deeper insight into the nature of thermoplastic polyurethane in terms of chemistry, properties and its applications is given.

Polymers are organic or semi-organic substances with a high molecular mass, this means they contain large molecules (macromolecules) which determine the polymers specific property profile [71]. Their basic materials are oil, natural gas and coal as carrier of carbon (C), hydrogen (H), oxygen (O) and substances that include nitrogen (N), chlorine (CL), sulphur (S) and fluorine (F). There are various possibilities to manufacture such polymers, leading to high variation in their final properties [72].

2.2.1 General Classification of Polymers

A polymers' properties result from their chemical constitution as well as their physical structure, i.e. linear or branched molecule chains (thermoplastics) and lightly cross-linked or heavily cross-linked molecules (elastomers and

thermosets) [73]. In Table 2 the general classification of polymers and their corresponding properties are represented.

Type	Structure	Features	Examples
<i>Thermoplastics</i>	linear crystalline/ amorphous	Un-cross-linked polymers with high strength and low strain under load. Soften or melt on heating, and do not lose their ability to be re-melted on warming, even after repeated heating and cooling cycles	Polyamide, Polypropylene, Polyethylene
<i>Elastomers</i>	cross-linked	Lightly cross-linked polymers, exhibit highly reversible strain under low stress. They cannot be re-melted due to cross-links.	Vulcanized natural rubber
	crystalline/ amorphous	Combine the processing properties of thermoplastics and the performance of cross-linked elastomers. They can be re-melted and are highly reversible under low stresses.	Polyetherester Polyurethane Polyetheramid
<i>Thermosets</i>	heavily cross-linked	Exhibit high mechanical strength and low strain after curing. Re-melting after curing is not possible.	Cured epoxy resins Polyesters

Table 2: Classification of polymers [74, 75]

2.2.2 Physical Structure of Polymers

At temperatures above their crystalline melting point polymers exist as amorphous melt. This means their macromolecules are present in a disordered pattern as the segments of the polymer chain exhibit a relatively large degree of mobility when molten [76]. When the polymer undergoes cooling, the molecular mobility decreases and the viscosity of the material increases. Exceeding the

glass transition temperature (T_g), the viscosity increases by several decades as the molecular rearrangements “freeze” with only the vibrations typically for a solid remaining. Below its T_g a polymer is hard and relatively brittle [77, 78]. Being stored between their melting temperature and T_g , polymers can undergo crystallization as the elongated molecules are forced to fold back on themselves. In this process of chain folding the chains are often present as layers of lamellas with amorphous material or material that is no longer able to further crystallize between them (amorphous regions). Polymers with alternating crystalline and amorphous layers are referred to as semi-crystalline polymers, whereas polymers that are unable to crystallize are amorphous [74]. Figure 9 shows the schematic structure of amorphous and semi-crystalline arrangements.

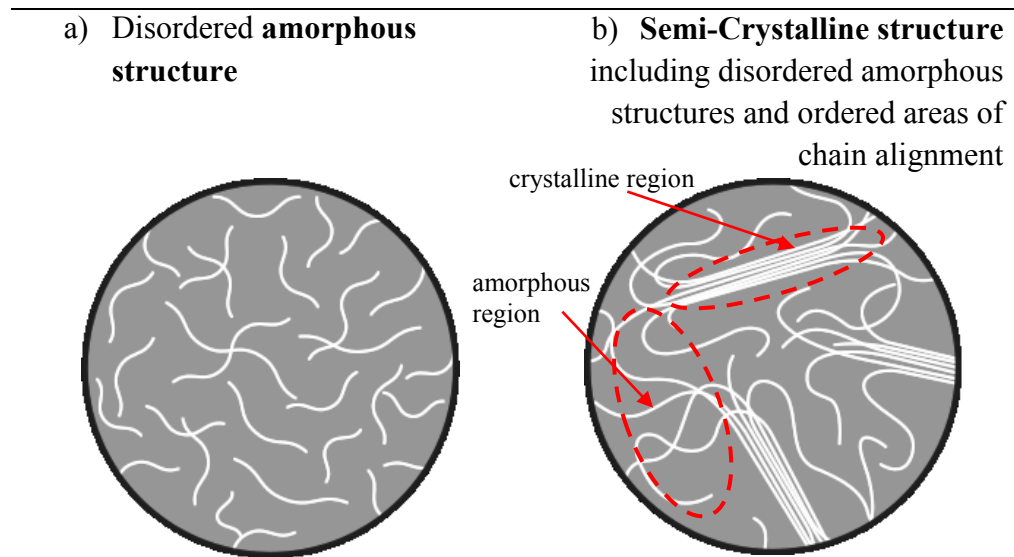


Figure 9: Example of a) amorphous and b) semi-crystalline structures [79]

Depending on the structure of the macromolecules, the chain folding or parallel alignment of the lamella is pronounced to a greater or lesser extent. This process of chain arrangement and the principle structure and length of macromolecules determines the crystal size and the melting temperature of a semi-crystalline polymer [78, 80].

2.2.3 Thermoplastics

Thermoplastic polymers have the special ability to be plastically malleable or brought to flow when heated. As described in section 2.2.1 this process is reversible so that the polymer solidifies after cooling. They consist of linear

macromolecules that are spatially un-cross-linked and are subjected to only low intermolecular forces (Van der Waals forces). These molecules are either randomly coiled “amorphous thermoplastics” or partly ordered as crystallites “semi-crystalline” thermoplastics [80, 81].

Amorphous thermoplastics are characterized by a completely unstructured and entangled order of their molecule chains (see Figure 9 a). As depicted in Figure 10 a, below their T_g amorphous polymers are stiff, rigid or even brittle and remain in that condition as far as exceeding their T_g . When the introduced thermal energy prevails over the intermolecular forces, the softening of the polymer begins and it becomes viscoelastic. This process is not happening abruptly rather it's occurring in a certain range of time and varying temperature. On further heating, the viscosity decreases without a distinct melting point [82].

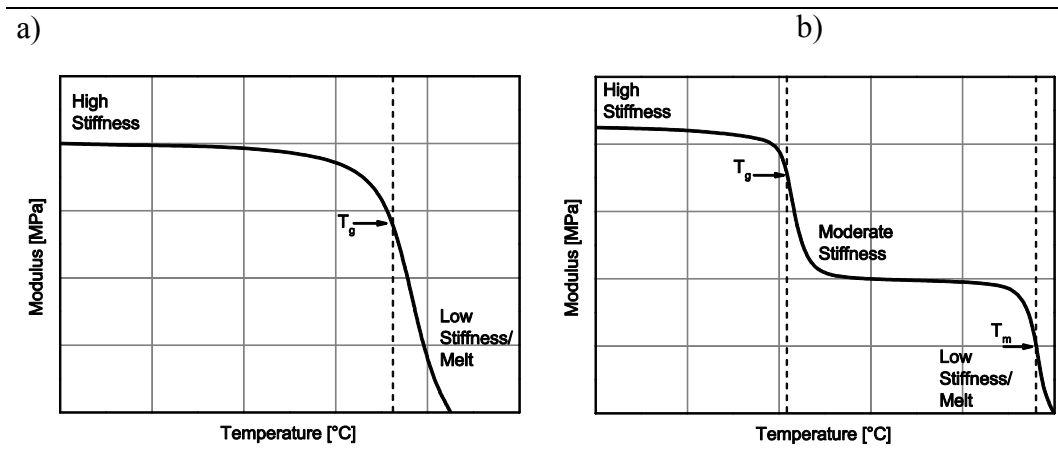


Figure 10: Schematic representation of the possible range of states represented by modulus vs. temperature of a) an amorphous thermoplastic and b) a semi crystalline thermoplastic, adapted from [76, 83]

The operating temperature of such polymers should be significantly lower than the T_g in order to have useful material performance.

Semi-crystalline thermoplastics consist of highly ordered macromolecules with amorphous regions between the crystallites (see Figure 9 b). Besides the glass transition, this structure induces an additional softening area with a sharp melting point (T_m)[84].

The melting behaviour and the specific T_m is of great importance for its processing and the parameters used. The melting temperature is the temperature where the last crystallites melt and is determined by the size distribution of the

crystallites (small crystallites melt first). As shown in Figure 10 b, these types of polymers show useful properties above the T_g and are fully molten when exceeding the T_m [85]. While being heated or cooled down and depending on the density of chain alignment, semi-crystalline polymers change their specific volume to a higher extent than amorphous polymers do [86].

2.2.4 Crystallization

When a semi-crystalline thermoplastic is melted and cooled it can re-crystallize under the influence of different process variables such as temperature, cooling rate, pressure and additives. When a relaxed melt is cooled down, disorganized macromolecules from the molten state reaching temperatures below their crystallization temperature can go back to an orderly structure while their specific volume decreases disproportionally. In the processing of polymers this change in volume is known as shrinkage [75, 76]. The crystallization process takes place over three sections – it's being initiated by the *nucleation* that leads to *crystal growth* which represents primary crystallization and the *post crystallization* or secondary crystallization. As a consequence of nucleation successive lamellar layers of the polymer chains fold together and begin to grow in a radial direction during the primary crystallization. The cohesion of the single macromolecules is thereby achieved by secondary valence forces [27, 87]. A schematic representation of a spherulite is given in Figure 11.

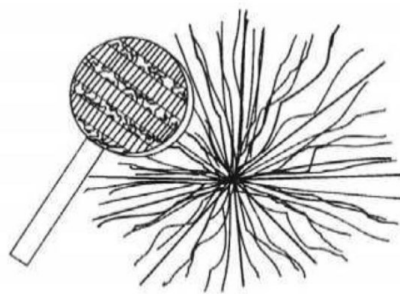


Figure 11: Schematic representation of a spherulite consisting of lamellarly arranged macromolecules [86]

From a thermodynamic perspective, the parallel chain arrangement increases the order of the system that in turn decreases the degrees of freedom meaning the

entropy of the system. The driving force behind this constitutional change is the free Gibb's Enthalpy [88].

$$\Delta G = \Delta H - T * \Delta S \quad \text{Eq. 11}$$

ΔG	Free Enthalpy	[J]
ΔH	Inner Enthalpy	[J]
ΔS	Entropy with $S \geq 0$	[JK ⁻¹]

At a very small value for ΔG the system reaches its energetically stable state that is being accomplished during the parallel arrangement of the macromolecules. As shown in Figure 12 enthalpy decreases with increasing temperature for both the amorphous and the crystalline phase, although at a different rate.

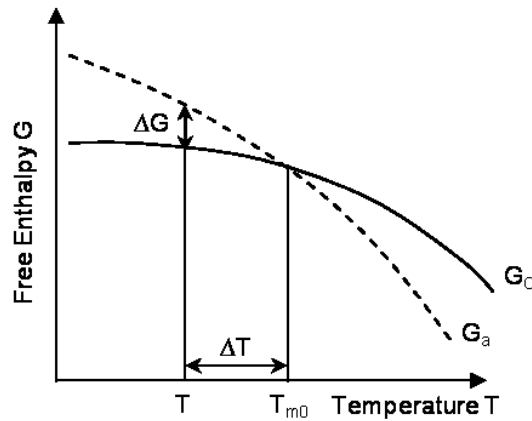


Figure 12: Schematic course of free enthalpy of an amorphous phase G_a and a crystalline phase G_c depending on temperature [27].

At their intersection point T_{m0} they reach a favourable energetic state, the equilibrium melting temperature, following the theory of a perfect polymer crystal [59, 89]. This theoretical superposition leading to complete crystallization, though, is not possible in a non-ideal environment. Thus, for example, amorphous areas emerge between crystals and free chain ends [90]. The shape of crystals thereby is influenced by nucleation and germ growth. A distinction can be made between homogenous nucleation, which results from the close arrangement and amount of perfect chain segments, and heterogeneous nucleation, which is the more probable to be observed. Not only can the

heterogeneous nucleation be initiated from, for example contamination within the polymer melt, but also additional nucleating agents or crystals that were not fully melted can cause crystallization [86, 90]. In the case where a germ exceeding the critical minimum size emerges, the germ growth is initiated. Therefore, molecules have to be transported towards the interface of the germ by means of diffusion and subsequently accumulate there. Due to the fact that the diffusion and the accumulation run at different speeds, the total speed of the germ growth is limited by the slower of the processes. It is for that reason that the germ growth can be categorized into “interface-controlled” growth (nucleation-process) and “diffusion-controlled” growth (transport-process). The product of nucleation and crystal-growth, represented as crystallization rate G , is shown in Figure 13. Thereby, crystallization towards lower temperatures is limited by T_g not allowing molecular motion exceeding this point and therefore no diffusion process could take place. On the other hand, at high temperatures above the T_m no stable germs can form. Within the range between T_g and T_m the diffusion rate increases with increasing temperatures while the nucleation rate decreases, so that a maximum crystallization rate is given in the middle of the glass transition and melting temperature. The crystallization rate G can take identical values at different temperatures although forming differently sized spherulites. As a consequence, at lower temperatures many small spherulites form whereas at higher temperatures larger but lower amounts of spherulites emerge [86].

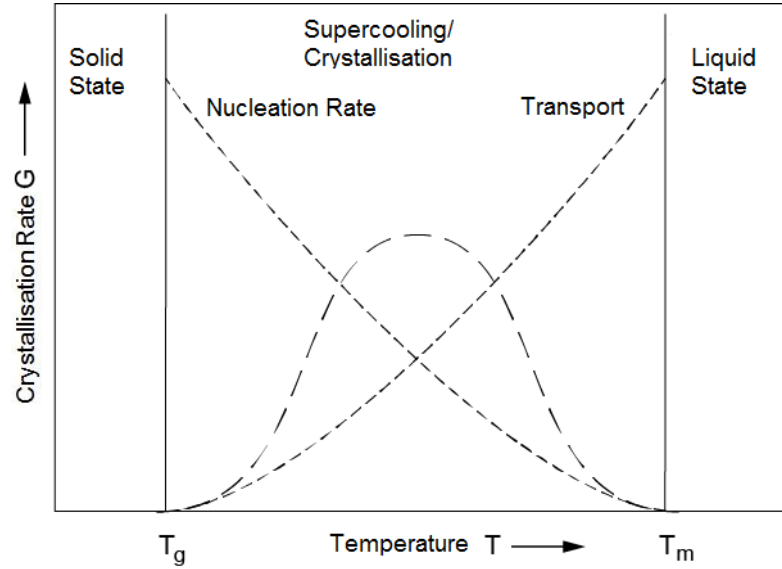


Figure 13: Resulting crystallization rate G from nucleation rate and transport in dependence of temperature [86].

After the primary crystallization is completed it is followed by post-crystallization in which further lamellas in the remaining gaps of the spherulites can be formed. Thereby, amorphous molecules accumulate at the parallelized chains of the crystalline structures around the transition point between crystalline and amorphous regions [86, 91].

Due to the thermodynamically favourable terms, nucleation preferably starts within areas of stronger hypothermia and the crystals primarily grow towards the highest temperature gradient as shown in Figure 13. Besides temperature the time available for crystallization is also of great importance [92]. As already indicated, crystallization has to be initiated by hypothermia below T_m without passing the range between T_m and T_g too fast as otherwise the macromolecules rate of diffusion is not sufficient to allow for the orderly structure of a crystal.

The relationship between crystalline volume V_c and the maximum attainable crystalline volume V_∞ of a polymer after infinite tempering time is defined as degree of crystallization ε [32].

$$\varepsilon = \frac{V_c}{V_\infty} \quad \text{Eq. 12}$$

The prediction of the crystallization is difficult due to the strong temperature and time-dependency. On the basis of an isothermal crystallization the primary crystallization can be described by the Avrami-equation. Assuming a constant nucleation rate alongside a constant and linear germ growth the Avrami can be presented as follows:

$$X(t) = 1 - e^{(-k \cdot t^n)} \quad \text{Eq. 13}$$

$x(t)$	Degree of Crystallization	[%]
n	Avrami-Exponent	[-]
k	Reaction Rate in dependence of temperature	[s ⁻¹]
t	Time	[s]

The spherulites resulting from crystallization can be made visible in polarized light having a diameter ranging from 1µm up to a few millimetres [86]. Many of a part's properties thereby are highly dependent on a polymer's crystallization behaviour and its resulting structure. The impact of an increased degree of crystallization is shown in Table 3.

Increase of:	Decrease of:
• Melting Temperature • Density • Tensile Strength • Hardness and Young's Modulus • Resistance towards Solvents	• Elongation at Break • Co-efficient of heat expansion • Transparency • Melting Range

Table 3: Effects of the degree of crystallization on part properties [76, 93]

The crystallisation behaviour of a polymer alongside the corresponding processing conditions e.g. temperature and time always have a significant influence on the part properties in many of the polymer processing technologies and have to be considered when designing components [77, 94, 95].

2.2.5 Thermoplastic Elastomers (TPEs)

An elastomer is a polymer that exhibits high elastic or viscoelastic deformation. However, this advantage in material performance is offset by its complex manufacturing process [96]. As a result, TPEs have been developed, combining the processing properties of thermoplastic polymers alongside with the application performance of elastomers [90]. Their macromolecules are linked physically not cross-linked as they are within typical elastomers, i.e. natural rubber (see Table 2). The linking points, formed by the semi-crystalline areas, ease when heated as they do for typical thermoplastics and reach their plastically formable state with a further increase in temperature [76, 97]. These reversibly linked elastomers therefore are fusible providing many processing options but also some limitations concerning their operating temperatures [91]. In comparison to pure and highly cross-linked elastomers, the maximum elongation of TPEs is also lower. Their special properties are a result of their two-phase composition [98]. Regarding their structure, TPEs can be divided into two groups, the elastomer alloys/polymer blends and the block copolymers [74]. Elastomer alloys consist of un-cross-linked or cross-linked elastomer particulate domains in a matrix of thermoplastic resin [99]. Their molecule chains consist of different sectioned building blocks, the so-called “hard” and “soft” segments. As these different blocks are incompatible among themselves it comes to a segregation of these areas on a microscopic or sub microscopic level. Thereby, the matrix is formed by the soft segments in which the hard segment is present as a dispersed phase. The hard segments are physically connected (thermo-reversible) building the amorphous or crystalline “cross-linking” (thermally labile, physical interaction) or reinforcement area in the TPE matrix [96]. As examples of these thermoplastic elastomers, copolymers on the basis of styrene (TPE-S), polyether/-ester (TPE-E), polyether (ester)-block-amides (TPE-A) and polyurethane (TPU) could be named [74, 100].

2.2.6 Thermoplastic Polyurethane

Polyurethane (PU) is a general term used for a class of polymers derived from the condensation of polyisocyanates and polyalcohols [101, 102]. PUs were first discovered by Prof. Otto Bayer and registered for patent approval in 1937 [98]. They have a broad property/diversity spectrum due to the variation possibilities

of their raw materials and the possible ways for manufacturing them. These types of polymers are therefore present in many aspects of modern life and have found use in a wide spectrum of applications in medical, automotive and other industry fields especially for seals or abrasion-resistant applications [103, 104]. In the following sections, the chemistry, properties and applications of PU will be described in more detail.

2.2.7 Chemistry of Thermoplastic Polyurethane (TPU) and TPEs

TPUs are block copolymers consisting of aromatic polyurethane-blocks (hard segment) and aliphatic polyester or polyether-blocks (soft segment) [74]. As indicated by Figure 14, the connection between the segments of a macromolecule in the form of urethane-binding results from a nucleophilic addition reaction between the cyanate and alcohol group of its raw material [98].

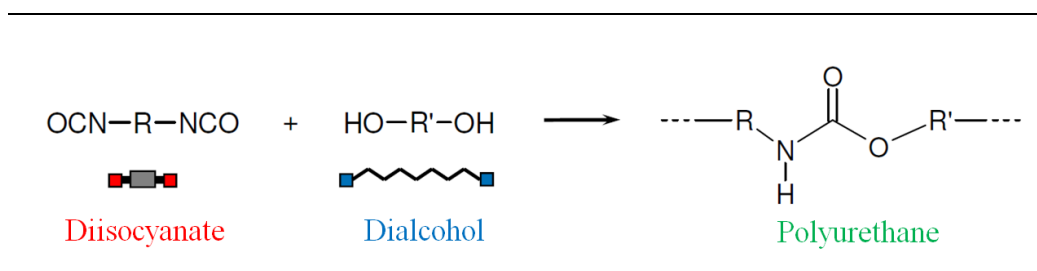


Figure 14: Formation of a polyurethane by addition reaction between diisocyanate and dialcohol [98]

By adding a surplus of diisocyanate during the reaction the resulting linear polyurethane strands are linked together under allophanate formation to a chemically reversible polyurethane elastomer that can be thermoplastically processed (see Figure 15).

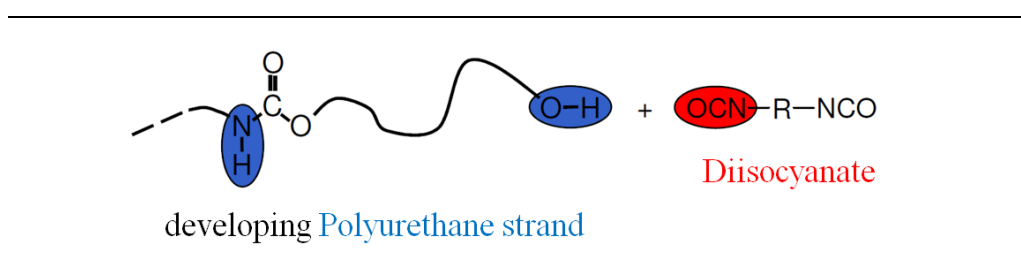


Figure 15: Allophanate formation as a side reaction of polyurethane production [98]

Besides its chemical linkage, there are physical links present in the form of semi-crystalline hard segment blocks that emerge between the aromatic diisocyanate groups and the low molecular diols [74]. Depending on the nature, length and structure of its components (i.e. the applied polyisocyanate or possible additives) the physical, chemical and mechanical properties of thermoplastic polyurethanes are decisively influenced. The hard segments of TPUs are generated from aromatic or aliphatic diisocyanate in combination with chain extenders that in addition function as physical networks in the semi-crystalline region [76]. The soft segments of TPUs are represented by polyols with a molecular weight between 200 and 10000 g/mol. Alcohols with a varying amount of hydroxyl groups are used in order to control the level of chemical linking. Amongst others, water scavengers, catalysts or inhibitors, stabilizers, emulsifier and surfactants are used as additives [91, 105].

2.2.8 Properties and Applications of Thermoplastic Polyurethane

As mentioned in Section 2.2.6, PUs are some of the most multipurpose polymers in existence today. They can be turned into PU-foams or TPUs that can show the property profile of a soft and flexible material but also of a rigid polyamide-like polymer [76, 106]. The global demand for polyurethanes is expected to grow at a Compound Annual Growth Rate (CAGR) of 5.8% from 12,018,579 tons in 2010, to 16,882,412 tons in 2016 [107]. Some examples for its actual applications are spring seats, seals for any type of component, dashboard membranes, and abrasion-resistant coatings up to activated carbon filters [98]. The properties of TPUs vary depending on their basic building blocks. As described in section 2.2.7, TPUs exhibit an alternating sequence of hard segment consisting of polyisocyanates plus chain extenders and soft segments comprising long-chain polyols.

As illustrated in Figure 16, an increasing share of soft segments (i.e. dialcohol with long chains) within the polyurethane network elasticity and chemical resistance is enhanced while an intensified proportion of hard segments (i.e. dialcohol with short chains) leads to higher hardness and strength.

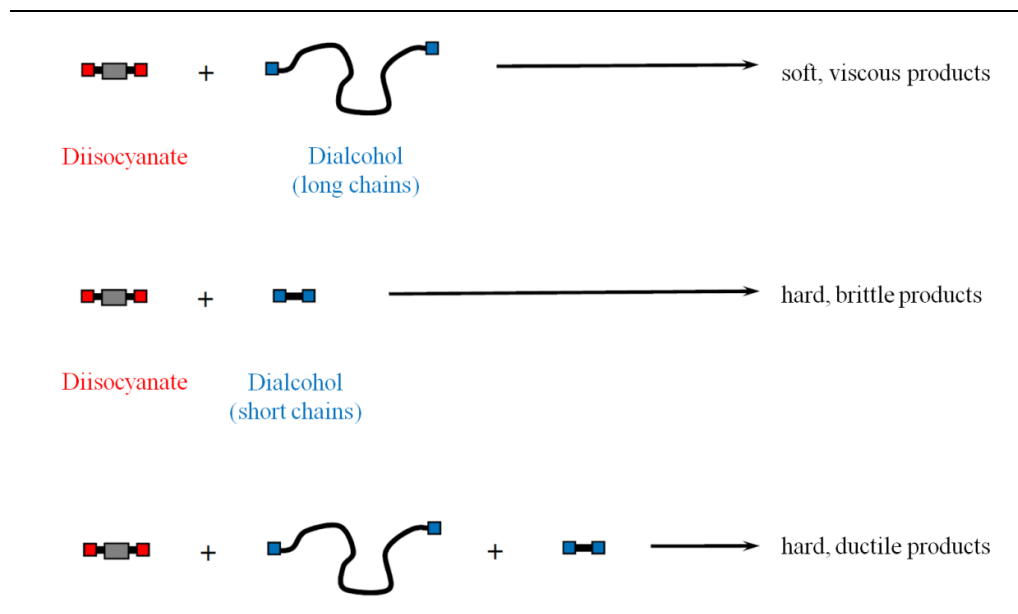


Figure 16: Possible variation of polymer structure within a thermoplastic polyurethane [98]

TPUs have relatively high impact strength and tear propagation resistance, damping characteristics as well as abrasion resistance. Their optical appearance ranges from translucent to opaque or crystal clear [76, 106].

2.2.9 Ageing Behaviour of Polymers

The term ageing summarizes all chemical and physical changes of a polymer over time. These changes influence the durability of a polymer or the time given to process it under certain conditions like heat, oxygen content and moisture [108]. The DIN 50035 for example defines the ageing of polymeric materials as the entirety of all irreversible, chemical or physical changes, also considering thermo-reversible effects (often referred to as physical ageing effects), of a material in the course of time. A distinction is made between inner and outer as well as chemical and physical ageing effects, which will be explained in more detail within this section [109]. However, a distinct differentiation between these effects is not always possible as they often go hand-in-hand [91].

So called *inner* ageing processes are best described by instable thermodynamic states of the polymer which can cause material ageing without external influences. These include incomplete polymerisation of monomeric components of the polymer as well as residual stresses due to fast or irregular cooling,

inhomogeneous density distribution or anisotropic shrinkage. The term *outer* ageing processes, refers to chemical, physical as well as microbiological based environmental influences on the polymer. They can be induced by heat or light radiation, chemical influences and mechanical stresses. In addition weathering can affect the polymers durability in combining the effects stated above in combination with the damage caused by microorganisms [91, 109].

Chemical ageing processes cause irreversible changes in the chemical composition of the polymer's molecular structure as well as its molecule size. Induced by thermal load, radiation or reactions with oxygen, ozone or water it comes to chain scission, cross-linking or formation of cyclical bindings. The main changes due to chemical ageing can be summarized in three groups [110, 111]:

1. *Change in molecular structure*: reduction of the molecular weight; variation in molecular weight distribution; formation of branches or cross-linking
2. *Formation of functional groups*
3. *Separation of low molecular weight by-products*: depolymerisation; separation of side groups

In combination with heat and oxygen it comes to *thermo-oxidative* degradation, while the decomposing effect in the presence of water is called *hydrolysis*. Within the process of LS, working at temperatures close to the polymers' melting point, the *thermally induced* ageing or degradation might be the most relevant. Due to the increasing shrinkage of the atoms at higher temperatures, it comes to splitting of the main chains of the macromolecules leading to a shortening of the chains in the first stage of *thermal degradation*. The chain scission preferably emerges at weak links of the polymer chains and is statistically distributed over the whole molecule. Therefore, not only short polymer chains are formed, it also comes to the formation of low molecular weight, volatile decomposition products such as methyl or hydrogen groups. The resulting products can promote the further oxidative breakdown possibly introducing cross-linking or ring

formation increasing the overall molecular mass of the polymer [110]. During the degradation of polymers, for example for polyamides, it can come to chain scission and chemical post cross-linking in addition increasing the molecular weight and the viscosity of the material [112].

A pure thermally induced degradation of macromolecules, the so called *pyrolysis*, can only take place in an inert atmosphere in the absence of oxygen and water. In practice this process is usually accompanied by oxidative reactions and hydrolytic splitting of polymer bonds. Besides temperature, the thermal degradation is dependent on the chemical composition and therefore the intermolecular binding energies of a polymer [113, 114].

Despite chemical ageing processes, *physical* ageing can lead to reversible as well as irreversible changes to the microstructure, molecular order, concentration ratios of certain components or the outer form and structure as well as the physical properties of a polymer. It does not affect the chemical composition of the macromolecules. These physical changes can be the following [91, 115]:

- *Relaxation or decrease in physical tension*
- *Post-crystallization: change in degree of crystallization and characteristics of crystals*
- *Segregation or phase separation in multi-component systems*
- *Loss of plasticizers due to diffusion out of the polymer*
- *Agglomeration: becomes apparent in the polymer in the form of efflorescence or the sweat out of single components*

Physical ageing that specifically influences the polymers morphology often appears when it is cooled down from a temperature above its T_g to a temperature that is lower than its T_g . The polymer loses its thermodynamic equilibrium due to its increased entropy or the enlargement of the specific volume [84, 116]. This material state is reversible upon melting it again [109].

Post-crystallization of semi-crystalline polymers is favoured at higher temperatures but it can also be present at room temperature for thermoplastic

elastomers or rubbers. Thereby, post-crystallization leads to an increase in the degree of crystallization, the thickness of the lamellas as well as a denser packing between amorphous and crystalline areas. Orientations of macromolecules or physical tension between them that emerged during processing of a polymer, e.g. injection moulding, do settle at temperatures above their T_g but go hand in hand with shrinkage of the material [91].

The chemical and physical ageing phenomenon can have an impact on the *material characteristics* and the *part performance*. Visible and measurable effects can be [109, 113]:

- *Deformation or crack formation:* i.e. due to tension or fatigue
- *Change of mechanical properties*
- *Change of melt rheology*
- *Different shrinkage behaviour*
- *Fracture formation:* due to local embrittlement or fatigue
- *Discolouration*
- *Change in surface gloss level*
- *Different chemical performance in terms of dissolving*

In principle, chemical ageing processes lead to a change in the molecular composition of the polymer which are linked directly to its mechanical properties, such as tensile or bending strength, elongation at break and toughness [76]. Alternatively, mechanical performance is also influenced by physical ageing.

Due to the formation of functional groups induced by for instance thermal degradation a discoloration can occur, in addition to changed electrical conductivity, whereas the separation of components with a low molecular weight leads to odour formation and different mechanical properties. Most importantly with respect to the LS process, chemical changes can influence the flow characteristics of the polymer melt and its viscosity as it affects its molar mass. A clear relationship between molar mass and the zero viscosity is often described by the power law in Eq. 14 [91, 117].

$$\eta_0 = K \cdot M_w^{3,4} \quad \text{Eq. 14}$$

η_0	Zero Viscosity	[Pas]
K	Constant	
M_w	Average Molar Mass	[g/mol]

From this mathematical relationship it becomes obvious that even a slight modification of the molar mass due to thermal loads can highly influence the viscosity of the polymer melt.

2.2.10 Ageing Behaviour of Thermoplastic Polyurethanes

Most polyurethanes show a moderate thermal stability degrading at temperatures from 200-300°C [74, 76]. In general ester-based thermoplastic elastomers show enhanced resistance towards oxidation, whereas, ether-based TPEs are more resistant towards hydrolysis while showing more pronounced oxidative reactions when exposed to thermal loads in atmospheric oxygen [118, 119]. The thermal weak point of polyurethanes is the hard segment of the macromolecules, the urethane bond. It becomes unstable and tends to dissociate at elevated temperatures [120]. Grassie *et al.* [121] examined the thermal degradation of polyester based polyurethane with a variable hard and soft share and found that for polyurethanes with a negligibly low share in soft segment the decomposition peak occurs at around 308°C. Their thermal stability was increasing to a maximum of 400°C with a polyester content of 90.7 % building the soft segment of the polyurethane. The same trend in the polymers' degradation behaviour could be observed in thermogravimetric analysis (TGA) (10 mg per sample, Heating Rate of 10K/min) under dynamic nitrogen supply (70 ml/s) as the macromolecules degraded at significantly lower temperatures for TPUs with a higher share in soft segment compared to the lower proportion of polyester [121]. At the same time, the heating rates applied in these standard analysis methods might not be quantitatively transferrable to the dynamics within laser sintering, the principle context of the material composition at higher heating rates, though, should be given. Further TGA measures were undertaken by Petrovic *et al.* [122] in analysing the effect of different soft segment chain lengths and concentrations

on the activation energy of degradation, pointing out that the initial process of the loss in mass is dominated by the hard segment degradation. To this end they noted that the interpretation of the results on the complex decomposition processes of segmented polyurethane is difficult when trying to take the structure-composition-relation into account. However, it can be concluded from these observations that polyurethane-based polymers with a higher share of soft segments show a lower initial mass loss and the onset temperatures of thermally induced degradation are higher under the applied conditions.

A distinction on thermal decomposition of polyurethanes has to be made depending on the surrounding atmosphere the process takes place in [123]. For decomposition in nitrogen atmosphere there are two pathways to be considered and within oxygen atmosphere, three pathways. In the first decomposition stage in a nitrogen atmosphere, dissociation of isocyanate groups under formation of CO_2 occurs. In the second stage the decomposition products between polyester and polyether base polyurethanes differ considerably from each other. As a consequence, polyether based TPUs form water, hydrogen cyanide, acetonitrile and a mix of 1,4-butanediol and polyether bonds. Polyester based TPUs, however, create a broad variety of decomposition products, mainly including methane, water and nitrile cyclopentanone. During the decomposition of the urethane bond it must be differentiated between two substantial processes. These are the *depolymerisation* back to its initial components alcohol and isocyanate and the *splitting* of urethane's C-O bond in a cyclical mechanism under the formation of primary amines, olefin and CO_2 [105, 124]. Other studies report on the development of secondary amines under the separation of CO_2 in a second step [125, 126].

Amongst others, the temperature ranges of the single pathways of decomposition are dependent on the chemical composition of the polyurethane. The three major steps of TPU decomposition are given below [125, 127]:

- *Dissociation: rearrangement of hydrogen to isocyanate and alcohol*

$$-R-NH-CO-O-R' \rightarrow -R-NCO + HO-R'$$
- *Dissociation into primary amines, olefin and carbon dioxide*

$$-R-NH-CO-O-R' \rightarrow -R-NH_2 + CO_2 + CH_2=CH-R'$$
- *Formation of secondary amines under separation of carbon dioxide*

$$-RNH-CO-O-R' \rightarrow -R-NH-R' + CO_2$$

The thermal degradation under formation of (often yellow) fume was observed by Woolley [128]. He found that at temperatures between 200-300°C rapid loss of the tolylene diisocyanate unit occurred under the development of a volatile nitrogen containing yellow smoke leaving a polyol residue. With a further temperature increase the molecules increasingly split into low molecular weight products with fume containing nitrogenous, toxic molecules like acetonitrile or hydrogen cyanide. These findings were later supported by other authors whom examined the thermal decomposition of PU with TGA-MS (thermogravimetric analysis coupled with a mass spectrometer) [129, 130]. Moreover, the yellowing of polymers exposed to high thermal loads is a known phenomenon. Shieh *et al.* [105] investigated the thermo-oxidative decomposition of a thermoplastic polyurethane based on 4,4'-Diphenylmethane Diisocyanate (MDI) and found that it shows a tendency towards yellowish to brownish discoloration. The studies have shown that this is referring back to a rearrangement of the conjugated double bonds of the single molecule chains. They also observed another important effect, the scission of molecule chains into small components of TPUs during thermal decomposition. The thermally induced chain degradation that leads to a reduction of the molecular mass was detected and verified using gel permeation chromatography (GPC). The molecular weight reduction increased

with duration and temperature of the thermal stresses under both nitrogen and oxygen atmospheres.

2.2.11 Ageing Behaviour of Polymers in Laser Sintering

As it is highly connected to the process stability and efficiency as well as the quality and properties of parts produced in LS, the ageing mechanisms of polymer powders for LS is an often discussed topic and an important field of AM research in recent years [24, 131, 132]. Therefore, this section discusses the current state of knowledge on the ageing of LS polymers. As polyamides are the most commonly used materials in LS, the majority of previous literature has focused on this material. In addition the current state of research regarding the degradation of TPEs within LS will be discussed.

During LS the polymer often spends hours close to the crystallite melting point and is therefore exposed to high thermal loads. Although the process is running in an almost inert atmosphere it results in ageing of the polymer powder hindering its reuse for subsequent production cycles. In order to guarantee reproducible part properties, a “refresh rate” (defined as the ratio between virgin and used material) of around 50% for PA12 has proven itself in the past [132, 133]. The ageing or degradation effects manifest themselves in a decomposition of the polymer. Chemical changes due to ageing are even further supported by the oxygen and water molecules contained within the polymers. Kühnlein *et al.* [132] described the ageing process of polyamides that tend to chain scission as well as chain branching or cross-linking undergoing recombination processes starting with the formation of radicals at temperatures close to the melting point. The radicals emerging in this so-called auto-oxidation process can continue to react in different ways and build out cross-linking or chain scission. When two radicals recombine it comes to cross-linking that coincides with an increase in molecular weight and termination of the reaction [134]. Accordingly, a shift in crystallization and crystalline melting temperatures was determined, two key parameters for stable processing in LS of semi-crystalline polymers. Depending on the type of polymer applied, chain breaking or cross-linking dominate the oxidation process. Generally, chemical and physical ageing processes are manifested in changing melting, crystallization and flow characteristics of the polymer melt [135].

Pham *et al.* [24] investigated the effects of the deterioration of polyamide powder during laser sintering. They found that powder with a lower melt flow rate (MFR) produced a poor ‘orange peel’ texture and a higher shrinkage. For PA2200 they proposed that an acceptable powder quality, which would guarantee a relatively good surface finish and the absence of ‘orange peel’, is a blend of virgin and used powder with a MFR higher than 25–27 g/10 min .

Refreshing the PA powder with virgin material helps to control the material state but also leads to inhomogeneous powder compositions. In another publication, Kühnlein *et al.* [135] showed that the storage of the PA powder in an oven with conditions aligned to the one in the build chamber of a LS system lead to distinctive changes in particle size distribution and the corresponding bulk behaviour. It was shown that there was a decrease in mean particle diameter [135]. A study published in 2012 by Wegner *et al.* [21] investigated the ageing of PA 12 in the LS process over four ageing cycles in an EOS Formiga P100. The effects on the powder properties were measured with the Hausner ratio (HR) on bulk scale, melt flow was analysed by means of melt volume rate (MVR) and mechanical properties were measured using tensile testing. A significant increase in MVR with an increasing number of processing cycles was found due to cross-linking and post-polymerisation reactions. The sharpest drop in MVR at around 200 cm³/10 min equalling 55% of the initial value of the virgin powder was reached in the first ageing cycle that lasted 25 hours. This significant decrease of the MVR over ageing cycles is the result of cross-linking and post-polymerization reactions [21]. After a processing time of 75 hours the value for the MVR decreased to a lesser extent and levelled off at 60 cm³/10 min. In characterising the powder flow they found a continuous increase in HR that exceeded the threshold from high flowability to reduced flowability at a value of 1.25 in the second ageing cycle. Similar to the MVR results, the most rapid increase in HR took place from virgin material to powder that was processed one time. The observed changes in the flow behaviour were explained by the change in particle size distribution (PSD) and particle shape. Moreover, they found that the mechanical properties of the manufactured specimen changed with increasing processing cycles. Depending on the energy density applied, the ultimate tensile strength (UTS) for specimens built in the x-y-direction dropped

more or less rapidly from 50 N/mm² (virgin material) down to 30 N/mm² (four times processed material) and so did the Young's modulus as it decreased from 1800 N/mm² down to 1100 N/mm².

This correlates with another study published by Kühnlein *et al.* [136] investigating the effects on mechanical properties of PA12 (PA 2200 by EOS) being conditioned at building temperatures for different periods. Young's modulus and percentage elongation at break (%EaB) decreased over multiple processing cycles due to the ageing induced changes of the material such as a shift in the crystalline melting towards higher temperatures leading to insufficient melting.

Similar experiments examining the changing powder and part properties of PA12 (DuraForm®PA by 3D Systems) over a build time of 300 hours under the influence of varying laser power (high, medium, low) have been carried out by Choren *et al.* [131]. The objective was to determine the maximum powder life cycle. An increase in the laser power relative to its ageing state was aimed to maintain part quality. The laser power was increased with additional ageing cycles in order to reach a constant degree in melting as viscosity increases. They found that the notched impact strength increased up to an ageing duration of 168 hours to then drop significantly after exceeding this point even at higher levels of laser power marking the point at which the ageing induced effects dominate the possibilities of energy input

The ageing and its corresponding recyclability scenarios of thermoplastic polyurethane during the LS process is sparsely reported in literature so far. In 2012 Plummer *et al.* [137] published a study on the recyclability of a TPU with respect to changing particle size distribution, melt flow as well as the polymer's thermal and mechanical properties. In the scope of the study four LS builds were performed and samples were taken after each build. The sample's recyclability was investigated by means of particle size analysis, differential scanning calorimetry, hot-stage microscopy of particle pairs, melt flow index, tensile test sample manufacture and tensile testing. It was concluded that the observed TPU showed that processing the thermoplastic polyurethane bed powder in LS was possible over the four builds without any significant degradation or reduction in properties.

2.3 Particulate Systems

As LS is one of the main powder-bed based additive processes, the materials used are solids consisting of fine particles with various properties. This section introduces important characteristics and interactions within such particulate materials, which take an exceptional position regarding their chemical and physical properties [138, 139]. Dependent on the environmental conditions, powders have a diverse range of properties in that they can deform elastically and plastically like a solid, flow like liquids under the influence of shear stress or can be compressed like gasses [140, 141]. Many of a bulk system's properties are highly dependent on the particle size. With increasing particle diameter the bulks' porosity and the inter-particle bonding strength decreases while flowability is enhanced. Generally, dry powders are considered non-cohesive or free flowing when their particle size exceeds 100 μm and show cohesive behaviour below that mark [142]. Serving as a value for quality standards within food or pharmaceutical industry, flowability is of high technical interest. Besides the particle size, flowability is influenced by many other factors. The most important ones are the chemical and physical properties such as particle shape, adhesive forces, surface quality, the proportion of fine grains and the environmental conditions the powders are processed in [139, 143-145]. With respect to the amount of fines, adhesive forces are of particular importance for the flowability of powders as it shows a functional dependence on the present adhesion forces. The adhesive forces almost behave inversely proportional to the particle size so that fine powders show a high tendency to agglomerate [143, 146]. Thus, resulting from inter-particle interactions a majority of fine bulk materials indwell a tendency to form agglomerations and insufficient flowability leading to difficulties during processing [147].

2.3.1 Particle Characteristics

The field of granulates made up of large sized particles is well studied, while the physics of very small particles such as fine or superfine powders concerns the majority of industrial applications [148, 149]. The following particle properties are normally studied and used for correlation with bulk behaviour, as they are

known to affect product performance, processability, stability and appearance of the end product and are [150-153]:

- *Particle size*
- *Size distribution*
- *Shape*
- *Surface morphology*

Not only does the shape of particles influence the performance of bulk solids in many ways, it also can be characterized by a wide range of values and parameters that are described elsewhere [154, 155]. The values to quantify shape applied within this project were dependent on the analysis method applied and the most reliable ones were derived within a preliminary sensitivity study (see appendix A.1.1). Many researchers argue that particle size, size distribution and shape has a major influence on the rheological properties of powders [156-158], while others say particle shape and surface texture primarily impact the bonding mechanisms and the surface energy between the particles and as a result influence it's rheology [153, 159]. The mechanical strength of granular medium relies on friction between particles. In general, angular particles with low sphericity tend to mobilize more friction than rounded particles. On the other hand, rounded or spherical particles in often tend to pack together more effectively to create denser bulks [160, 161]. In the subsequent sections a deeper insight into particle interactions is given.

2.3.2 Inter-Particular Forces and Interactions

Inter-particular forces are occurring between particles of a bulk system. Although there is significant published work existing on this topic and research activities have been carried out for decades, especially within the pharmaceutical industry, it is still impossible to accurately predict the forces between fine powders [144, 162, 163]. One of the reasons is the lack of knowledge on the following topics [148, 164]:

- *The exact magnitude of the molecular forces involved*
- *The exact morphology of the contact*
- *The mechanical properties of the materials in contact*

In addition, experimental results have shown that the figures indicate high deviations up to a factor of 1000 in terms of total force that can occur for particles of the same size. Due to the experimental difficulties during analysis these high deviations are not yet explained in any detail neither are they satisfactorily explained. Therefore, more indirect, secondary factors, such as particle size distribution or shape are normally studied and used for correlations with the particle interactions. In the following sections the most important definitions and forces affecting the bulk performance are going to be explained [165, 166].

Bonding surface area and surface energy

The dominating bond mechanism and the surface area over which they can interact are the two primary factors on the inter-particular interactions and the behaviour of the bulk systems i.e. in terms of packing [165, 167, 168]. The term *bonding surface area* describes the effective surface over which the inter-particular interactions take place. In the case of solid bridges, this surface area can be defined accurately and corresponds with the true contact area between two particles. On the contrary, the surface area for intermolecular forces is hard to define and can seldom be estimated from any direct measurement especially for fragmented or even porous particles [165, 169, 170]. Thus, in addition, the surface area is a function of secondary factors such as particle size, particle size distribution as well as plastic and elastic deformation [165]

In general forces or *bonding mechanisms* within a particular system can be divided into interactions due to contact that is established between adjacent particles (referred to as solid bonds) and bonds that act over distances (referred to as intermolecular bonds).

Van der Waals forces

The most important and predominant attraction forces between solid surfaces, such as powder particles, are a consequence of the attraction between molecules and are called van der Waals forces. In dry bulk systems they are omnipresent and dominate the inter-particle interactions [171, 172]. Van der Waals forces can be understood as a class of molecules possessing different types of electronic configurations giving them dipole character and consequently attract each other. They conclude three types of forces - the Debye-forces (induced forces) arising between one induced and one permanent dipole, the Keesom-forces (orientation forces) between two permanent dipoles and the London-forces (dispersion forces) [164, 173]. London, whose theory is based on the interactions between two induced dipoles, obtained the following equation by a quantum mechanical treatment of this phenomenon for the mutual attraction energy V between two molecules.

$$V = -\frac{3}{4} h \nu_0 \frac{\alpha^2}{d^6} \quad \text{Eq. 15}$$

V	Attraction Energy between two Molecules
α	Constant (polarizability)
ν_0	Characteristic Frequency (response towards i.e. electromagnetic radiation)
d	Separation Distance
h	Planck's Constant

These dipole-dipole forces have a short range of approximately 100 nm and their attraction force decreases with the sixth power of increasing separation distance [174, 175].

By assuming the individual intermolecular interactions are additive, a microscopic theory is given by Hamaker. The mathematical expression calculates the interaction energy between two semi-infinite solid bodies at a

separation distance H , by summarizing all the possible individual molecular interactions. The macroscopic material properties of the two solids observed are taken into account by the Hamaker-coefficient [176]. Another macroscopic approach for the interaction energy between solid bodies in vacuum and in a liquid medium based on the optical properties of the interacting solids is given by Lifshitz [171, 177]. Both theories lead to a measure for the van der Waals forces. In Eq. 16 the relation between the material-constant A following Hamaker and the Lifshitz-coefficient, $\hbar\bar{\omega}$ is given:

$$A = \frac{3}{4\pi} \hbar\bar{\omega} \quad \text{Eq. 16}$$

A	Hamaker-coefficient (a measure to establish the magnitude of the dispersion forces)
π	Circle Constant Pi 3.1415...
$\hbar\bar{\omega}$	Lifshitz-coefficient

This theory today is accepted and from a physical perspective is more useful but hard to apply with the need for the additional optical data. Thus, generally the microscopic Hamaker-theory is applied. Van der Waals forces shall only be effective in case their contact distances are small and the particle size is below $100\mu\text{m}$, otherwise the weight forces prevail [175, 178].

Capillary forces due to moisture

Within highly humid environments it comes to adhesion of powders due to capillary condensation of the fluid in the gap between two particles at low separation distances as illustrated in Figure 17 [179].

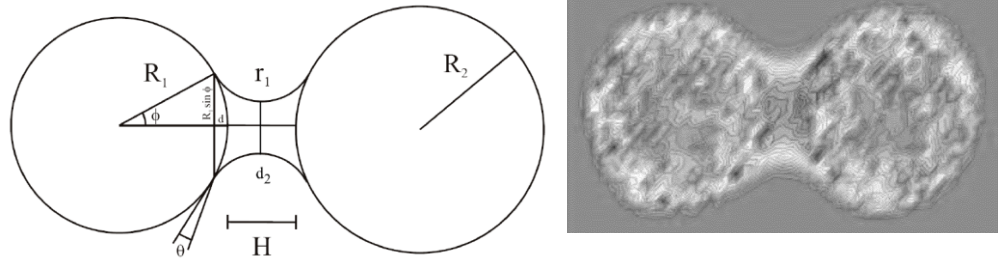


Figure 17: Capillary condensation of a liquid between two spherical particles with the radius R_1 and R_2 , adapted from [180] (left) and sketch for the water capillary formation between two silica nanoparticle, taken from [181]

While in dry bulk systems the previously described van der Waals forces prevail, the capillary forces replace them as the dominating attraction at an ambient humidity of approximately 60% [182, 183]. Unlike the van der Waals forces liquid bridge bonds can be “adjusted” by modifying the environmental conditions, such as temperature and relative humidity, and the properties of the liquid that is present in the free gas phase of air. Moreover, moisture bonds are more complex compared to van der Waals forces due to their static (surface tension) and dynamic (viscosity) characteristics. Surface tension can contribute both positively and negatively to a powder’s relative movement (flowability). However, increasing viscosity of the liquid always creates an opposing force to the powder’s movement reducing its flowability [172, 184, 185].

Electrostatic forces

Electrostatic forces can also have a strong influence on the cohesion of particles and their bulk behaviour due to triboelectric charging (particle-particle or particle-wall contact) causing potential differences between the particles resulting in charges and electrostatic forces. In principle the force F interacting between two charges Q_1 and Q_2 with the distance $d_{1,2}$ is described by the Coulomb equation as shown in Eq. 17.

$$F_{el} = \frac{1}{\pi \epsilon_0} \frac{Q_1 Q_2}{(d_{1,2})^2} \quad \text{Eq. 17}$$

F_{el}	Electric Force between two Point Charges
π	Circle Constant Pi 3.1415...
ϵ_0	Vacuum Permittivity/Electric Constant $\epsilon_0 = 8,854 * 10^{-12}$ Farad/meter
Q	Electrostatic Charge
$d_{1,2}$	Distance between two Point Charges

For triboelectric charges between a spherical particle of radius R having a charge Q interacting with an adjacent uncharged particle at separation H, the maximum electrostatic force on a particle is based on the classical Coulomb equation as follows [186]:

$$F_{el} = \frac{Q^2}{16\pi\epsilon_0 H^2} \left[1 - \frac{H}{\sqrt{R^2 + H^2}} \right] \quad \text{Eq. 18}$$

F_{el}	Electric Force between two Point Charges
π	Circle Constant Pi 3.1415...
ϵ_0	Vacuum Permittivity/Electric Constant $\epsilon_0 = 8,854 * 10^{-12}$ Farad/meter
Q	Electrostatic Charge
H	Separation Distance
R	Particle Radius

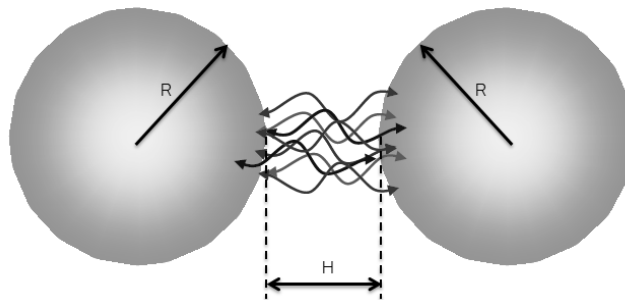


Figure 18: Electrostatic forces between two particles over a distance H following [187]

As a general remark, in powders the electrostatic forces on a particle are usually lower than the capillary forces for particles smaller than 100 μm and lower than

the van der Waals forces for particles smaller than 30 μm [148, 188]. Moreover, humid environments cause a discharge of the system and therefore lead to a significant reduction of the Coulomb attraction forces [162, 173, 189].

Solid State Bridges and Sintering

Besides adhesive bonds without elemental material connection, the connections creating solid state bridges, in particular enhance the binding strength between particles. They can arise from sintering or chemical reactions. Due to friction it can come to plastic deformation at roughness peaks and contact points within bulk powders sometimes locally even reaching the melting temperature of the material. Thereby, the areas of contact are increasing and lead to melt bridges [190, 191]. Alternatively, solid state bridges can also arise from increase in temperature promoting the mobility of the atoms that lead to diffusion processes as a consequence [192, 193]. The basics of sintering technology for a variety of materials are well described in literature [194, 195] so that the focus here is kept on polymer sintering. An inter-particle neck caused by sintering forces can become permanent and withstand breakage forces caused by the relative movement of solids and gases within the bulk system. This indicates how important the sintering behaviour of a material is during processing and for the mechanical capabilities of the manufactured parts. Thereby, the sintering process is faster at higher temperatures or pressures. The consolidation behaviour of two polymer particles was optically observed by Bellehumeur *et al.* in 1996 [196]. In 1949, Eshelby corrected the Frenkel model, which is based on Newtonian viscous flow under the action of surface tension, by satisfying the continuity equation. The model, subsequently referred to as Frenkel-Eshelby model, helps to quantify the subjective impression during the imaging observation of the particle coalescence as follows [196, 197].

$$\frac{x}{a} = \left(\frac{t\Gamma}{\eta a_i} \right)^{1/2} \quad \text{Eq. 19}$$

x	Half Neck Thickness
a	Particle Radius during Sintering
t	Sintering Time
Γ	Surface Energy
η	Viscosity
a_i	Initial Particle Radius

In Figure 19 this model is graphically described by assuming spherical particles.

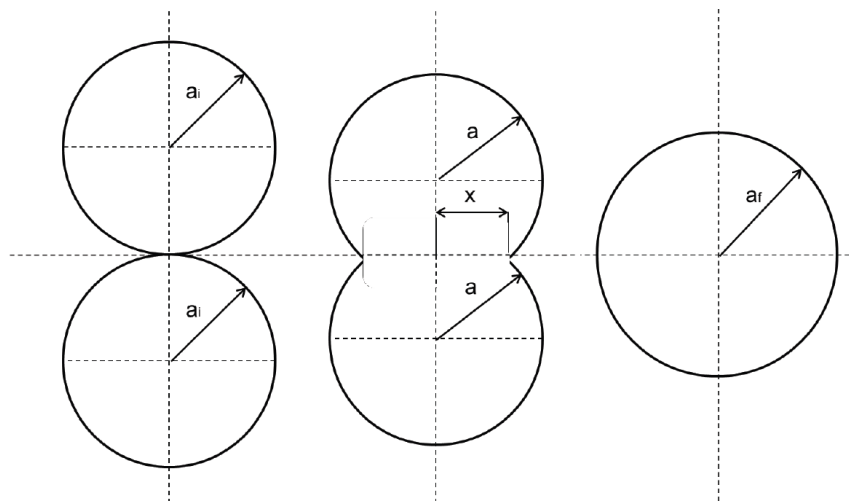


Figure 19: Idealized representation of two polymer particles' neck growth during sintering, adapted from [196]

The initial stage of the model describes the contact of the two solids, subsequently starting to build out a neck alongside with a reduction of their initial radius until a homogenous melt film originates in the final stage.

Mechanical interlocking

The term mechanical interlocking is used to describe the physical hooking and catching of particles leading to increased cohesivity within a bulk system. As depicted in Figure 20, this effect is highly dependent on the shape of the particles.

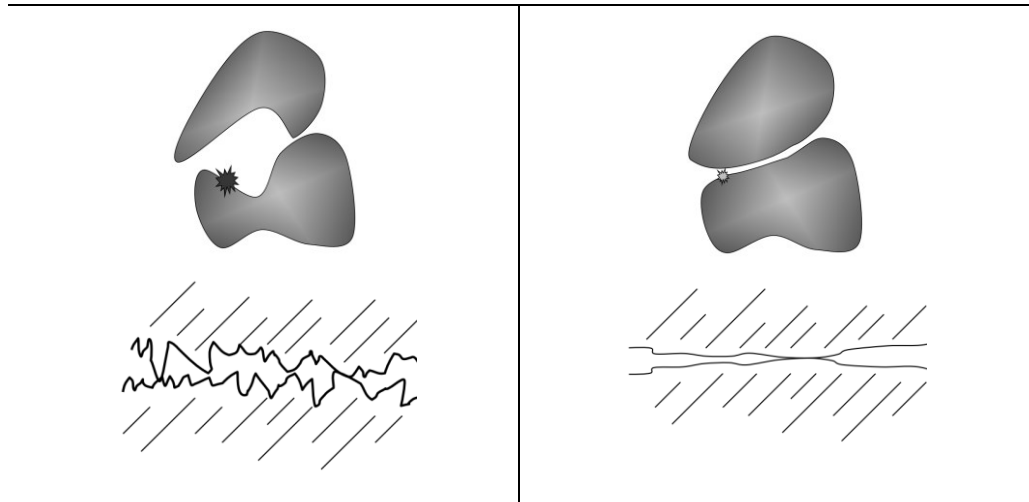


Figure 20: Representation of mechanical interlocking between two particles with irregular shape and surface exhibiting strong interlocking (left) and more spherical shape and smooth surface with weak interlocking (right), adapted from [187]

Irregular shaped particles with irregular surfaces have a higher tendency to interlock than spherical particles. A similar effect, more closely related to surface roughness, can also cause frictional forces that inhibit powder flow [158, 198, 199].

Comparison between the inter-particle Forces

As described in the above sections, particle interactions are of a complex nature and highly dependent on a variety of characteristics. As an illustration for the magnitude and range of inter-particle forces, with regards to bulk properties such as particle size and separation distance, there are several idealized models (representing interactions between plate-plate, sphere-plate, sphere-sphere) existing in literature [144, 200]. The models relevant for the scope of this thesis and the LS-process are the idealized models for sphere-plate and particle-particle interactions and are going to be described in more detail within this section. A comparison of the different inter-particle forces in dependence of the particle diameter for the particle-wall adhesion is shown in Figure 21. The hatched area indicates the range in particle sizes for LS polymer powder between 10 – 100 μm with a percentage of particles below 10 μm being less than 3%. The capillary forces consisting of liquid moisture bridges represent the dominating force in a humid environment. For dried materials the van der Waals forces dominate the bulk behaviour for particles smaller than 90 μm . For particles exceeding this mark the electrostatic forces surpass the van der Waals interactions. For the

sphere-plate relationship the weight forces have a negligibly low influence. In theory and under ideal conditions every smooth sphere with a diameter below 1 mm would have to stick on a flat and ideally smooth wall. All adhesive forces have in common that they linearly decrease with decreasing particle size [147, 201, 202].

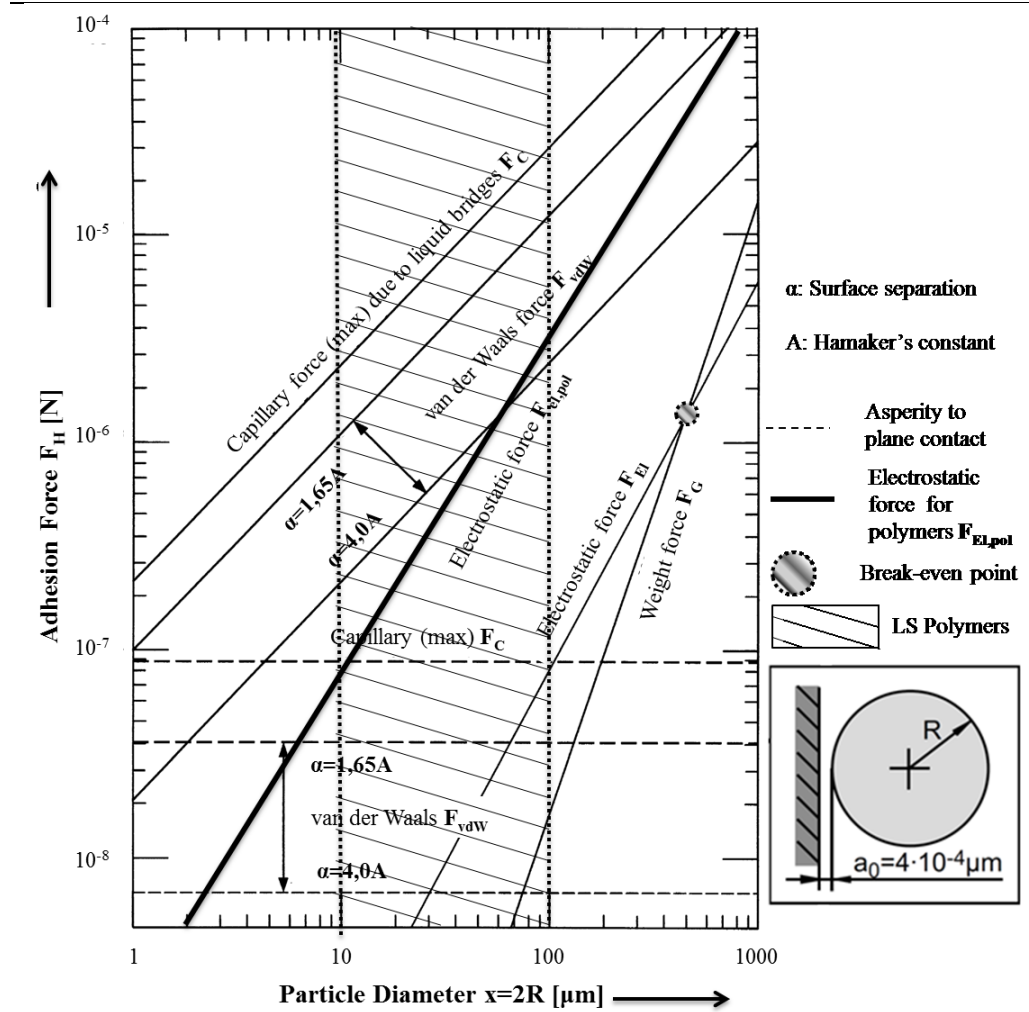
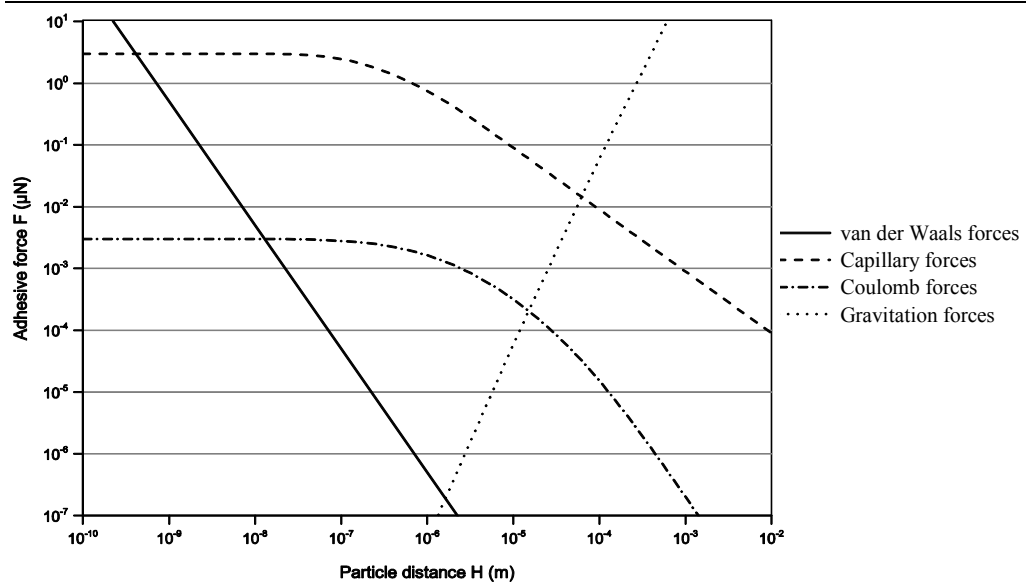


Figure 21: Magnitude of the adhesion forces depending on particle diameter, adapted from [32, 144, 188, 201]

For a powder bulk and the interactions between its particles that directly influence its performance i.e. flowability and packing, a model referring to the sphere-sphere relation is of higher relevance [203, 204]. A comparison of the adhesive forces in the sphere-sphere-model between two particles in a separation distance H is given in Figure 22. It shows that that besides the nature of the force the distance between the interaction particles is decisive for its strength [180].

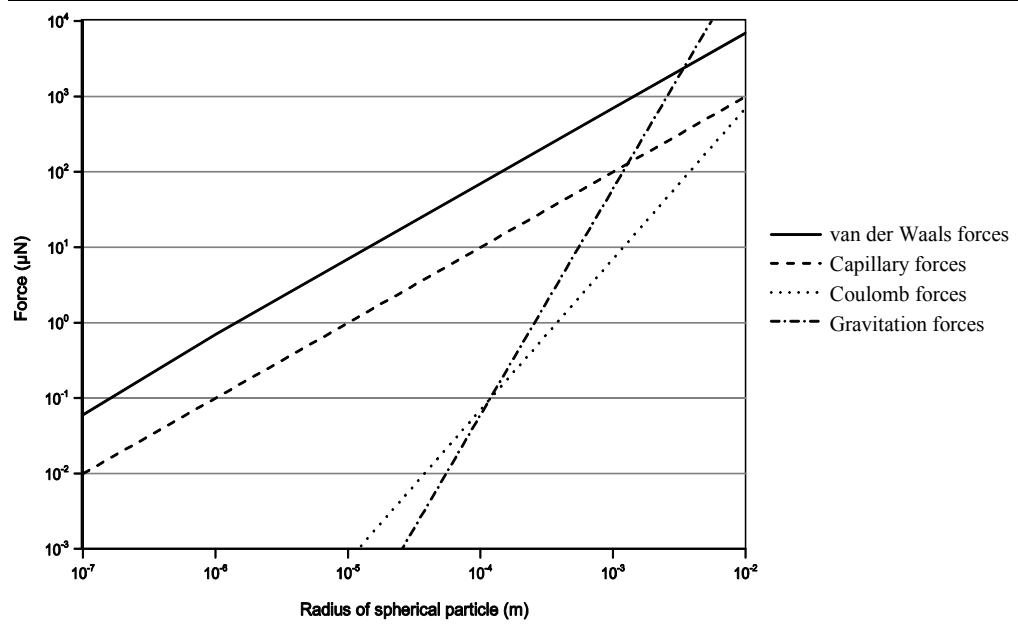


Particle radius $R_1 = R_2 = 5 \text{ } [\mu\text{m}]$; Hamaker-constant $A = 8 \cdot 10^{-19} \text{ [J]}$; surface charge density $\sigma_0 = 100 \text{ [e} \cdot \mu\text{m}^{-2}]$; specific density $\rho = 1.48 \text{ [g} \cdot \text{cm}^{-3}]$; surface tension of water $\gamma = 72.0 \text{ [mJ} \cdot \text{m}^{-2}]$

Figure 22: Comparison of the adhesive forces in dependence of particle distance H presented by the sphere-sphere-model, adapted from [180]

The van der Waals forces again are the dominating force for small particle distances H decreasing rapidly with increasing separation distance and reach a negligibly low magnitude at around 100 nm. In contrast, the electrostatic forces are effective up to distances around 1mm, though their amount is approximately 2 magnitudes lower than for van der Waals forces. Electrostatic forces do have a positive influence on compaction processes but are not of major importance at very close particle contacts as they are dominated by van der Waals forces. In moist powders, capillary forces due to liquid bridges are the dominating forces. For dry bulk materials, the gravitational force surpasses the impact of Coulomb forces at distances at around 10 μm [200, 205].

Not only the separation distance but also the size of the interacting particles does impact the predominant forces. At constant separation distances it becomes obvious that the van der Waals forces are the dominating forces in bulk systems as shown in Figure 23.



Particle radius $R_1 = R_2 = 5 \text{ } [\mu\text{m}]$; at constant separation distance $H = 4 \cdot 10^{-10} \text{ [m]}$; Hamaker-constant $A = 8 \cdot 10^{-19} \text{ [J]}$; surface charge density $\sigma_0 = 100 \text{ [e} \cdot \mu\text{m}^{-2}]$; specific density $\rho = 1.48 \text{ [g} \cdot \text{cm}^{-3}]$; surface tension of water $\gamma = 72.0 \text{ [mJ} \cdot \text{m}^{-2}]$; contact angle towards water $\theta = 5 \text{ } [^\circ]$; aperture angle $\varphi = 20 \text{ } [^\circ]$

Figure 23: Inter-particle forces in dependence of particle radius at constant separation distance, adapted from [180]

The influence of the gravitational force behaves proportional to the increase in particle radius and according to the theoretical sphere-sphere-model begins to dominate the adhesive forces initially at particle sizes of approximately 4 mm. Previous studies, though, have shown that this effect could occur at much smaller particle sizes, which is due to the idealized approach of the model not taking into account the particles' surface roughness. Other studies, investigating the packing of coarse particles, have been primarily concerned with particle packing dominated by the gravitational force, which under certain packing conditions, is mainly controlled by the particle size and shape [31, 206]. Moreover, with increasing surface roughness, in turn increasing particle distance, the strength of the adhesive forces (especially the van der Waals forces) relative to the gravitational forces decreases and packing increases [174]. Within engineering applications, the capillary and the van der Waals forces have been identified as the most important [207]. These two forces of cohesive nature cause restricted movement of particles and thus often lead to formation of agglomerates, in turn affecting the packing of bulk powders remarkably [182, 208]. How to take these forces into account and especially how to control them during processing of

powders is one of the biggest challenges within powder technology [180, 209, 210].

Effect of Flow Additives

The relationship between adhesive forces, the bonding surface area and the separation distance has been taken advantage of within the pharmaceutical industry [147]. Thereby, the inter-particle forces have been reduced by the addition of nano-scale particles. Former studies attributed their positive effect on powder flowability to a “ball-bearing-effect” which might be applicable for powders that tend to mechanically interlocking [144, 211]. Today it is known that flow regulators function as an artificial surface roughness and lead to a reduction of the adhesive forces by increasing the separation distance and reducing the contact areas the forces would be able to be effective. There is limited data existing on the field of research regarding flow regulators and therefore their application is mainly based on empiricism [146, 211, 212]. Figure 24 gives a qualitative representation of the effect of flow regulators for two different particle pairs. The Flow Energy in mJ, measured with a powder Rheometer, thereby equals the force and torque absorbed by a blade moving through a defined volume of powder over a certain distance. The Flow Energy behaves inversely proportional to the inter-particle adhesive forces indicating enhanced flow at low flow energy [213].

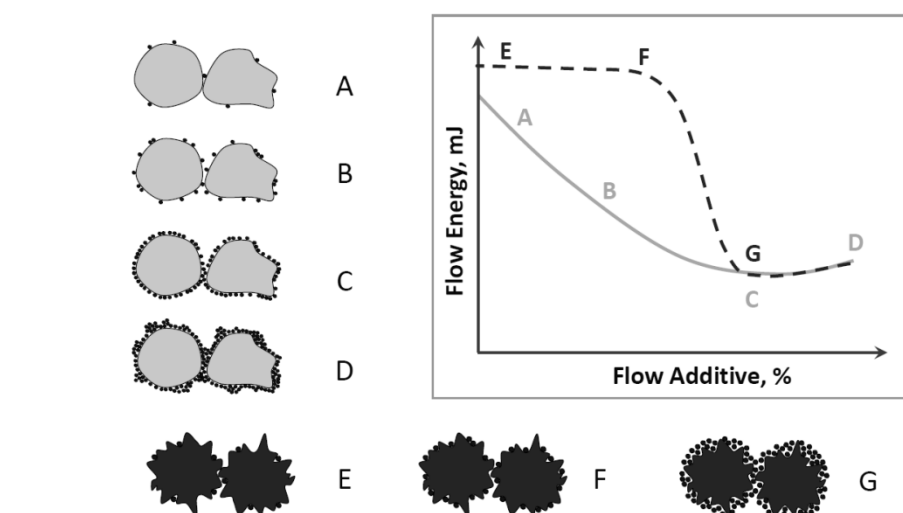


Figure 24: Flow Energy vs. Additive & Morphology, adapted from [187]

From A to C the degree in surface covering with a flow agent is increased for rather spherical shaped and smooth particles. As described before, for these types of particles the van der Waals are the dominating adhesive force and their adhesive powder is decreased with an increasing amount of flow additives due to the increased separation distance of the particles. As shown in Figure 22, the magnitude of the adhesive forces decreases rapidly with increasing separation distance as to be seen from A to B [145, 180, 214]. At C it reaches an optimum as the inter-particle forces can't be effective anymore over this distance. With a further addition of flow additive they lose their spacing effect and begin to interact underneath each other, turning around their operating principle. Besides the fact that flow agents or glidants tend to have poor flow themselves and they can be difficult to readily disperse onto host particle surfaces uniformly as indicated by sample D [180, 215, 216]. By comparison, the particles marked by the characters E to G represent rather rough surfaces and jagged particle shapes. As surface roughness represents a "natural" space between particles reducing the van der Waals forces can be reduced for particles that are smaller or similar in size compared to the asperities. For particles larger than their asperities the particle size and its corresponding inter-particle adhesive forces as well as the mechanical interlocking also play an important role [217-220]. In the last case the particles illustrated by the characters E to F are not influenced by the flow additive as either their adhesive character or the friction between the particles are still dominating their flow regime to rapidly drop from F to G reaching their optimum amount allowing the particles to slide past each other more easily.

Summary – Powder Characteristics affecting Bulk Behaviour

Identifying the flow properties of particulate materials constitutes a complex and difficult area of research due to the amount of parameters forming the bulk behaviour [179, 221]. In order to give an overview of the particle characteristics and material properties influencing powder flow, Figure 25 concludes the most important interactions.

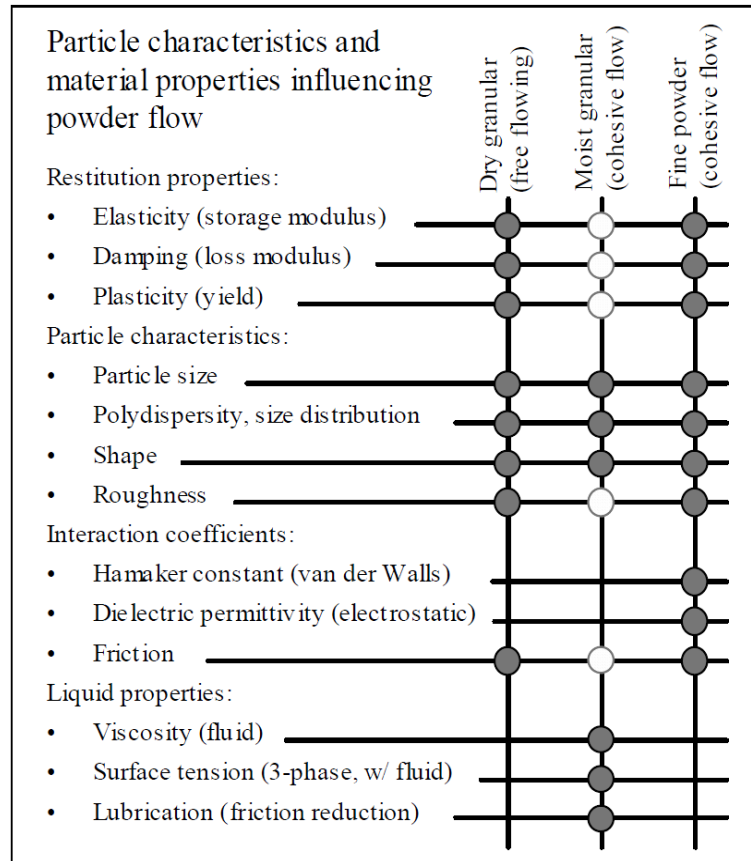


Figure 25: Overview of particle characteristics and material properties affecting the various types of bulk flow behaviour (the darker connection points indicate significant relationships), from [186]

The models that have been introduced in the previous sections are helpful for building correlations and are used to predict flow behaviour for example for scale-up in industrial applications. However, due to the fact that every material might behave differently from what the models predict or what former data on similar material indicates, the effects of particle size, size distribution and the consolidation on bulk flow are not evident from single particle characterization. In reality it requires statistical analysis on ensemble particle packing to create useful linkages between micro-scale characteristics and bulk behaviour [222].

2.4 Major Findings and Knowledge Gap

Compared to the world of conventional polymer processing, the existing database for LS, mainly based on PA12, only touches the surface in terms of materials available as well as the knowledge about the key process/material interactions, consequently the process requirements that have to be fulfilled. In

order to contribute to a deeper understanding of new polymers for LS as well as a substantial LS-database, alternative polymers have to be analysed to the same extent in order to gather an equal understanding. Furthermore there is still demand in finding the right process-adapted methods to analyse the process behaviour of polymers used in LS in order to reveal the important interactions as described in section 1.1. In the following sections the major gaps identified within the literature review are going to be addressed.

2.4.1 Pre-Process – Powder Interactions

As discussed in section 2.1.3, the importance and the magnitude of properties of the bulk material as well as the dynamic flow of powders processed in LS has only been observed in previous studies to a small extent. However, no investigations that were directly correlating and quantifying the bulk properties and its effects on part quality have been carried out.

The main fields of research identified here are:

- identifying suitable analysis for the quantification of the powder characteristics as well as their static and dynamic flow properties in order to reveal important interactions between process and powder
- experiments looking into correlating the obtained laboratory scale quantitative data with processing behaviour and quality of the resulting parts for validation of the magnitude of powder properties

2.4.2 In-Process – In-situ heating rates and effects on polymer during exposure

In addition to the deposition of powder, the temperature control as well as the actual melting of the material during the build are vital for the quality and the property profile of the manufactured parts [52, 56, 223]. The idealized process leads to the model of quasi-isothermal laser sintering in which melt and powder both exist alongside each other [224]. When taking a closer look at the thermal processes in LS, material properties such as glass transition, crystallization and melting rank among the most important ones [32, 225]. In order to detect these material properties current researchers apply DSC analysis at a heating rate of 10 K/min. Conventionally applied heating rates in other fields of research often range between 1 K/min and 20 K/min [226]. However, in the study at hand the

actual in-situ heating rates during LS were found to go up to 7,200 K/min depending on the material as well as the processing parameters and therefore differ significantly from the capabilities of conventional DSC runs [227, 228]. Thus, the data from the DSC at lower heating rates are not directly nor quantitatively transferable to the dynamics in LS as the melting and re-crystallization characteristics can change significantly at different heating rates and maximum temperature applied during the analysis [32, 229, 230].

The use of TPEs in LS implies different and new interactions and reaction mechanisms that demand for specific analysis. TPEs for example have a broader melting peak at lower overall crystallinity and the idealized scenario of the quasi-isothermal LS is not given for this type of polymer not holding the often described requirement of the “two-phase mixed zone” (see Figure 26) of typical semi-crystalline LS polymers such as PA12.

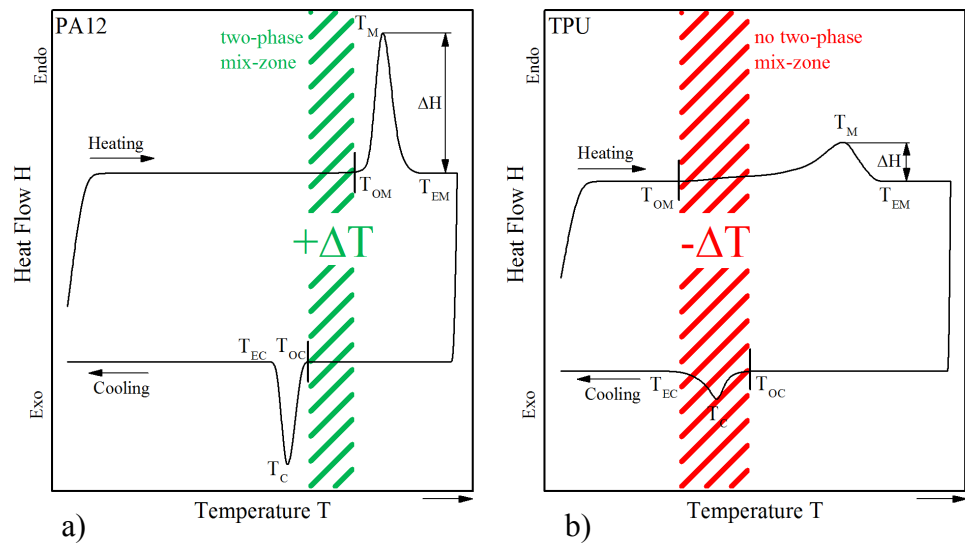


Figure 26: Schematic comparison of DSC run and the delta between onset of melting and onset of crystallization of a) PA12 and b) TPU, adapted from [32]

As a consequence, the effects of changing build chamber temperatures on the overall energy input and part properties need to be detected and described specifically for this type of polymer. As described in section 2.1.4, for this purpose the Energy Melt Ratio (EMR) has already been applied on three different TPEs by Vasquez [13]. However, only the effects of different energy densities applied during laser exposure on part properties were investigated but

no evidence has been presented whether the approach is valid for varying build temperatures.

The main fields of research identified here are:

- Determining the in-situ temperatures and quantification of the corresponding thermodynamic phenomenon especially the isothermal crystallization of the TPU compared to PA12 in a process adapted manner
- Experiments to assess the effects of varying processing conditions especially the build chamber temperatures on the part quality in terms of tensile properties and crystallinity

2.4.3 Post-Process – Ageing of LS Polymers

As introduced in section 1.2, the Post-Process observations in this thesis are considering the ageing behaviour of the observed TPEs. Similar to the In-Process, the current state of research is mainly based on PA12 powders.

Previous studies were useful in order to indicate the tendency of TPEs to ageing in the LS process but the numbers of processing cycles don't seem to be sufficient in order to represent an actual manufacturing environment that is striving for a high material efficiency and the accompanying reusability. In addition, it suffers from excluding the analysis of possible chemical or physical changes of the polymers observed. In consequence, there is an important gap in knowledge when it comes to the ageing of TPEs in LS.

The main fields of research identified here are:

- Investigation of the thermal stability, the potential chemical or physical changes and the powder life of TPEs as well as the qualification of suitable analysis.

3 Research Aim and Novelty

3.1 Aim of the Research

To evaluate the specific processing characteristics of thermoplastic elastomers (TPEs), a group of polymers novel in their use in powder bed fusion, throughout the laser sintering processing chain.

3.2 Objectives

The research objectives of this thesis are going to be presented following the logic of the LS processing chain as introduced in section 1.2 and are representing the essence from the understanding of the literature review (chapter 2). This holistic approach was applied aiming to determine the important interactions on the powder scale, material-process scale (in-situ LS) and the effects on the parts as well as the material quality after being processed.

3.2.1 Pre-Process

- To understand the effects of varying powder qualities on their static and dynamic bulk properties.
- To characterise the effects of powder properties on process and parts by interconnecting the bulk and flow behaviour with the part quality in terms of tensile properties, in-situ powder packing, thermal conductivity and part density.

3.2.2 In-Process

- To investigate the temperatures (in-situ LS) and the corresponding heating/cooling rates, in order to understand and quantify the thermodynamic phenomenon especially the isothermal, time-dependent crystallization in a process adapted manner. Consequently, disclosing the different crystallization behaviour between thermoplastic polyurethane and polyamide 12.
- To reveal the important process parameters during the processing of TPEs in LS in order to describe the material-process interactions and to evaluate a method allowing for prediction of part properties.

3.2.3 Post-Process

- To investigate the thermal stability of the TPEs at the in-situ processing conditions.
- To characterise the physical and chemical ageing of TPEs in LS in order to gain a deeper insight into the polymer ageing behaviour and the use of suitable analysis methods following that aim.

3.3 Methodology and Contribution to Existing Knowledge

As described throughout chapter 2, there is very little literature available describing powder behaviour of LS materials and how it affects the process as well as the parts' quality. In this study the magnitude of powder properties on processability as well as the resulting part quality is investigated as represented in Figure 27. This will help to contribute to the knowledge on requirements and design of new LS powders.

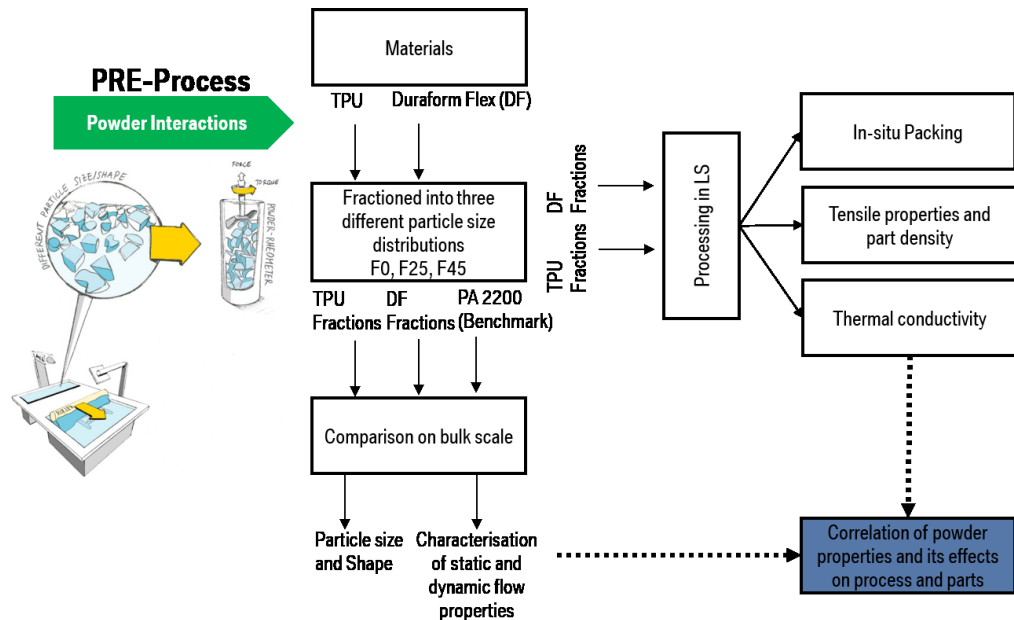


Figure 27: Overview of Pre-Process Objectives

Although there is significant understanding of the processing specifics and requirements for PA12 in LS, there is very little awareness of other polymer types, which not only hold totally different powder characteristics but also

various intrinsic properties such as melting and crystallization. By determining the in-situ heating and cooling rates as well as melting temperatures, the calorimetric differences between TPEs and a typical semi-crystalline PA12 are investigated for the first time by high speed thermal analysis.

Based on this increased understanding of the material behaviour a DOE employing an overall energy approach was derived as indicated in Figure 28. The effects of temperature control on resulting part properties were investigated in order to reveal the most influential process parameters and allow for prediction of part properties.

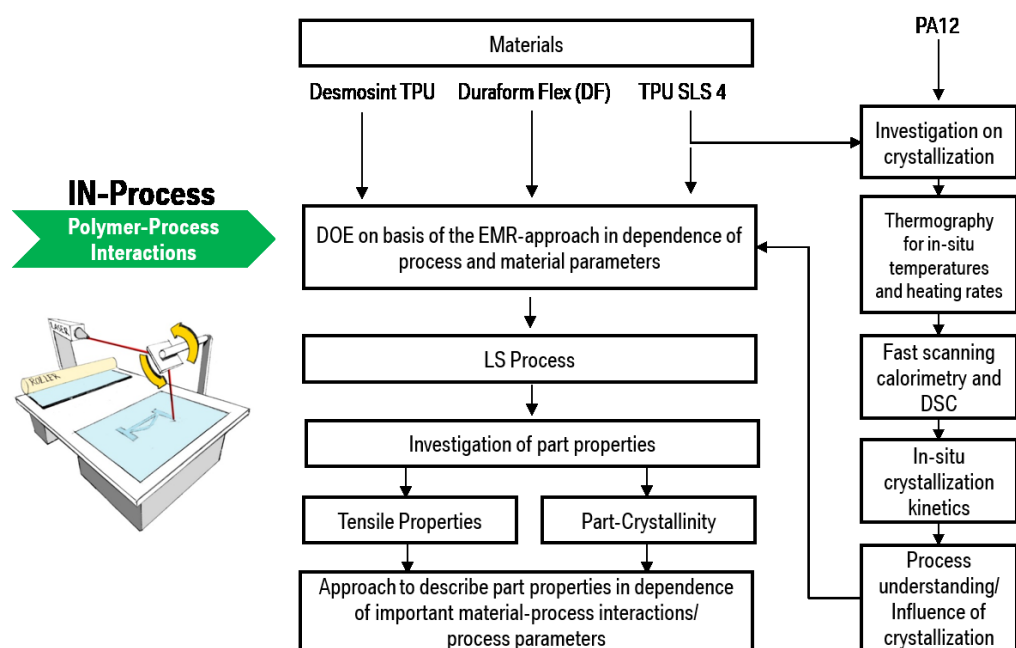


Figure 28: Overview of In-Process Objectives

Previous studies on ageing of TPEs within LS did not investigate the physical or chemical degradation effects. In this thesis these effects are examined by repeatedly processing the materials without refreshing them with virgin powder. The changes in part and powder properties as well as the changes of the material on a macromolecular scale served to validate and characterise the ageing behaviour. A schematic overview of the Post-Process execution is given in Figure 29.

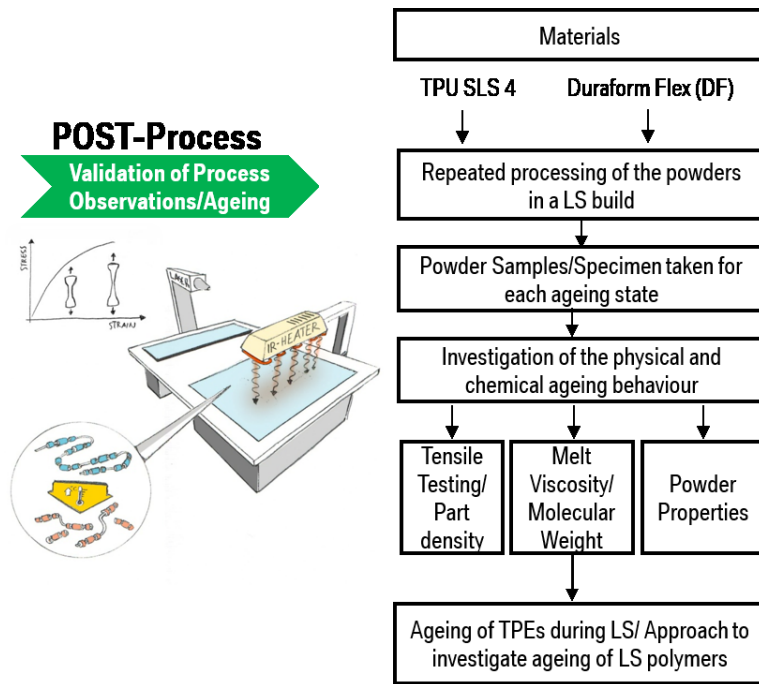


Figure 29: Overview of Post-Process Objectives

Consequently, the comprehensive analysis of *Pre-Process* conditions, *In-Process* parameters and *Post-Process* effects to understand the material requirements for successful laser sintering of new TPE-based LS polymers presents the novel contribution to existing knowledge. In addition, by investigating a new group of polymers for the use in LS applying process adapted analysis, this research contributes by furthering the knowledge on accessibility of alternative materials and feed into the existing LS database.

4 Experimental Methods and Analysis

In accordance with the overall thesis structure, this chapter introduces the experimental methods and the analysis applied throughout the initial as well as the principle investigations of the PhD studies.

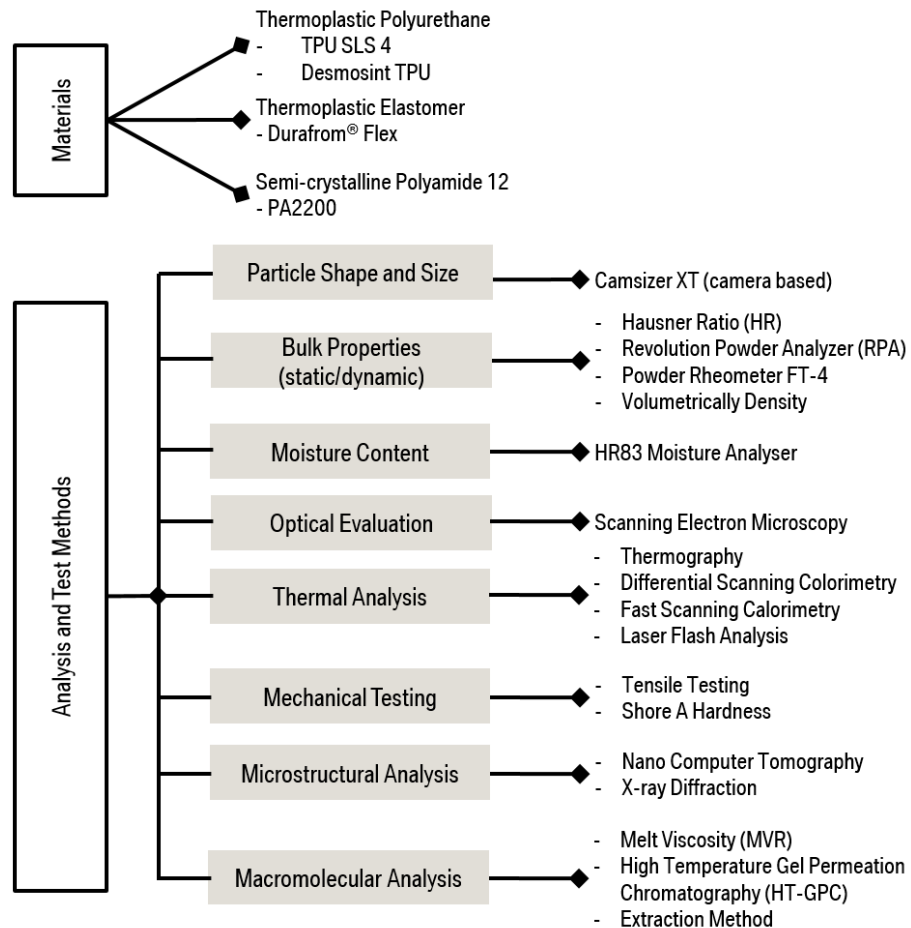


Figure 30: Experimental Methods used in this study

Figure 30 provides an overview of the materials and experimental methods applied in this study. The analysis methods used helped to characterise the materials prior and after processing and helped to characterise and validate the different experiments in terms of material properties and processing parameters.

4.1 Materials

The materials investigated in this study are introduced throughout this section and an overview is given in Table 4.

Trade name	Distributor	Polymer type	Investigated throughout
TPU SLS 4	non-commercial	TPU (thermoplastic polyurethane)	Pre-, In-, Post-Process Objectives
DuraForm [®] Flex	3D Systems	TPE-E (copolyester-compound) no official information available	Pre-, In-, Post-Process Objectives
Desmosint	Lehmann & Voss& Co.	TPU (thermoplastic polyurethane)	In-Process Objectives
PA2200	EOS	Polyamide 12	Pre-, In-Process, Objectives

Table 4: Materials investigated in this study

As previously introduced, the focus of the PhD project was on the investigation of thermoplastic elastomers combining the processing properties of a typical thermoplastic polymer with a rubber-like material. A detailed description of TPE-based polymers was given in the sections 2.2.5 – 2.2.8. The fact that TPEs are plastically deformable makes them particularly interesting for the use in LS while offering supplementary part property profiles to PA12.

The TPU SLS 4 (Freudenberg Forschungsdienste SE & Co. KG) is an aliphatic, ester-based (building the soft segment) block copolymer (polyurethane building the hard segment) without ether linkages. As it was developed in the scope of this project it is not commercially available. However, to this state it offered a new type of TPE for LS and an interesting benchmark towards the commercial DuraForm[®] Flex (hereinafter referred to as DF) as it also allows for production of flexible, rubbery parts by the LS process and has very similar mechanical properties at ambient temperatures. DF is distributed by 3D Systems and was the first commercially available TPE for the use in LS. The IR-analysis carried out in this study suggests that the DF also is a block copolymer based on aromatic ester blocks (building the hard segment) and aliphatic ether blocks (building the soft segment). Desmosint (Lehmann&Voss&Co) is a TPU type elastomer and first came to the market as a commercial LS powder in 2012. Regarding its

chemical basis it is known that it is an ester-based TPU and therefore constitutes a chemical equivalent to the TPU SLS 4 [231].

PA 2200 (hereinafter referred to as PA 12) served as benchmark LS material in terms of powder performance as it is known for stable processing and repeatable properties of the manufactured components in terms of mechanical capability and surface roughness [6, 28]. For the purpose of finding reliable shape indices in the scope of an initial experiment in section 4.2.2, additional materials are introduced providing a range of different powder shape characteristics. As they are only relevant for the initial experiment they are not being introduced here. Within the initial In-Process investigations in section 4.3.2, the PA 12 served as reference material as it was of major interest to disclose the differences in the crystallization kinetics as well as the in-process thermal dynamics of a thermoplastic elastomer compared to a typical semi-crystalline polymer. The comparison of the TPU SLS 4 and the DF made particularly sense in the course of the Post-Process observations as they differ from a chemical perspective. As the TPU SLS 4 is an ester-based polymer and the DF as an ether-based TPE they are expected to show different degradation behaviour being exposed to repeated processing cycles within LS.

4.2 Pre-Process – Investigation of the Bulk and Flow Behaviour

4.2.1 Introduction

As described in section 2.1.3, the properties of parts manufactured in LS are amongst others dependent on the flow and packing efficiencies of the processed powders. At first, section 4.2.2 introduces an initial experiment to assess reliable shape indices for the subsequent correlations of shape and its effects on the powder behaviour. Subsequently, in accordance with the main objectives (section 3.2.1), the experimental methods and analysis applied in order to investigate the influence of the bulk and flow characteristics of TPU SLS 4 and DF on the resulting part properties are introduced. All powders thereby were used in their virgin state. In addition, throughout the Pre-Process investigations, the TPU SLS 4 and the DF powder samples were modified in terms of particle size distribution before analysis in order to detect the effects of different size

distribution on the packing and flow characteristics. Therefore the original batches were divided into three different particle size fractions (F0, F25 and F45) by applying an air classification process. The fraction F0 therefore refers to the standard distribution out of the manufacturing process; F25 and F45, respectively, indicate that most of the fine particles below 25 μm or 45 μm are sifted out. In order to allow for comparison on powder scale, the materials are going to be compared to the standard LS powder PA 12.

4.2.2 Initial experiments to assess Powder Quantification Indices

As introduced throughout section 2.3.2 there are several factors that influence the static and dynamic powder behaviour such as packing and flowability. The nature of each powder is different and even the manufacturing process of each polymer powder can affect its inter-particle interactions [39]. In order to allow for quantification of the effects of particle shape on bulk behaviour for fine powders it is essential to apply accurate and reliable analysis. It is essential to find an appropriate analysis method to quantify the characteristics of fine powders. Within static image analysis, for example, the particles are applied on an object slide and are captured by a camera as shown in Figure 31a. The picture generated thereby only shows the particle in a two-dimensional representation. A second disadvantage of this approach is that it can only explore several hundred particles that are of very low statistical relevance [232, 233].

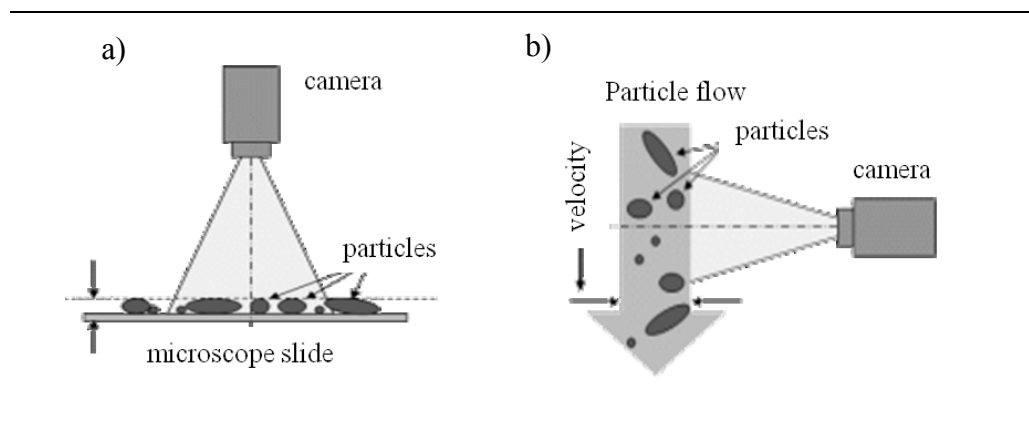


Figure 31: Comparison between a) static image analysis according to ISO 13322-1 and b) dynamic image analysis acc. to ISO 13322-2, adapted from [234]

In contrast to the two-dimensional image based systems, the dynamic image analysis devices specified in Figure 31 b, captures the particles during free fall which enables it to provide a three-dimensional representation of the investigated powder at a reduced number of overlapping particles. The disadvantage compared to the static method is that this is only possible with a moderate depth of sharpness. However, resulting from the moving powder stream, it is able to capture millions of particles with a maximum error below 1 % according to ISO 14488:2007 and therefore gives a representative and statistically relevant result for the observed sample [232, 235, 236]. The aim of this preliminary study on quantification indices is to find the most precise shape parameter of the dynamic image analysis applied.

Materials

For the purpose of finding reliable shape indices in this initial experiment, six materials significantly differing in terms of particle shape were compared. The materials observed are listed in Table 5 in the order from rather jagged edged shape (DuraForm®Flex) to most spherical particles (iCoPP).

Trade name	Distributor/ Manufacturer	Type of polymer	Powder Manufacturing process
DuraForm [®] Flex	3D Systems	TPE-E (no official information available)	Cryogenic milling (no official information available)
TPU SLS4	Freudenberg Forschungsdienste SE & Co. KG	TPU	Cryogenic milling
Rilsan Invent Black	Arkema	PA11	Milling (no official information available)
PA2200	EOS GmbH	PA12	Precipitation
Orgasol	Arkema	PA12	Probably precipitation (no official information available)
iCoPP	Trial Corporation	PP	Probably precipitation (no official information available)

Table 5: Materials used for shape indices comparison

These materials have been chosen on the basis of SEM/incident light microscope pictures that were taken for preliminary optical evaluation prior to analysis of their particle shapes. From this rather subjective approach it was possible to identify powder particles that already differ significantly in terms of their shape derived from the SEM pictures in order to relate it to the results from the dynamic image analysis.

Particle Shape Analysis

In order to identify the shape characteristics of the powder particles a Camsizer XT (Retsch Technology GmbH, Haan, Germany) was employed according to

the Machinery Directive 2006/42/EC [232, 237]. It applies a high resolution camera system that consists of two digital cameras, one to detect the size and shape characteristics of fine particles, while the second camera is optimized for the analysis of large particles.

For the analysis of fine bulk powders, especially for those with a broad particle size distribution, it is very important to ensure representative sampling. Therefore, each powder sample is taken with a sample splitter according to DIN 51701 before it was analysed in the Camsizer XT [238]. The software of the Camsizer is able to evaluate a range of different shape characteristics that are briefly introduced in Table 6 below.

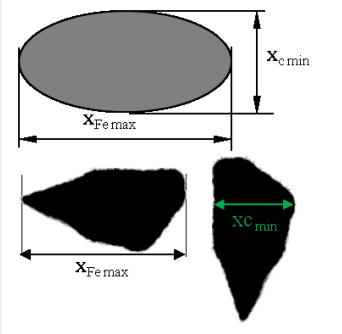
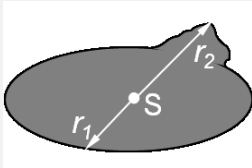
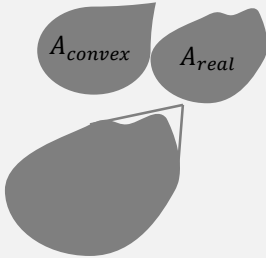
Shape Characteristic	Graphical Representation	Description
<u>Breadth to length ratio</u> (b/l):		$\frac{b}{l} = \frac{x_{c \min}}{x_{Fe \max}}$ $x_{c \min}$ and $x_{Fe \max}$ over all measured directions
<u>Sphericity</u> (SPHT): $\frac{4 \pi A}{U^2}$		U: measured circumference of a particle projection A: measured area of a particle projection
<u>Symmetry</u> (Symm):		Symm $= \frac{1}{2} \left[1 + \min \frac{r_1}{r_2} \right]$ r_1 and r_2 are the distances from the centre of area S to the borders
<u>Convexity</u> (Conv):		$Conv = \sqrt{\frac{A_{real}}{A_{convex}}}$ Ratio of the real area of the particle projection and its convex area.

Table 6: Shape Indices image-based Particle Analysis (Camsizer XT) [232]

Following below in the results section, the most precise and reliable shape factor was aimed to be identified by comparing the different available characteristics

over a range of varying powder particles that are clearly distinguishable already from an optical evaluation on basis of the SEM pictures.

4.2.3 LS System and Production of Test Samples

A DTM SinterStation® 2500 plus (3D Systems, Rock Hill, USA) as well as the parameter setup shown in Table 7 was employed for the fabrication of specimens for mechanical testing and the evaluation of shore hardness and part density according to ASTM F2921(2011) [1]. The parameters were qualified within the scope of a preliminary study described in appendix A.1.2.

Parameter description	Parameter value	
	TPU	DF
Left and right feed heater set point	55°C	55°C
Part heater set point	125°C	160°C
Powder layer thickness	0.1 mm	0.1 mm
Left and right feed distance	0.38 mm	0.38 mm
Fill laser power	18.75 W	18.75 W
Fill scan count	1	1
Outline laser power	5 W	5 W
Outline scan count	1	1
Slicer fill scan spacing	0.15 mm	0.15 mm
Scan speed	5 m/sec	5 m/sec

Table 7: LS parameters used for the production of the TPU and DF test specimens

In order to counteract the influences due to storage, as well as agglomerates and inhomogeneity of the samples, all the powders were sieved (mesh size 200 µm) before being processed. Five type S2 tensile test specimens were fabricated according to DIN 53504:2009-10 (2009) [239] and International Standard ISO 37:2011 [240] in XYZ-direction according to ASTM F2921-11e3 (2011) [1] in order to assure a flat build not demanding for a high amount of powder. Five cylindrically shaped specimens – later also referred to as shore cylinders – (diameter 35 mm and thickness 6 mm) were used for the evaluation of the shore hardness according to DIN ISO7619-1 (2012) [241]. The tensile specimens were also used to detect their surface quality measuring three points along the long

sides' centre line on each of the samples top and bottom surface. The mean values have been calculated for the representation of the results. Finally, a centrally positioned cube with an edge length of 4 cm was manufactured for the determination of the part density.

4.2.4 Conditioning and Sampling

For the conditioning of LS powders no quantitative data exists within literature and there are no standardized scenarios within industry describing their conditioning. Therefore, within a previous study conducted by Freudenberg Forschungsdienste SE & Co. KG (FFD) in the scope of this project, the TPE-based powders' flowability was investigated in dependence of moisture content. Thereby, the powders especially the TPU SLS 4 showed a tendency towards electrostatic charges due to tribo-electrical effects in a dried condition. It was found that at their equilibrium moisture (between 0.3-0.4 %) they showed the best performance [242]. On account of this and in order to achieve similar and homogenous exposure towards environmental humidity, the powders were conditioned prior to the investigations for approximately 15 ± 1 hours in a stable environment of the standard atmospheres for conditioning and testing of polymers as described by DIN EN ISO291 [243] and ISO 23529 [244]. Before analysing them, every powder sample that was taken out of the powder reservoirs was selected using a powder sample splitter to ensure that the powder samples were representative of the entire powder bulk in terms of PSD [238].

4.2.5 Moisture Content

For the determination of the materials' moisture content (MC), a HR83 Moisture Analyser (Mettler-Toledo AG Laboratory & Weighting Technologies, Greifensee, Switzerland) was employed. The operating principle is based on drying of a powder sample using a thermocouple and measuring the released moisture of a material at a resolution of 0.001% MC by monitoring the change in weight with a precision balance with a resolution of 0.1 mg [245].

4.2.6 Optical Evaluation

A scanning electron microscope (SEM), FEI Quanta 200 (FEI Company, USA), was used for the initial optical characterization of the particle shapes and surface morphology.

4.2.7 Particle Size and Shape

For the identification of the physical characteristics of the powder particles dynamic image analysis (Camsizer XT), was employed according to the Machinery Directive 2006/42/EC [237]. The particle size within this study is presented as x_{cmin} [μm] that equals the shortest maximum chord x_c of a particle projection measured from all directions in space (also referred to as “width of particle projection”). The PSD is presented as the frequency distribution $q_3(x)$ [%/ μm] based on volume. The diameters D_{10} , D_{50} , D_{90} correspond to the particle sizes equal or lower than 10%, 50% and 90% of the PSD, respectively. As a result of a preliminary investigation shown in appendix A.1.1, the particle sphericity (SPHT) was used as a measure of the particle shape as it represented the most reliable and sensitive shape value. SPHT is defined as the ratio between the diameter of a sphere with the same volume as the measured particle and the diameter of the circumscribed sphere [155].

4.2.8 Bulk and Flow Behaviour – Static and Dynamic Powder Behaviour

For the calculation of the packing density as well as the flow efficiency under dynamic conditions, three experimental methods were applied. A brief indication on the working principles is given in Figure 32. The Hausner ratio (HR) test was performed according to ASTM D7481 (2009) [246] with manual tapping of a powder sample as described by Liu *et al.* [247] and Schmid *et al.* [248]. The ratio between the poured and tapped bulk densities, called HR, thereby classifies the powders flowability as described in Eq. 20.

$$\text{Hausner Ratio (HR)} = \frac{\text{bulk volume}}{\text{tapped volume}} = \frac{\rho_{\text{tapped}}}{\rho_{\text{poured}}} = \frac{V_{\text{poured}}}{V_{\text{tapped}}} \quad \text{Eq. 20}$$

$HR < 1.25$ high powder flowability
 $1.25 < HR < 1.4$ decreased powder flowability
 $HR > 1.4$ cohesive powder

ρ_{poured}	poured density of powder sample
ρ_{tapped}	tapped density of powder sample
V_{poured}	poured volume of powder sample
V_{tapped}	tapped volume of powder sample

As the HR is highly dependent on the user due to the manual tapping of the powder samples [249], three repetitions were completed for this technique in order to increase its statistical outcome. The Flowability Test of the Revolution Powder Analyzer (RPA) (Mercury Scientific Inc., Newton, USA) was operated in accordance with the ASTM D7481 standard (2009) [246] and the manual provided by Mercury Scientific Incorporation (2010) [250]. Its operation, described by Krantz *et al.* [251] and Amado *et al.* [28], is based on the calculation of the avalanche angle and the surface fractal for a powder sample inside the rotating drum with the aid of a digital camera. The avalanche angle thereby serves as a measure for cohesion and thus gives a reflection on the flowability of the powder analysed. The surface fractal corresponds to the fractal dimension of the free surface of the powder and provides an indication of how rough the powder surface is [28].

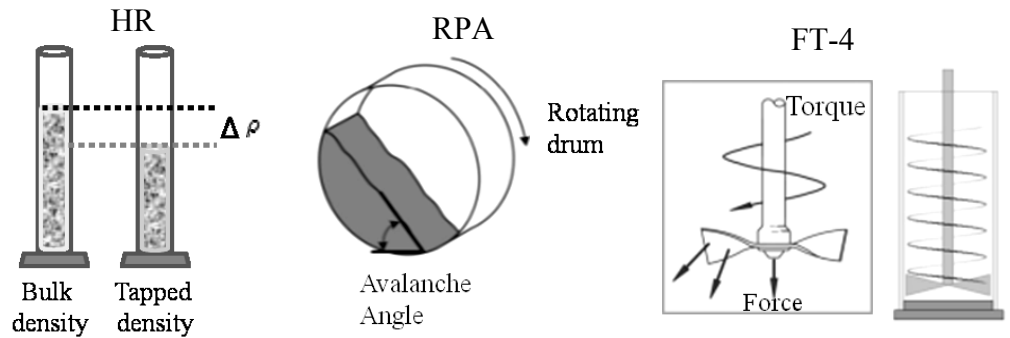


Figure 32: Working principles of the powder analysis methods used in this study, adapted from [248, 251, 252]

The Stability Test of the FT-4 Powder Rheometer (Freeman Technology, UK) was operated in accordance with the ASTM D7481 standard (2009) [246] and the manual of Freeman Technology (2007) [252]. The Basic Flowability Energy (BFE) [mJ] is the energy required to establish a compressive high stress flow pattern in a conditioned, precise volume of powder inside the vessel and it is calculated during the downwards movement of the blade through the powder bulk. It correlates with the cohesive character of a powder. On the other hand, the Specific Energy (SE) [mJ/g] is a measure of the powder's flow efficiency or the mechanical interlocking between the powder particles in an unconfined stress environment and is calculated during the upwards movement of the blade. The Conditioned Bulk Density (CBD) [g/ml] corresponds to the density of a precise volume of powder measured inside the vessel of the FT-4 after the initial conditioning cycle of the bulk, thus gives indication on packing efficiency of a powder [213, 253, 254]. Due to the high repeatability of the results obtained from the RPA and FT-4, two repeats were completed with these methods. The operating principles and the characterization indices of these three experimental techniques were described in more detail in literature [249]. According to recent studies, the values of the corresponding analysis methods can adequately be correlated with bulk or powder properties respectively as shown in Table 8 [249, 255].

Analysis methods/ Powder characteristics	Packing efficiency	Cohesion	Flow efficiency
HR	Poured/tapped density of HR [g/ml]	HR [-]	-
RPA	-	Avalanche angle [°]	Surface Fractal [-]
Rheometer	CBD [g/ml]	BFE [mJ]	SE [mJ/g]

Table 8: Analysis methods and characterization indices used to identify the powder properties

4.2.9 Effects of PSD on In-Situ Packing, Mechanical Properties, Part Density and Surface Roughness

For the investigation of the packing density inside the build platform small “density cubes” which include un-sintered powder were built. Four density cubes were distributed over the centre of the build chamber, as in this area the deviation of powder bed temperature is found to be the lowest, hence effects of temperature on different packing were reduced. After the completion of the build job these cubes were opened and the density of the powder was measured. Thereby, the density was calculated as follows. First the density cubes with the powder inside were weighed in a balance (accuracy of 4 decimal digits) and their mass was noted. The cube was then cut open in three places at which parts of the walls at constant dimension have been replaced, in order to identify the as is wall thickness of the cube equalling the axis in the LS process (D: Depth, W: Width, H: Height, see Figure 33). The wall thickness was detected in order to allow for the calculation of the actual volume as it might differ from the information of the 3D digital model and this would lead to a higher error in the calculation due to e.g. different shrinkage or curling [41].

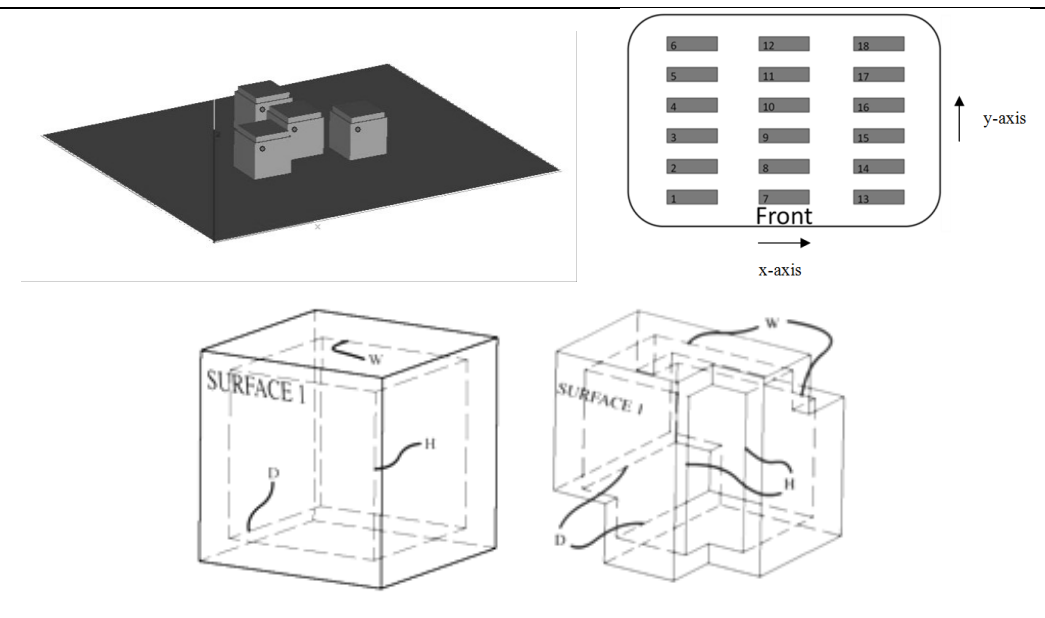


Figure 33: Positioning of density cubes in the LS process in correlation to Figure 92 (top) and procedure for cutting the density cubes in order to allow for replacement of inherent powder and later measurement of actual wall thickness (bottom)

After calculating the actual volume, the empty cubes with the spare parts were weighed again in the balance. The difference of the two masses was the mass of the powder. The same process was followed for each cube of the TPU und DF fractions.

The mechanical properties were determined by means of tensile testing with a S2 shoulder bar according to DIN EN ISO 53504 harmonized with ISO 37:2005 [239]. First small plates are manufactured and the actual specimen is subsequently punched out using a standardized punching die (ZCP 020, Zwick GmbH & Co. KG, Ulm, Germany). This procedure ensures constant and reproducible dimensions (linear and width) over all specimens and was performed in consideration of ISO 23529 (2010) [244]. The ultimate tensile strength (UTS), percentage elongation at break (%EAB) and E-modulus were measured using a tensile testing machine Z005 (Zwick GmbH & Co. KG, Ulm, Germany) equipped with a 5 kN load cell and an optical extensometer (lightXtens[®], Zwick GmbH & Co. KG, Ulm, Germany) at a testing speed of 200 mm/min. The Shore hardness was measured with a digital shore hardness testing device and was calculated according to DIN EN ISO868 (2003) [256] and DIN ISO 7619-1/-2 (2012) [241, 257]. A 3D laser scanning coloured microscope of the VK-9700 Series (Keyence Corporation, Belgium) was employed to optically determine the surface quality of the specimens [258]. The values for roughness were determined over three central points on the top and bottom sides of the longitudinal axis of the sintered parts. For each side of the specimens the mean value for R_a , R_q and R_z was calculated from the three measured points. A more detailed description for these values and the measurement procedure is given by Westkämper and Volk [259, 260]. The densities of the sintered cubes were calculated volumetrically (ratio of mass to volume). As this method of density measurement can lead to a significant measurement error as a result of the rough surface of the parts and small pores that are hardly taken into account while weighing the samples, it was decided to also measure the density with the aid of computer tomography (CT). A computer tomograph GE Nanotom 180 (180 kV / 15 W nano-focus X-ray tube) (GE Sensing & Inspection Technologies GmbH, Huerth, Germany) with a molybdenum target suitable for the detailed examination of plastic components was used [261, 262]. CT allows the

generation of 2D and/or 3D reconstructions of the internal microstructure of an object [263]. In capturing numerous layers of a specimen and stacking them together in a three-dimensional x-ray image, it is possible to detect differences in the parts' density and likely porosity [264, 265]. The image can be visualized as a grayscale or as a pseudo-colored image, depending on the best contrast that can be generated for each object. To achieve a high resolution and contrast, it is necessary to set a proper threshold between the gray levels of air (no attenuation) and polymer (attenuation due to sample) that leads to a differentiation within the gray level histogram [265]. While analyzing samples out of just one type of material, as was the case in this study, it is possible to reach a maximum error of around 0.01% [266, 267]. For this analysis, cubes with an edge length of 10 mm were used to achieve a CT resolution of around 3 μm throughout the sample dimension. The evaluation of the scanned data was accomplished with the Software VG Studio Max 2.1 (Volume Graphics GmbH, Heidelberg, Germany).

4.2.10 Effects of PSD on Absorption and Thermal Conductivity

As introduced in section 2.1.4, during LS the thermal conductivity as well as absorption has a decisive influence during exposure as well as for the distribution of the inserted energy [27, 46, 268]. The absorption was analysed in a previously conducted study, in which the diffusive reflection of the materials was detected employing the integrated sphere method and the absorption was calculated subsequently as described in literature [269-272]. However, the results (see appendix A.5) did not show a clear systematic trend nor did they indicate a significant change for the materials observed in dependence of PSD. Therefore, and as in literature contact conductivity is described as the main influencing factor on the powder bed's effective thermal conductivity during sintering (see section 2.1.4), the focus was consequently set on the phenomenon of thermal conduction. For the determination of the influence of varying PSDs on the thermal conductivity of the two powders and their corresponding PSDs (TPU SLS 4/TPU F0, F25, F45), the thermal conductivity was determined at feed and build chamber temperature using laser flash analysis (LFA) according to DIN EN 12667:2001-05 [273]. Thereby, the LFA is an indirect analysis method detecting the thermal diffusivity at the preferred temperature. Inserting the

specific heat capacity c_p as well as the bulk density of a material of interest in Eq. 21 subsequently allows for calculation of the thermal conductivity k [274].

$$k = \alpha * \rho * c_p \quad \text{Eq. 21}$$

k	Thermal Conductivity	[W/mK]
α	Thermal Diffusivity	[m ² /s]
ρ	Bulk Density	[kg/cm ³]
c_p	Specific Heat Capacity	[J/kg K]

The bulk density used for the calculation here was the in-situ density determined from the cubes described in section 4.2.9 in order to apply a process adapted value. The specific heat capacity was determined using a DSC 204 F1 Phoenix® (NETZSCH-Gerätebau GmbH, Selb, Germany). A LFA 457 MicroFlash® (NETZSCH-Gerätebau GmbH, Selb, Germany) was applied for the analysis of thermos-physical properties (thermal diffusivity). In order to heat the sample, it was irradiated from below with short beam pulses of a Nd:YAG (Energy up to 18 J, Pulse Width: 0.3 ms). A temperature delta was detected on the sample surface and the thermal diffusivity α was then calculated from the chronological sequence of the temperature increase of a sample with a defined thickness [274-277]. The sample was placed in a sample holder (two aluminium plates, coated with graphite for increased absorption) without applying external stresses. Each material, the TPU SLS 4 and DF and their corresponding fractions, were fired and measured in a “five-shot” principle and the thermal diffusivity was calculated from the mean value of the individual measurements.

4.3 In-Process – Investigation of the Process-Material Interactions

4.3.1 Introduction

Within this section the investigations on the process-materials investigation are described. In the scope of an initial experiment the crystallization kinetics between TPU SLS 4 and PA12 were aimed to be studied at process-adapted conditions. It was of major interest to disclose the differences in the isothermal

crystallization kinetics as well as the in-process thermal dynamics of a thermoplastic elastomer compared to a typical semi-crystalline polymer, the PA12 which has been well described in literature.

For the investigation of important process parameters and its effects on the part qualities an overall energy approach was applied and is going to be introduced in more detail in the course of this section. The materials thereby observed were TPU SLS 4, the Desmosint TPU as well as DF. Comparing these polymers makes particular sense, as the two TPUs are equal from a chemical perspective, while showing a significantly different degree in crystallinity (TPU SLS 4 = 20 %; Desmosint = approximately 1-2 %) and different melting characteristics manifested by a broader melting peak of Desmosint (onset of melting approximately 30K lower compared to TPU SLS 4 at a comparable melting peak temperature at around 150 – 155°C). On the other hand, the DF differs from a chemical perspective compared to the TPUs, though having a similar crystallinity as the TPU SLS 4 combined with a possible processing range that is comparable to the one of Desmosint (approximately 30 K). Hence, the materials provide useful references in order to gather information on the processing specifics in dependence on material properties.

4.3.2 Initial experiments to assess the In-Situ Heating Rates and Simulation of In-Situ Crystallization Kinetics

Within section 2.1.4, build chamber temperature was found to be one of the most influential process parameters in LS not only affecting process stability but also the quality of the manufactured parts e.g. with regard to degree of crystallinity or part density. Hence, the in-situ temperatures for the polymers observed were investigated using infrared thermography (IT). IT is an image based method allowing the contactless measure of surface temperatures. The aim of the investigations was to detect the temperature distribution over the exposed areas and the characteristic temperature-time-profile during melting of the powder bed surface during LS. The heating and cooling rates that could be calculated from these investigations served as input for a fast scanning calorimeter (Flash DSC) that is capable to adapt to this high in-situ thermal dynamics during heating or cooling respectively. Fast scanning calorimetry (FSC) is an advancement of conventional differential scanning calorimetry (DSC) and research on

substances like polymers will benefit from its capability to not only use a spectrum of scanning rates of around 10^6 times broader (see Figure 34) but especially the very high scan rates up to 40,000 K/s [278, 279].

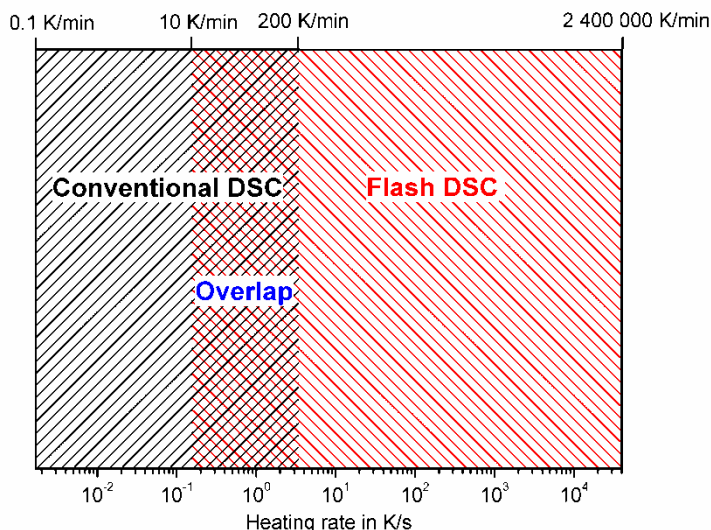


Figure 34: Range of scan rates of Flash DSC (Mettler Toledo AG, Schwerzenbach, Switzerland) of more than seven decades [278]

As the structure of polymers is dependent on the cooling conditions and reorganization of crystals at specific heating rates, it is important to be able to apply the in-situ dynamics in order to get feedback on the actual material behaviour in the process applied [278]. Another advantage of high heating rates is the suppression or minimization of the previously mentioned reorganization as not enough time to reorganize is allowed [278, 280-282]. In Figure 35 the conventionally applied heating rate for the detection of the melting enthalpy of 10 K/s is compared with a significantly higher heating rate of 5000 K/s in order to indicate its effect on the resulting melting enthalpy and the melting peak formation for the TPU SLS4. Due to minimized reorganization in the form of annealing of small polymer crystals, a broader melting peak can be observed that also leads to a slightly higher enthalpy in this case [281, 282]. This already indicates the different material behaviour for higher heating rates as present in LS [283]. In addition, due to the limitation of the cooling rates and the signal time constant of a conventional DSC, isothermal crystallization can only be studied for slowly crystallizing materials. For polymer samples which have been

processed, hence crystallized at very high cooling, reorganization of the crystalline portion upon heating is a major issue

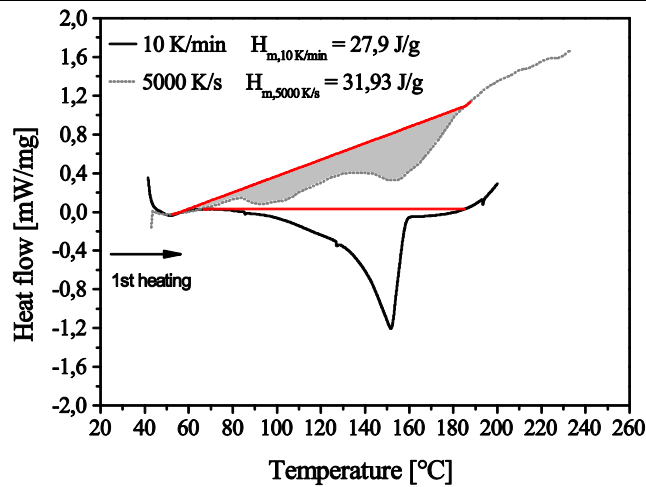


Figure 35: Comparison of heating rates 10 K/s vs. 5000 K/s for TPU SLS4 measured in the Flash DSC 1 (Mettler Toledo AG, Schwerzenbach, Switzerland)

Due to the crystal perfection during the comparatively low heating in a conventional DSC, the melting behaviour subsequently measured is no longer related to the initial crystalline structure. On the contrary, in the literature fast scanning DSC was found to prevent or minimize the effect of reorganization during the heating measurement subsequently to crystallization as a result of the high heating rates applicable [281, 282, 284].

Consequently, in employing this process as a characterization method of the melting and crystallization behaviour, it should help to gather more useful results for a deeper process understanding and important material behaviour for the TPEs processed in the LS process.

The aims of this initial study were:

- to disclose the differences in the thermodynamic kinetics between TPU SLS 4 and PA12 at
 - a. high cooling rates
 - b. isothermal crystallization subsequently to high heating/cooling in order to indicate magnitude of influence of crystallization during LS

These studies were carried out under adaption of in-situ LS heating and cooling rates respectively.

Thermography

By means of infrared thermography (IT), the temperatures of the powder layer prior to, during and after melting were measured for TPU SLS 4. For that purpose the material was processed with the optimum parameter set from section 4.2.3 (Table 7) on a DTM SinterStation® 2500 HS with an implemented high speed thermal imaging system Infra Tec Image IR 5300 at the University of Duisburg-Essen, Institute of Product Engineering [283]. In order to guarantee that the results were transferable to the machine (DTM SinterStation® 2500 plus) used for all further trials at BMW's Rapid Technologies Center, the machines' laser and heater outputs were harmonized in a preparatory step. Thereby, an additional pyrometer detected the temperature deltas between the two systems throughout a test job in order to adjust the processing temperatures of the DTM SinterStation® 2500 HS for the later thermography measurements on the level of the DTM 2500 plus. For the alignment of the two systems' laser outputs, a laser power measuring device (OPHIR F150A, Ophir Optronics Solutions Ltd) was applied to measure fill and outline laser power of the DTM 2500 plus and disclose potential differences that would be harmonized subsequently on basis of the intended parameter set. In final step, the properties of specimens in terms of shore hardness, tensile properties and scaling factors have been compared in order to validate the comparison between the two LS systems. All the results for these harmonization steps between the two systems can be found in appendix A.1.

The camera system implemented in the DTM 2500 HS has an optical resolution of 320 x 256 Pixels, a maximum temporal resolution of 3000 Hz using quad frame mode and a wavelength range from 2.5 – 5.5 μm . The camera was placed adjacent to the scanner head with an observation angle of 29°, allowing for the measurement of the melt temperature during exposure with the laser (see Figure 36). Compared to the systems described in the literature so far, the setup applied within this study allowed for characterization of the temperature-time profile before, during and after exposure at various points of the field of view. It therefore delivered information about the heating, the heating rate, the maximum melt temperature, the cool down and consequently the temperature after the melt cooled down to ambient conditions.

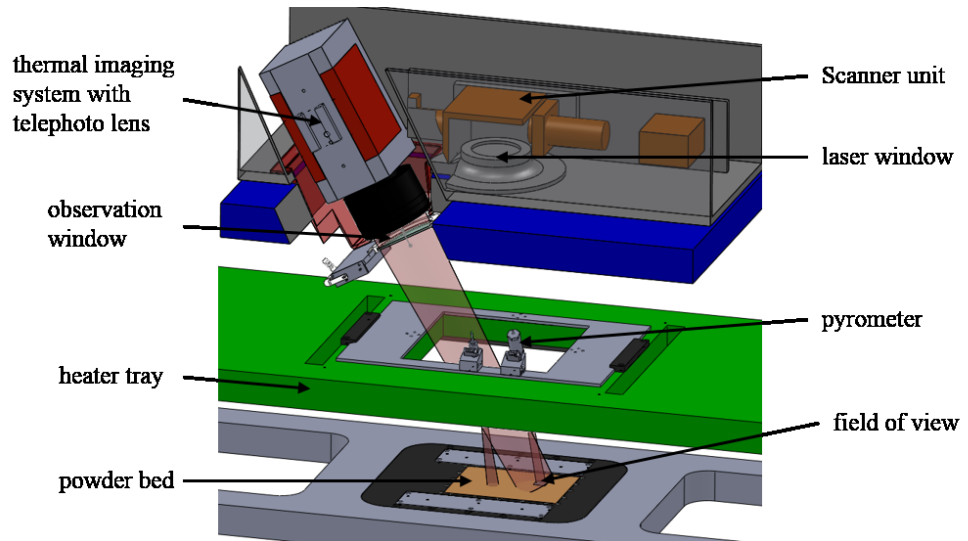


Figure 36: Cross section schematic of the experimental setup for measuring the surface temperature in a SinterStation® 2500 HS [285]

For this purpose, a telephoto lens with a focal distance of 100 mm and a 500 mm close up lens was employed, resulting in an optical resolution of 0.147 mm at a distance of 490 mm, which is the ideal resolution for the laser focus diameter of 0.45 mm. As a result of that setup, the effective field of view was limited to a size of 11.8 by 9.4 mm. This only allows for measuring temperatures in single points or a small area of real parts but allows for determination of the melt temperature during exposure. For the final calibration of the imaging system it was necessary to determine:

- the emissivity of the polymer observed in dependence of the camera wavelength in powder state and melted state at the corresponding processing temperatures
- transmission of the observation window
- reflected temperature of the heater tray
- ambient temperature of the imaging system

The direct measurements of emissivity were performed at DLR (German Aerospace Center, Institute of Planetary Research, Berlin, Germany) in detecting the polymers radiation wavelengths using a FTIR-spectrometer. According to DLR this setup allows for wavelength dependent analysis of the emissivity at an

error below 1% between wavelengths of 1 to 16 μm . A more detailed description of the measuring arrangement, its calibration and capabilities is given in literature [286-289] and in appendix A.3.4. For the determination of the maximum temperatures during the fill and outline scan, cuboids with an edge length of 8 mm and a height of 1 mm were analysed and the data was taken from three cross sections, though, excluding the very first layer due to the fact that it faces different thermal and measuring conditions [285]. Five single points uniformly distributed over the analysed field of view were evaluated for each layer. The measured data was used to determine the maximum temperature of the melt during laser exposure as well as the average melt temperature within the observed area ten seconds after laser exposure. Thereby the effect of the outline scan was neglected as the energy density used during this step of exposure does not significantly influence the peak temperature of the generated melt pool. On the basis of a temperature-time-curve it was also possible to calculate the heating and cooling rates during and following exposure.

Differential Scanning Calorimetry – Fast Scanning and Conventional DSC

As mentioned in section 4.3.2, FSC can go up to extremely high heating (up to 40,000 K/s) and cooling rates (up to 4,000 K/s). In contrast to conventional DSC its working principle is based on dynamic power-compensation. Thereby, the heating of the samples takes place in two separate devices and the temperature difference established during heating is then compensated by the power control [279, 290]. The measured difference in heater output consequently equals the change in the heat flow of the material [77]. Instead of using an oven as for conventional DSC, the FSC applies small sensors (see Figure 37) to heat the samples up using a heating resistor (Flash DSC 1 manufactured by Mettler Toledo AG, Schwerzenbach, Switzerland). In order to eliminate any interfering influences on the measurement caused by heat capacity or thermal conduction of the sample crucible itself, the samples are directly applied on the sensor and therefore the thermal lag during melting is limited to the actual sample being analysed.

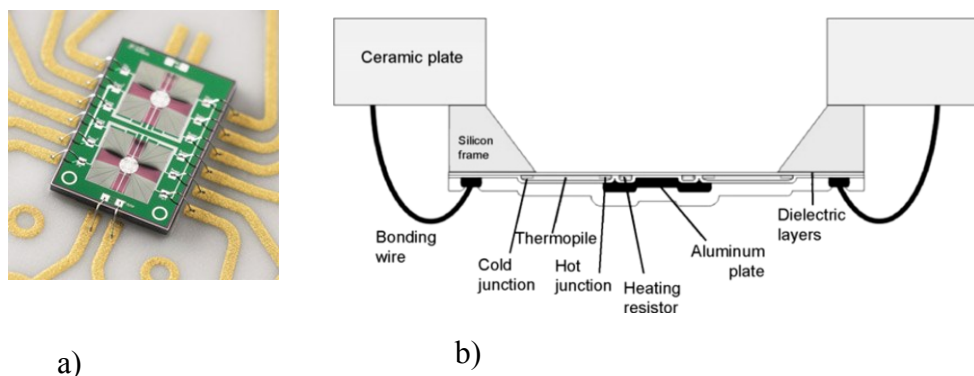


Figure 37: Flash DSC 1 sensor a) and schematic cross section not at scale b) (Mettler Toledo AG, Schwerzenbach, Switzerland) [279, 290]

Thereby, the size of the sample has to be selected in such a way that measurements at higher heating rates are still possible while the sample is still representative for the bulk material. According to Schawe the optimum sample mass for many applications is between 20 and 200 ng [280]. As the absolute sample mass in the range of ng to μg can't be weighed with conventional balances, within this study it was estimated on the basis of the thermal properties such as the melting enthalpy, the glass transition step height, or the heat capacity to estimate the sample mass [291].

Parameter	Value
Temperature Range	-95 °C – 420 °C
Heating Rates (typically)	30 K/min. (0.5 K/s) – 2 400 000 K/min (40 000 K/s)
Cooling Rates (typically)	-6 K/min. (-0.1 K/s – -240 000 K/min (-4 000 K/s)
Signal Time Constant	0.001 s
Resolution of Temperature Signal	2.5 mk
Sampling Rate of Temperature Signal	10 kHz
Sample Size	10 ng – 1 μg

Table 9: Specifications of Flash DSC 1 (Mettler Toledo AG, Schwerzenbach, Switzerland) [279, 290]

In order to guarantee a good thermal contact between the sample and the sensor, the sample needs to be fused on the sensor before the actual experiments. In this case, the original state (e.g. re-used particles with thermal history) of the sample is lost. Alternatively, the sensor can be covered by a thin layer of a contact medium (e.g., silicon oil). This allows for a reproducible contact between the sample and the sensor [280, 291]. However, in following the pre-melting of the sample onto the removable sensor Mathot *et al.* [279] showed that even under various conditions an excellent repeatability of measurements on cooling and heating of a polypropylene sample was achievable.

The samples used for the measurements were also fused onto the sensor (melting with 100 K/s up to 180°C; cooling to 25°C with 100 K/s) for a reproducible contact and weighed between 20 - 30 ng. In order to simulate the time dependent quasi-isothermal LS also taking into account the in-situ dynamics of the melting/exposure prior to crystallization, in the next step the crystallization volume at different isothermal holding temperatures was investigated. Sampling was performed analogous to the experiments on the thermal stability introduced above. Prior to the isothermal runs, the sensitivity towards increasing cooling rates was studied for both polymers in the first instance. Therefore, the PA12 and the TPU SLS 4 were heated from room temperature up to 250°C and 220°C respectively to reach full melting without degrading. In the next segment the melt was cooled down with varying cooling rates between 0.1 and 1000 K/s and the resulting crystallinity was determined semi-quantitatively in a subsequent heating run. The intention was to see whether crystallization may have taken place during the cool down step from the maximum melting temperature. For the determination of the time dependent crystallization during LS, the associated isothermal FSC runs were performed as shown in Figure 38 for PA12 at $T_{iso}=169^{\circ}\text{C}$ and TPU SLS 4 at $T_{iso}=105^{\circ}\text{C}$ respectively. In order to indicate the crystallization kinetics of the TPU under process adapted conditions an additional heating run with a maximum temperature of 290°C, equal to the in-situ peak temperature, was performed for the TPU SLS.

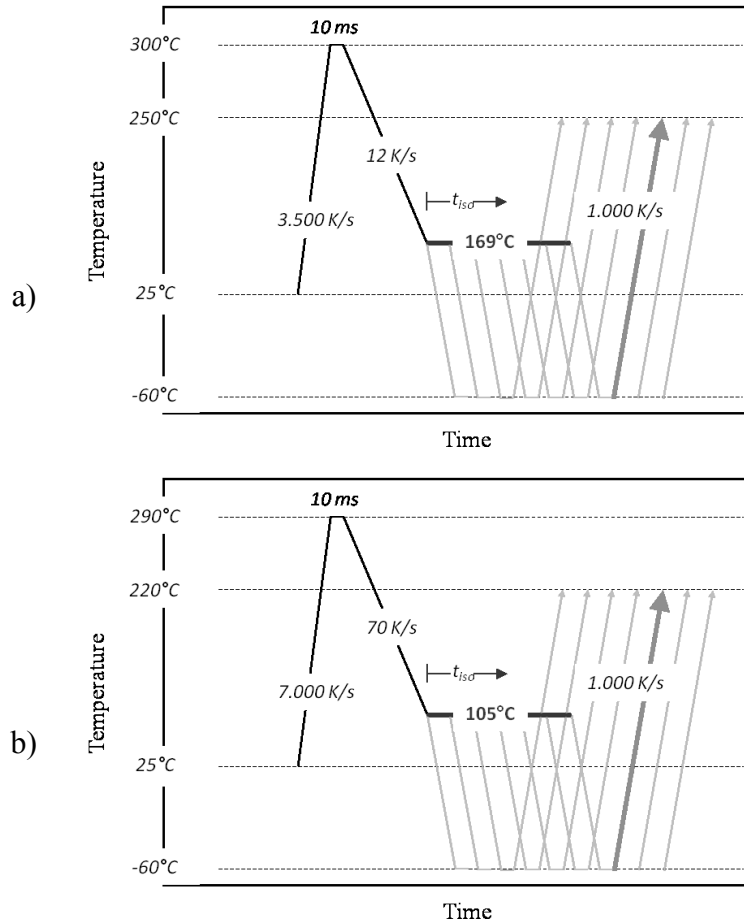


Figure 38: Schematic representation of the temperature programme for the analysis of melting enthalpy as a function of isothermal crystallization time (t_{iso}) for a) PA12 and b) TPU SLS 4

In conventional DSC, Rietzel [32] has shown that at relatively low temperatures ($\leq 167 - 168^\circ\text{C}$) the crystallization for PA12 occurred during cooling of the sample down to the isothermal holding temperature, as a consequence the calculation of the peaks was impossible. At an isothermal temperature of 168°C and higher, a clear peak for calculation was detected and therefore a temperature of 169°C was used for the FSC measurements in this section. For the calculation of the crystallization volume, the isothermal runs were interrupted after discrete intervals and the resulting crystallization $[\Delta H_c(t)]$ was analysed in the resulting heat flows $[\Delta H_m(t)] = [\Delta H_c(t)]$.

The heating and cooling rates for the TPU SLS 4 were calculated from the results of the thermography measurements (see section 6.2). The corresponding heating and cooling rates for the PA12 FSC runs were aligned for the corresponding

processing parameters in coordination with observations carried out by Wegner for PA 12 [227, 283, 292].

The reference measurements for the conventional DSC have been performed using sample sizes between 5-8 mg at heating/cooling rates of 20 K/min and 40 K/min respectively (gas flow 50 ml/min N₂) employing a DSC 204 F1 Phoenix® (NETZSCH-Gerätebau GmbH, Selb, Germany) according to DIN EN ISO 11357 (2010) [226]. For the analysis of the isothermal crystallization kinetics, the relative crystallinity $X(t)$ (weight fraction crystallinity) can be achieved by an integration of the transient normalized heat flow (isothermal crystallization exotherms) over the course of crystallization time [59, 293, 294].

4.3.3 LS System and Production of test samples

The LS System applied for studies was a DTM SinterStation® 2500 with a heater upgrade as presented in section 4.3.2. The lower temperature deviations over the build platform helped to reach a precise feedback on the effects of varying build chamber temperature on part properties. All materials were investigated for their minimum and maximum build temperatures in preliminary studies (see appendix A.1.2) (lower limit $\triangleq$ curling; upper limit $\triangleq$ glazing temperature). This was performed experimentally, as even for the PA12 based polymers no reliable analysis or model is available to predict these temperatures. The ranges for each of the materials are shown in Table 10.

Material	TPU SLS 4	Desmosint	DF
min. build temp. [°C]	115	90	130
ΔT [°C]	10	30	30
max. build temp. [°C]	125	120	160

Table 10: Experimentally determined minimum and maximum build chamber temperatures

In order to gain evidence on the development of the effect of increasing temperature, the areas with the most homogenous temperature distribution within the LS system were chosen, in order to be able to relate effects back on the build temperature variation. The build setup contained Type S2 tensile specimens in accordance to section 4.2.3. In addition massive cubes (35x35x20 mm) were built in order to measure the degree of crystallinity by means of X-

ray diffraction as well as the determination of the Shore A hardness (see appendix A.8).

Parameter	Desmosint	TPU SLS 4	DF
Laser power (L) [W]	11; 16; 21; 26; 31	6,2; 10,4; 14,6; 18,8; 23	6,2; 10,4; 14,6; 18,8; 23
Build chamber temperature (T) [°C]	90; 105; 120	115; 120; 125	130; 145; 160

Table 11: Machine parameters that have been varied within the design of experiments (DOE)

The parts were manufactured at varying energies (L1 – L5) at a constant build temperature (T) as shown in Table 11 and Table 12.

Nr. of experiment	Build temperature	Laser power
1	T1	L1
2	T1	L2
3	T1	L3
4	T1	L4
5	T1	L5
6	T2	L1
7	T2	L2
8	T2	L3
9	T2	L4
10	T2	L5
11	T3	L1
12	T3	L2
13	T3	L3
14	T3	L4
15	T3	L5

Table 12: DOE for the determination of varying parameter combinations on part properties

T1 – T3 $\triangleq$ levels of variation for build chamber temperature

L1 – L5 $\triangleq$ levels of variation for laser power

Thereby, it was aimed to validate varying energy melt ratio (EMR) described in section 2.1.4 with build chamber temperature as well as laser power. Hence, in

a separate experiment the influence of hatch spacing was validated as the EMR may be influenced by changing this parameter.

For a holistic description of the results, the EMR described in Eq. 10 was used. In using this approach, it was aimed to investigate a complete energy based description of the results with variation in material and machine parameters. The required input variables for the EMR were either taken from literature or determined with suitable analysis methods as shown in appendix A.8.2.

4.3.4 Mechanical Properties

The mechanical testing by means of tensile testing and shore hardness was performed in accordance to section 4.2.9.

4.3.5 Determination of Part Crystallinity

For the determination of the degree of part crystallinity as a result of the different parameter combinations, X-ray diffraction was used. The method uses the effect of coherent scattering in order to detect the crystallinity of samples on a basis of the arising diffraction interferences. More specifically this means that the atoms, excited by the X-rays, emit electromagnetic waves that are dependent on the nature and size of the crystalline structure. X-ray diffraction thereby measures the difference between emitted radiation and the radiation that arrives at the detector. The intensity is a measure for crystallinity and is plotted in a diffractogram with the angle between radiation source (X-ray tube) and the detector. A more detailed description of the method and validation of results is given in literature [295].

4.4 Post-Process – Investigation of the Ageing of TPEs in LS

4.4.1 Introduction

As described in section 2.2.11 it is known that polymers used in LS change their intrinsic properties due to processing conditions that are close to the crystalline melting temperature. The aim of the Post-Process experiments was to characterize the ageing processes of the newly developed TPU SLS 4 and compare it with the commercial elastomeric reference DuraForm® Flex (DF).

Both thermoplastic elastomers (TPEs) allow the production of flexible, rubbery parts by the LS process and have very similar mechanical properties at ambient temperatures. However, the chemical resistance and characteristics differ due to their chemical basis as introduced in section 4.1. Therefore, it is aimed to evaluate the tendency of the two polymers to be affected by the thermal loads within a LS build. In the scope of an initial experiment the stability, hence potential ageing effects, were studied in a process-adapted approach using fast scanning calorimetry (FSC). From this experiment, the main investigations of this section were derived. Thereby, the effects of ageing on the intrinsic properties, such as molecular weight, as well as the changes in the bulk material have been examined. In order to represent a real manufacturing environment, in which the materials have to reach maximum efficiency, the materials have been processed 14 times generating 15 different ageing stages of powder without refreshing with virgin material. The methods applied have aimed to gain a deeper insight into the polymer ageing processes and the use of suitable analysis methods following that aim.

4.4.2 Initial Experiment on Thermal Stability

The thermal stability of polymers is often observed by thermogravimetric analysis (TGA) in measuring weight gain or loss as a function of temperature and time using a highly sensitive microbalance [230]. However, considering the kinetics of a LS process, it also reaches the limits of its capabilities in terms of maximum possible heating rates that usually are equal to the commonly applied heating rates of DSC analysis. In addition the TGA measures reaction at which gaseous reaction products arise. As beginning depolymerisation is primarily characterized by shortened polymer chains that does not necessarily affect the overall weight, it cannot be determined by TGA [13, 134]. However, mechanical properties, flowability of the polymer melt as well as its ability to crystallize are highly dependent on a change in the chain build up, hence thermal stability and the crystallization behaviour were studied in dependence of the in-situ dynamics of the LS process by fast scanning calorimetry [113, 114, 280]. It was therefore aimed to give an indication on thermal stability and potential degradation phenomenon (e.g. cross-linking, depolymerization, oxidation, etc.) during laser

exposure and to reveal whether this provides a reasonable objective for the main investigations of this thesis.

Fast Scanning Calorimetry (FSC)

For the investigation on the maximum temperature at which the TPU SLS 4 would still remain thermally stable (does not degrade) the temperature program shown in Table 13 was performed in the FSC. The configuration of the system was the same as introduced in section 4.3.2. The determined melting enthalpy thereby served for evaluation of the thermal stability. In order to allow for a quantitative interpretation of the results the peak area of the end-thermal heat flows was calculated. This area equals the melting enthalpy $\Delta H_{T_{\max,i}}$ after heating to $T_{\max,i}$.

Segment-Nr.	Program	Comment
1	0.1 s at 25°C	stabilize
2	heating from 25°C with 1000 K/s to $T_{\max,1}$	heating to max. temperature
3	10 ms at $T_{\max,1}$	dwell time at max. temperature ($T_{\max,1}=180^\circ\text{C}$)
4	cool down from $T_{\max,1}$ with 1000 K/s to 180°C	cooling down to 180°C with high cooling rate in order to suppress crystallization
5	cool down from 180°C with 5 K/s to 25°C	constant conditions for all crystallization runs
6	0.1 s at 25°C	stabilizing
7	heating from 25°C with 1000 K/s to $T_{\max,2}$	analysis of the melting curve
8	similar to segment 3 but with $T_{\max,2}$ repetition of segments 4 to 7, although $T_{\max,i}$ increases by 10 K after completion of previous segment in the range between $180^\circ\text{C} \leq T_{\max} \leq 340^\circ\text{C}$	

Table 13: FSC Temperature program for detection of the maximum temperature at which the TPU SLS 4 remains stable

The ratio between the melting enthalpy after heating to $T_{\max}$ and the enthalpy after heating to 180°C ($\Delta H_{T_{\max}}/\Delta H_{180^{\circ}\text{C}}$) characterizes the potential changes in the sample.

4.4.3 LS System and Production of test samples

As before a Sinterstation[®] 2500 plus with the parameter setup from section A.1.2, Table 22 was used to generate the different ageing states and produce tensile test specimens for each of the materials observed. Again, type S2 tensile test specimens were produced in accordance to section 4.2.3. Specimens were produced according to ASTM F2921-11e3 to reduce the amount of powder required [1]. For CT analysis, cubes with an edge length of 10 mm were manufactured. As previously mentioned, as there is neither a specific scenario described in the literature as to how to condition LS powders for optimal processing, nor is it known how moisture affects the process, the powders for all builds were processed at equilibrium moisture between 0.3 – 0.4% in order to ensure comparable starting conditions and represent actual manufacturing environments. A total of 14 builds led to 14 different ageing states of tensile specimen and 15 different states for powder samples including virgin and aged powder. For the analysis of the fine powders, it was important to ensure representative sampling. Therefore, each powder sample was taken in accordance to the representative sampling scenario described in section 4.2.4.

4.4.4 Mechanical Properties and Part Density

The mechanical testing as well as the detection of part density by means of computer tomography (CT) was performed in accordance to section 4.2.9. Due to the amount of data and the measuring expenditure, for each material a sample manufactured out of virgin material, one for ageing state seven and one for ageing state 14 were analysed.

4.4.5 Analysis of Ageing Effects on Macromolecular Scale

For the correlation of potential changes in molecular weight with the change in the viscous flow of the polymer melt, the melt volume rate (MVR) was measured with a GÖTTFERT MI-4 (GÖTTFERT Werkstoff-Prüfmaschinen GmbH, Buchen, Germany) melt index tester according to DIN EN ISO 1133. The test

load applied for both polymers was 2.16 kg with a pre-melt time of 4 minutes. The TPU was tested at 170°C ($T_m = 150^\circ\text{C}$) and DF at 230°C ($T_m = 190^\circ\text{C}$) due to their different melting temperatures. All powder samples were measured at equilibrium moisture between 0.2 – 0.3%. The moisture content was analysed with a HX204 halogen moisture analyzer (Mettler-Toledo AG, Ch). In order to detect potential changes of macromolecules, the molecular mass distribution was measured over all 15 ageing states applying high temperature gel permeation chromatography (HT-GPC) [91, 135]. The separation column used was a PLXT-20 Rapid GPC (stationary phase was highly cross-linked polystyrene with defined pore sizes) with ortho-cresol used as the solvent for TPU at 140°C and trichlorobenzene for DF at 160°C.

For the investigation of low molecular weight fractions within the polymers, potentially emerging due to thermal cracking at chain ends, an extraction method was applied. The samples used were the remaining tensile specimens. The polar, volatile and aprotic solvents applied (tetrahydrofuran (THF) and acetone) served to leach out the monomers and oligomers of the sample parts but did not dissolve the high molecular weight chains of the original polymers. With this method it was investigated whether the concentration of low molecular weight fractions increased with ageing of the material over multiple processing cycles. An analysis balance (Mettler-Toledo AG, Ch) with an accuracy of 0.1 mg was used. The sample parts with the corresponding ageing states were dried by heating in an oven for 30 min at 80°C and subsequently for 30 min at 100°C. In order to further dry the samples they were sorted in a desiccator on top of hygroscopic concentrated sulphuric acid at room temperature for 18 hours. Fractions of the parts were put into glasses that also were dried for 3 hours at 100°C beforehand. The test samples ($n=3$ per ageing state and solvent applied) were then fully covered with the respective solvent and mildly agitated for 18 hours. After allowing loose particles to settle the solvent was decanted carefully and fresh solvent was applied. Afterwards the samples were stored for an additional two hours under mild movement. The particles that might have been replaced from the samples surface were allowed to settle for an hour and the solvent was again decanted off. After being dried for three hours at 80°C and subsequently for 1

hour at 100°C the weight of the samples was determined again and the material percentage weight loss compared to the samples' original mass was calculated. With Fourier Transform Infrared Spectroscopy (FTIR) it is possible to detect both chemical and physical changes of polymers, especially the ageing induced, oxidative degradation reactions [91, 296, 297]. The spectrometer employed in this work was a Nicolet 5700 (Thermo Electron Corporation) with an ATR-Crystal in reflective mode with a spectral resolution of 0.4 cm⁻¹ again investigating all 14 ageing states of the test pieces for both types of polymer.

4.4.6 Analysis of ageing effects on Powder Scale

In order to identify the physical characteristics of the powder particles, a Camsizer XT introduced in section 4.2.7 was employed. For the quantification of changing bulk properties the FT-4 Powder Rheometer, previously introduced in section 4.2.8 of this thesis, was used measuring the Conditioned Bulk Density (CBD) [g/ml] relative to the single ageing states. As a general remark, it is an important requirement for the analysis of fine bulk powders, especially for those with a broad particle size distribution, to ensure representative sampling. Therefore, samples were always taken out of a previously tumbled and well mixed bulk before being lead through a chute riffler in order to generate representative samples. From the literature it is known that the sampling with a chute riffler is a practical method leading to the second smallest standard deviation of approximately 1.10% below the state of the art splitting techniques [298].

5 Pre-Process – Powder Characteristics, Bulk and Flow Behaviour

5.1 Introduction

In this section, the results of the initial experiments on powder quantification indices are presented to derive the most reliable and accurate shape factors.

Subsequently, the effects of varying bulk properties on the powder's static and dynamic flow properties of TPU SLS 4 (F0-F45), DF (F0-F45) and PA 12 are investigated. Initially the powders' quality is characterised in terms of moisture content, particle size, size distribution and the particles' surface morphology. Subsequently their static and dynamic powder behaviour is studied. PA12 thereby serves as a valuable benchmark material on the bulk scale as it is known for good flow properties and stable processing. Later the effects on process and part quality of the two TPEs and its corresponding fractions are investigated in terms of the in-situ packing, thermal conductivity as well as the resulting tensile properties and part densities.

5.2 Initial Experiments to assess Powder Quantification Indices

The results for the comparison of the shape indices is presented in Figure 39. The convexity (Conv) values do not differ significantly for all powders observed despite a clear difference given by the optical SEM assessment. Looking at the breadth to length ratio (b/l) value it can be seen that it almost follows the trend of the visual assessment, although, it shows a drop for PA2200. Thereby, PA2200 is on the same level of the TPU SLS4 which however differs significantly according to the results of the SEM analysis.

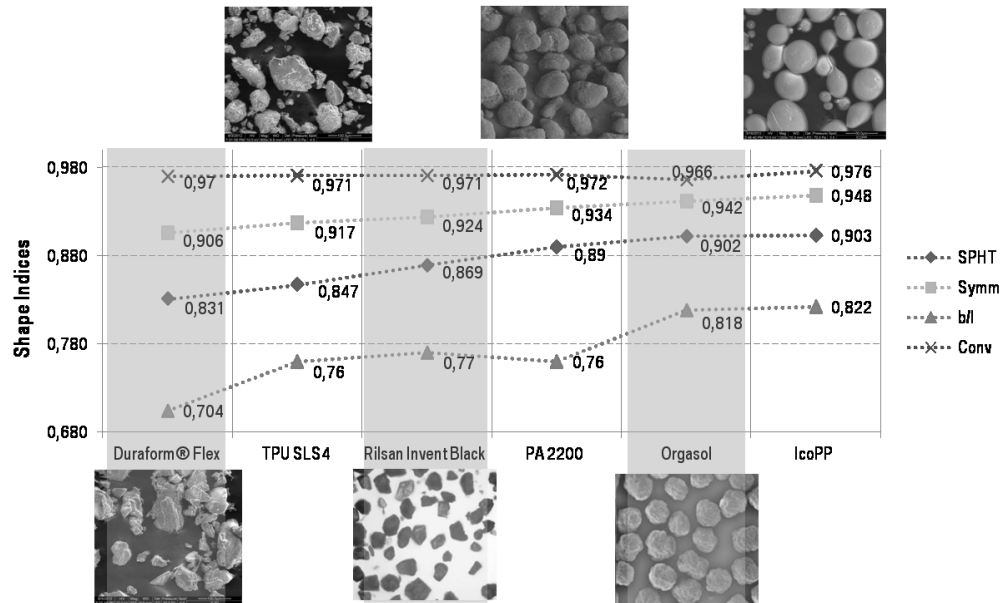


Figure 39: Comparison of Camsizer XT shape indices; Sphericity (SPHT), Symmetry (Symm), breadth to length ratio (b/l) and Convexity (Conv) over a variety of significantly different particle shapes in accordance with the corresponding SEM pictures – (the abbreviation F0 in TPU SLS 4 F0 stands for original size distribution as manufactured)

The sphericity (SPHT) and the symmetry (Symm) values follow the same trend that also matches the visual assessment of the observed powder shapes. Taking a closer look at the Symm values it can be seen that they vary in a narrow range (0.9042) from least round to roundest particle compared to the SPHT results (0.072).

5.3 Powder Characteristics

Optical Evaluation

For reasons of optical evaluation of the powders in the first instance, SEM images were taken for all the materials compared in this study (PA12, TPU SLS 4, DF and corresponding fractions of the TPEs). The SEM images of PA12 and TPU SLS 4 (F0, F25 and F45) are presented in Figure 40(a – d) a comparison of DF and PA12 in Figure 41(a – d) and an overview of the surfaces of all three materials in Figure 42(a – c). As a general remark, PA12 particles presented a smooth surface texture and a more spherical shape than the edgy and angular shaped particles of the TPU SLS 4 and the DF fractions as a consequence of their manufacturing process. The PA12 is a precipitation product whereas the other

two powders were cryogenically milled [299]. This manufacturing process per se leads to more jagged and edged particles. However, taking a closer look at the TPU SLS 4 fractions the fine particles in the F0 fraction ($<25\text{ }\mu\text{m}$) showed an irregular surface compared to the bigger grains and appeared less round and spherical than larger particles included in its original distribution.

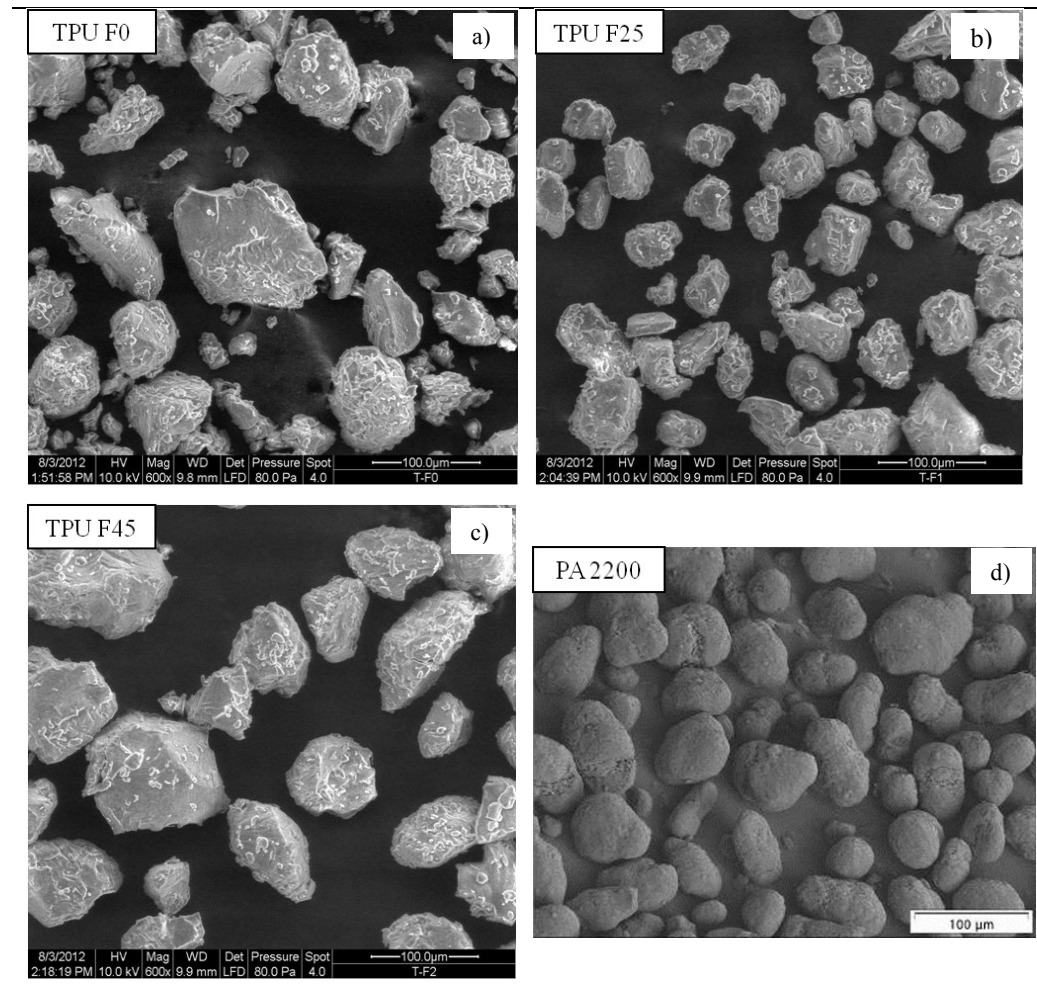


Figure 40: SEM images (100 μm resolution top four images and 5 μm resolution for the bottom two images) for TPU SLS 4 fractions (a – c) compared to PA12 d) (SEM for PA 12 is taken from [32])

This became even more obvious when TPU F0 was compared to F25 and F45 respectively. Within the powder fractions containing a lower fine proportion, the particles that were still edgy but less rough with clear edges. In further sieving out particles between 25 – 45 μm , the PSD of TPU F45 including only particle sizes $\geq 45\text{ }\mu\text{m}$ showed a rather mono-modal distribution as is known for PA12. Without the claim to be representative for the whole bulk, the surface morphology in

Figure 42 indicates the differences between TPU SLS 4 and PA12. The TPU SLS 4 still showed artefacts of the cryogenic milling while the PA12 surface seemed as a result from agglutination of small polymer particles. A similar pattern as for the TPU SLS 4 was observed when comparing the DF fractions. The reduced amount of fine particles became obvious from the optical observation for both polymers, although the particles in DF F25 and DF F45 respectively remained rather jagged and more angular with clear “crater-like” areas not showing the smooth fragments at the edges as for the corresponding TPU SLS 4 fractions.

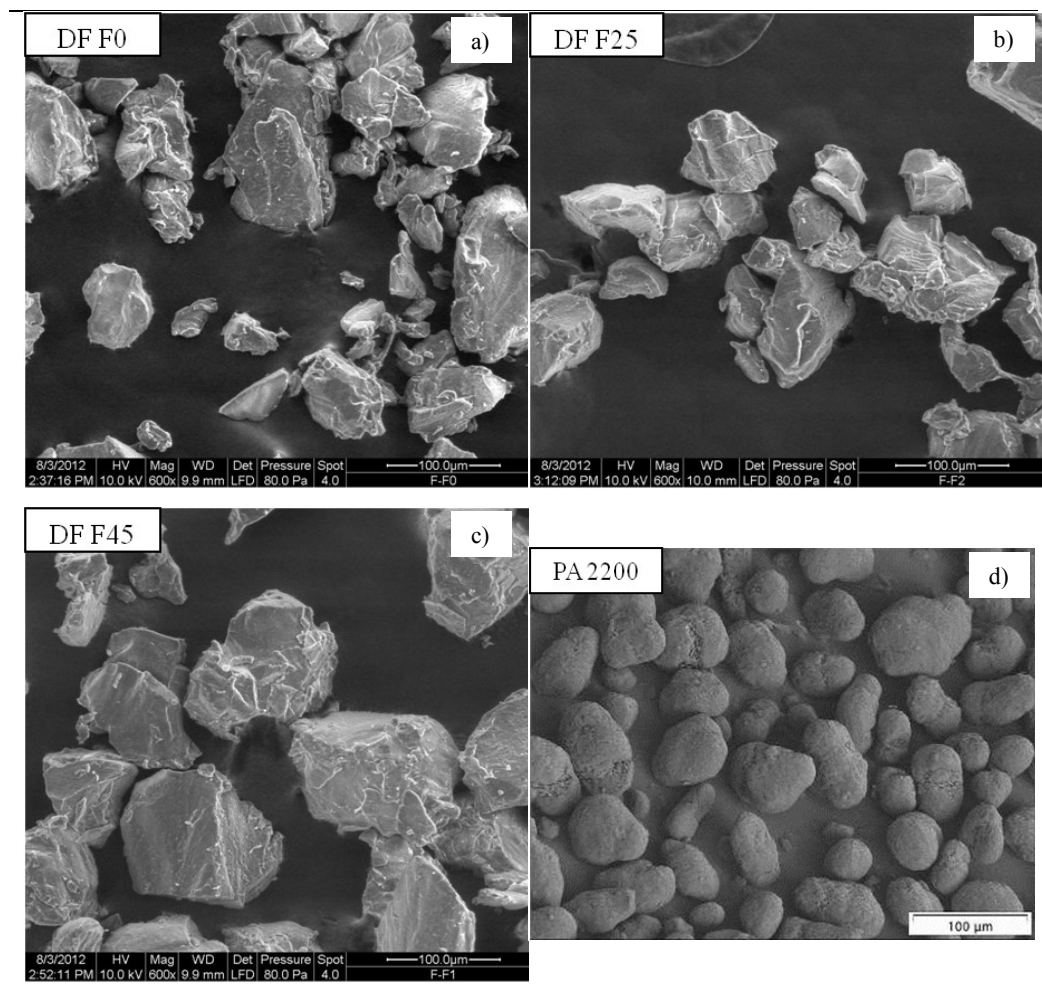


Figure 41: SEM images (100 µm resolution top four images and 5 µm resolution for the bottom two images) for DF fractions (a – c) compared to PA12 d) (SEM for PA 12 is taken from [27])

When comparing all figures (Figure 41a – d and Figure 42a – d representing shape and surface, Figure 42a – c depicting surface morphology) it is clear that

the ground materials result in irregular particles and depending on the processing characteristics and ductility of the polymer might break up with varying levels of brittle fracture that in turn results in rather sharp or fibrous/streaky edges respectively.

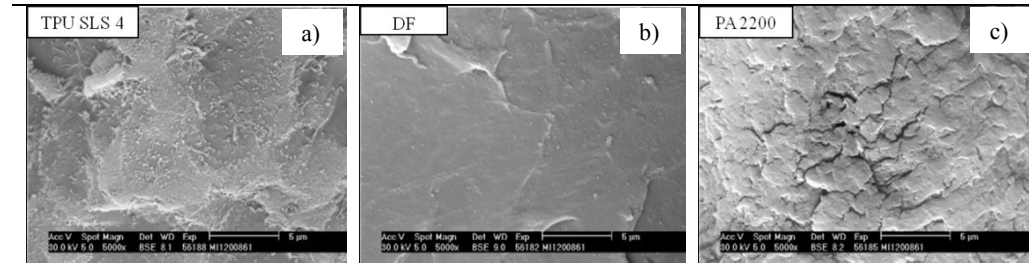


Figure 42: SEM images (100 µm resolution top three images and 5 µm resolution bottom three images) for comparison of TPU F0 a), DF F0 b) and PA12 c)

The images within this section are aimed to provide basic comparison of the surface texture and the shape of the particles by optical observation. It allows for a first impression of the influence of their specific manufacturing processes especially in terms of shape and surface morphology to support later discussion on the quantification of the shape as well as the packing or the dynamic flow behaviour.

Quantification of Moisture Content, Particle Size and Shape

Within this section, the results for the powder characteristics by means of moisture content, particle size distribution and shape are presented. In Figure 43a the normalized frequency distribution based on volume in dependence of particle size for PA12 in comparison to the TPU SLS 4 fractions is shown.

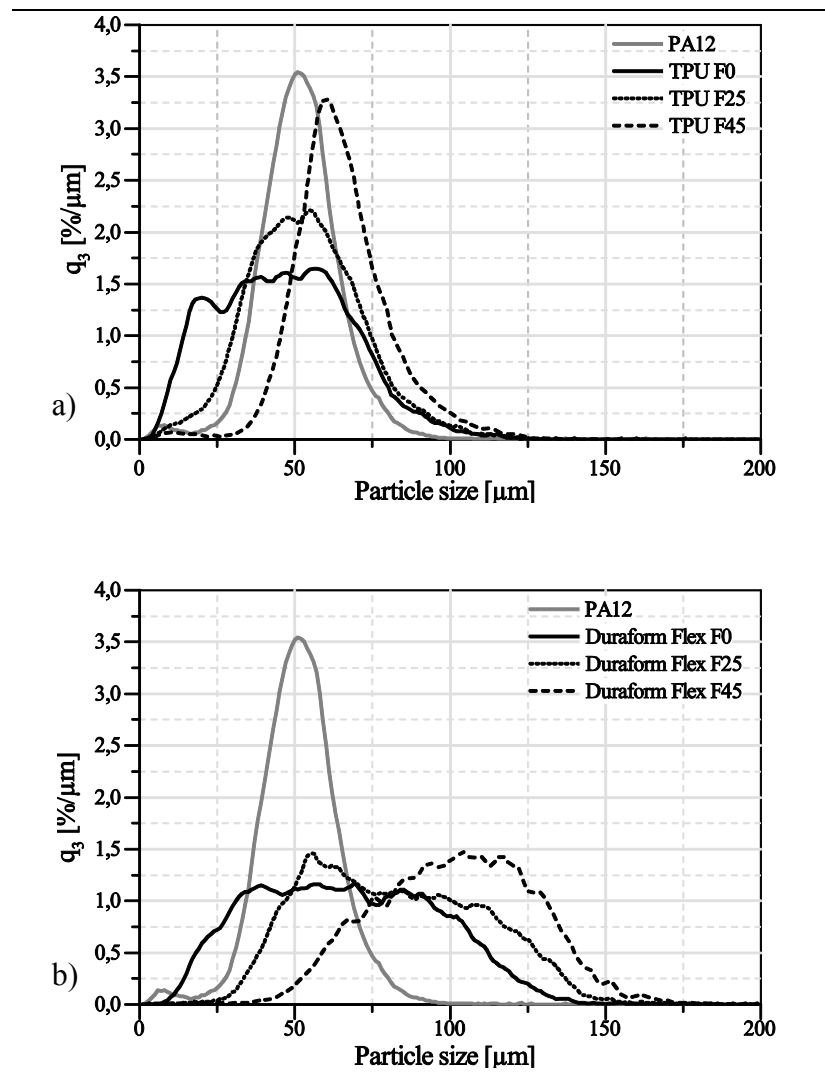


Figure 43: PSDs of the a) TPU SLS 4 and b) DF fractions over particle size in comparison to PA12

TPU F0 showed a multi-modal PSD while TPU F25 was bi-modal and TPU F45 became mono-modal, similar to PA12. The more that fine particles were separated from the original bulk F0, the narrower became the corresponding PSD. Approximately 90% of the particles for TPU F0 were between 5 – 100 μm and for TPU F25 approximately 90% of the population ranged between 25 – 100 μm . The particles of TPU F45 were in a narrow range of 45–120 μm and as a consequence approximately 90% of the population ranged between 45 – 100 μm . For all the TPU SLS 4 fractions the percentage of particles that lay between 100 and 120 μm was approximately 10%. With the decreasing amount of fine particles within the TPU SLS 4 fractions, the corresponding modality (number

of peaks) of their PSDs exhibited a decline and they aligned more and more to the PSD of the commercially available material PA12. In Table 14 the average values for D₁₀, D₅₀ and D₉₀ are shown for all powders. The TPU SLS 4 fractions showed differences regarding their particle shapes as shown by means of sphericity (SPHT) in Table 14. The average SPHT for TPU F0 was 2.81% lower than it was for TPU F25 and 3.86% lower than for TPU F45. The fine particles below 25 µm inside TPU F0 displayed a sharp surface and an irregular edgy shape (SPHT = 0.855) as indicated by the SEM image in Figure 40. The larger particles with sizes above 25 µm displayed SPHT values approaching the shape of a sphere and a smoother surface morphology for the optical evaluation, especially when comparing TPU F0 and TPU F45. A progressive decrease of fine particles between 25 and 45 µm led to a PSD with even more spherical and symmetrical particle shapes. Consequently, TPU F45 reached the highest SPHT value at 0.888 with less irregularities and edges over its particle surface. The SPHT value of TPU F45 was very close to PA12 (0.891).

Material/ Characteristic	PA12	TPU F0	TPU F25	TPU F45	DF F0	DF F25	DF F45
D ₁₀	36.5	17.9	31.1	47.7	35.3	45.8	66.7
D ₅₀	50.9	45.7	52.2	62.8	69.4	77.7	101.2
D ₉₀	66.3	74.1	76.2	84.2	108.7	119.6	132
SPHT	0.891	0.855	0.879	0.888	0.842	0.835	0.835
Moisture content	0.512	0.309	0.283	0.307	0.27	0.278	0.272

Table 14: Powder characteristics for PA12, TPU F0-F45 and DF F0-F45

The maximum PSD for the original DF fraction (DF F0) ranged between 0 – 175 µm, the PSD of DF F25 ranged from 25 – 175 µm and the PSD of DF F45 between 45 – 175 µm. All the DF fractions presented multimodal (multiple peaks) PSDs as depicted by Figure 43b. Their modality presented a small decline as the amount of fine particles was reduced. While the amount of particles above 150 µm was negligibly low for DF F0 and DF F25, for DF F45 it was approximately 10%. In contrast to the PSDs of TPU SLS 4, none of the DF fractions aligned to a pattern of the benchmark PA12. Moreover, the DF fractions showed differences regarding their particle shapes and surface

morphologies presented in Figure 41. The fine particles below 25 μm thereby exhibited a sharp and fibrous surface texture, while the particles above 25 μm displayed a rather smooth surface texture. However, the average SPHT of DF F0 was 0.84% lower than the SPHT of DF F25 and DF F45 which showed the same value.

When comparing the particle sizes of TPU SLS 4 and DF fractions from Figure 43a and b it can be seen that the DF fractions enclosed particles with sizes above 120 μm . This especially applies for DF F45, approximately 30% of its particles were above 120 μm . For all of the TPU SLS 4 fractions, 120 μm was the largest particle size overall. Moreover, from the values in Table 14 it became obvious that the average particle diameters of the DF fractions were larger than for the TPU SLS 4 fractions and in addition the SPHT values of all the DF fractions were lower.

Besides the physical characteristics of the particles, moisture was monitored. The differences in moisture between the fractions of the same material didn't show significant variations, while between the same fractions of TPU SLS 4 and DF the differences in moisture absorption ranged between 10 – 12% as shown in Table 14.

5.4 Effect of varying Powder Properties on Bulk and Flow Behaviour

Within this section the results of the varying PSDs on the powders bulk behaviour in terms of packing efficiency and their dynamic behaviour in terms of flow efficiency are presented according to the method introduced in section 4.2.8. In Figure 44 the results for the poured and tapped bulk densities determined during the HR measurements are depicted.

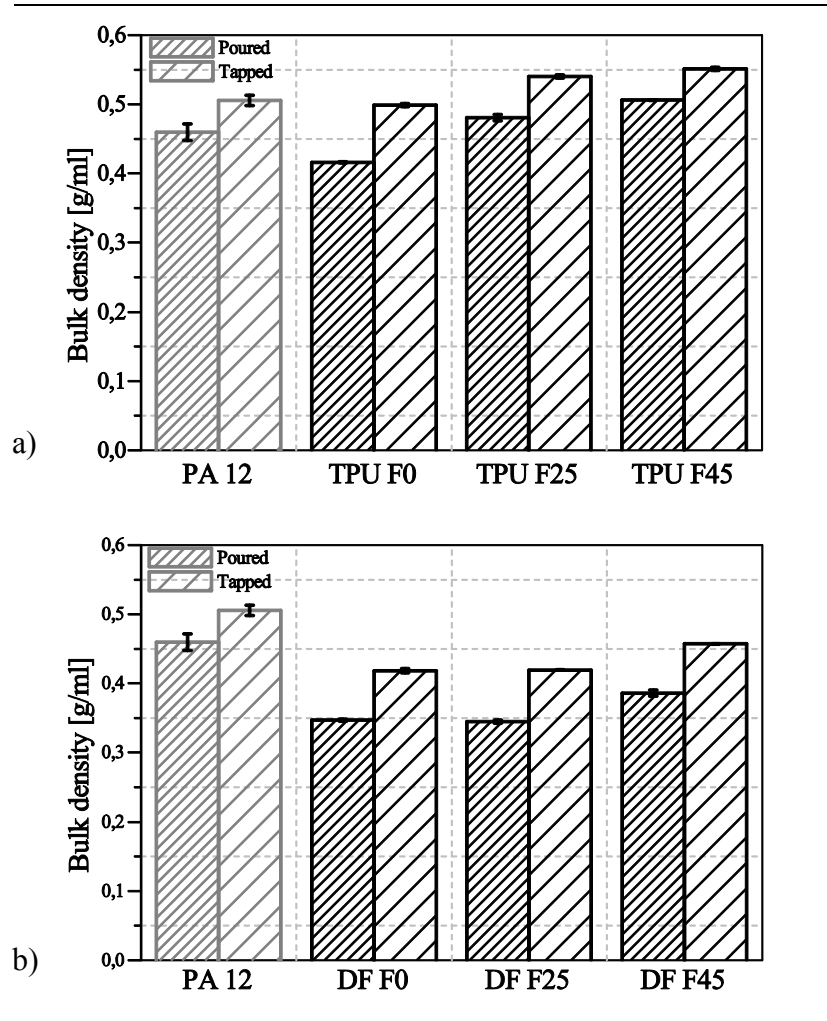


Figure 44: Bulk density of the powder samples in poured vs. tapped states measured by the HR method of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

According to Figure 44a, TPU F45 presented the highest packing density in ambient conditions within its own fractions (in poured state: $\text{TPU F25} = \text{TPUF0} + 15.54\%$, $\text{TPU F45} = \text{TPU F0} + 21.56\%$ / in tapped state: $\text{TPUF25} = \text{TPU F0} + 8.26\%$, $\text{TPU F45} = \text{TPU F0} + 10.53\%$). The packing efficiency of the TPU SLS 4 fractions, both in poured and tapped state, was increased with a decreasing amount of fine particles. Compared to PA12, the tapped TPU F0 fraction is only 1.33 % lower (poured density is 9.42 % lower). The TPU F25 (TPU F 25 $\cong$ 4.66% higher poured density and 6.82% higher tapped density) and TPU F45 (TPU F45 $\cong$ 10.11% higher poured and 9.06% tapped density) packed more efficiently compared to PA12.

The packing density between DF F0 and DF F25 did not change (differences less than 1%). However, an increase in the packing density was noticed for DF F45 compared to DF F25 and DF F0. DF F45 presented the highest packing density in ambient conditions (in poured state: DF F45 = DF F0 + 9.32%, DF F0 = DF F25 + 0.58% / in tapped state: DF F45 = DF F0 + 7.77%, DF F25 = DF F0 + 0.2%). The angular and irregular shape, the rough surface texture as well as the multi-modal PSDs of the DF fractions create a rather loose bulk density. As a result, the proportion of large particles should be higher compared to the proportion of the finer particles inside a PSD.

A comparison of the results for the HR is presented in Figure 45.

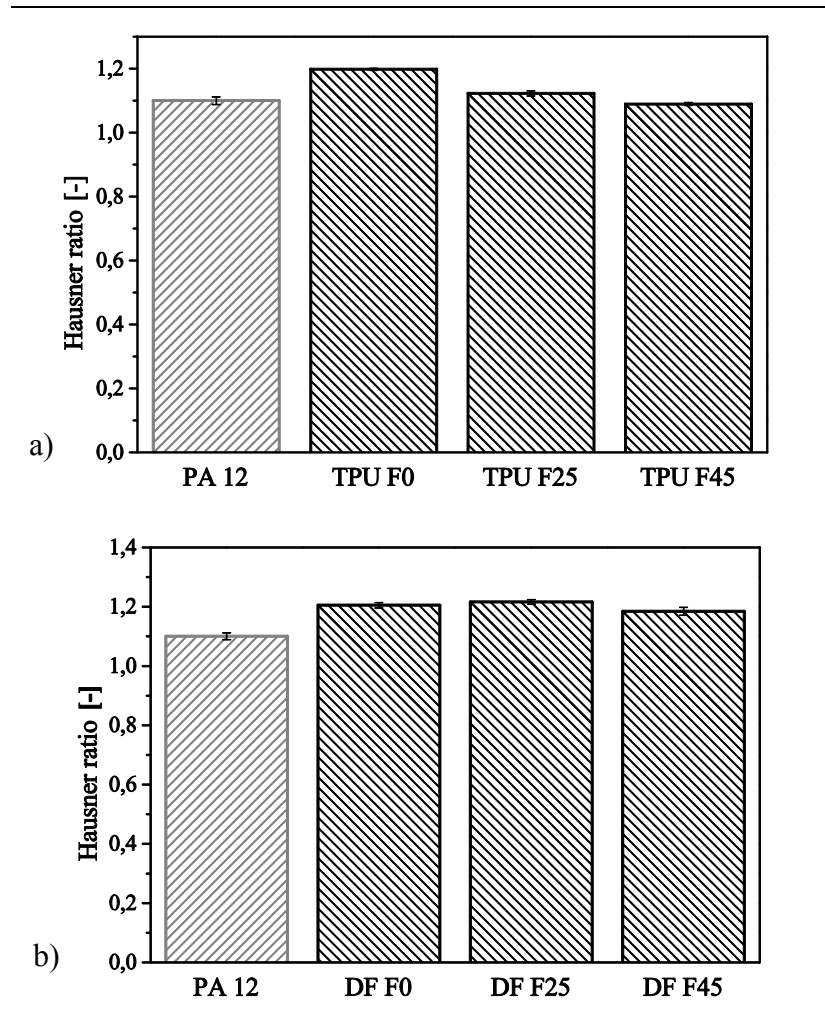


Figure 45: Hausner ratio of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

Amongst the TPU SLS 4 fractions as shown in Figure 45a, TPU F0 presented the highest HR of 8.91 % higher than PA 12 (TPU F0 = TPU F25 + 6.3%, TPU

F0 = TPU = F45 + 9.08%). This led to the following order of the powders' cohesiveness $TPUF0 > TPU\ F25 > TPU\ F45$ and consequently the flowability of the TPU SLS 4 fractions followed the exact opposite order with TPU F45 reaching the same HR as for PA12 (+ 1%). Consequently, TPU F0 had the greatest resistance to free flowing. As a result, for the TPU SLS 4 fractions, flow and packing efficiencies were improved when the fine particles below 25 μm were extracted from the PSD.

According to Figure 45b, DF F25 and DF F0 presented no differences within the measurement accuracy. It is clear that the multi-modal PSD of DF F25 could not reach a better flow rate compared to DF F0. However, the separation of particles between 0 – 45 μm enabled DF F45 to reach the most efficient flow pattern amongst the DF fractions with a HR of 1.71% lower compared to DF F0.

Another objective was to correlate the bulk density values of the HR method with the Conditioned Bulk Density (CBD) calculated from the FT-4. The results are depicted in Figure 46. Since the CBD is a user independent value and proved to show the most reliable results for the powder packing in LS, it is of interest to compare the trends of poured density from the HR method and the CBD in terms of reliability. TPU F45 presented the highest CBD amongst the TPU SLS 4 fractions ($TPU\ F25 = TPU\ F0 + 8.11\%$, $TPU\ F45 = TPUF0 + 12\%$), following the same trend as the bulk densities measured with the HR (poured and tapped). In particular, the tapped density values (HR) showed a good correlation to the CBD values of the TPU SLS 4 fractions.

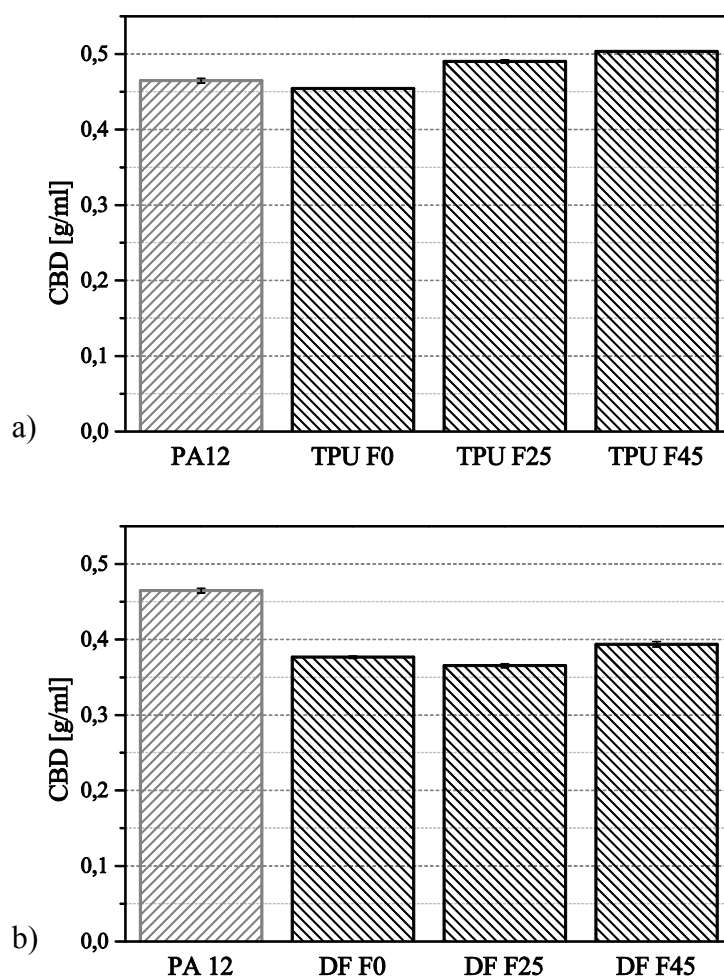


Figure 46: Conditioned Bulk Density (CBD) of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

While the CBD of TPU F0 was only around 2% lower than the value of PA12, the CBD of TPU F25 was 8.11% higher and even 12% higher for TPU F45 compared to TPU F0.

The results for the DF fractions shown in Figure 46b again matched with the corresponding performance in the HR measurements. DF F45 presented the highest CBD amongst the DF fractions (DF F45 = DF F0 + 4.86%, DF F0 = DF F25 + 2.59%). It therefore follows that DF F25 presented the loosest packing amongst the DF fractions. The DF F45 fraction's CBD thereby was still around 19 % lower than the CBD of PA12.

According to the basic flowability energy (BFE) values shown in Figure 47a, TPU F45 presented the highest flow efficiency amongst the TPU SLS 4 fractions that was even 20.28% higher than the BFE of PA12.

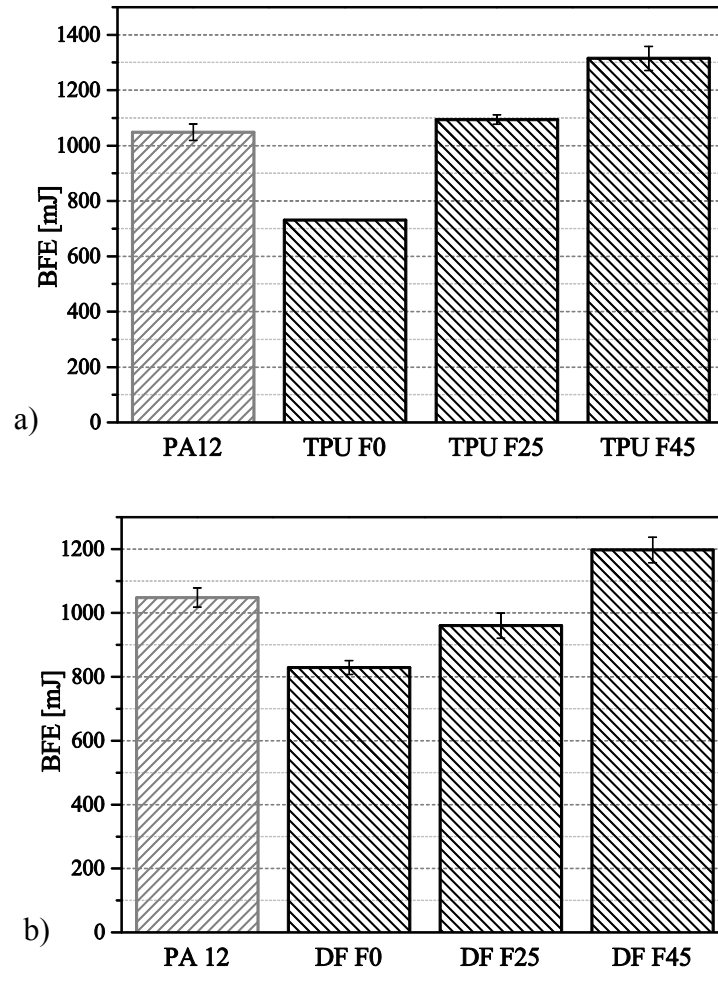


Figure 47: Basic Flowability Energy (BFE) of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

The BFE value for TPU F25 was 33.21% higher compared to TPU F0 and for TPU F45 was even 44.43% higher compared to the original PSD of TPU F0. Figure 48 shows a similar trend for the specific energy (SE) results (TPU F0 = TPU F25 + 10.13%, TPU F0 = TPU F45 + 11.38%).

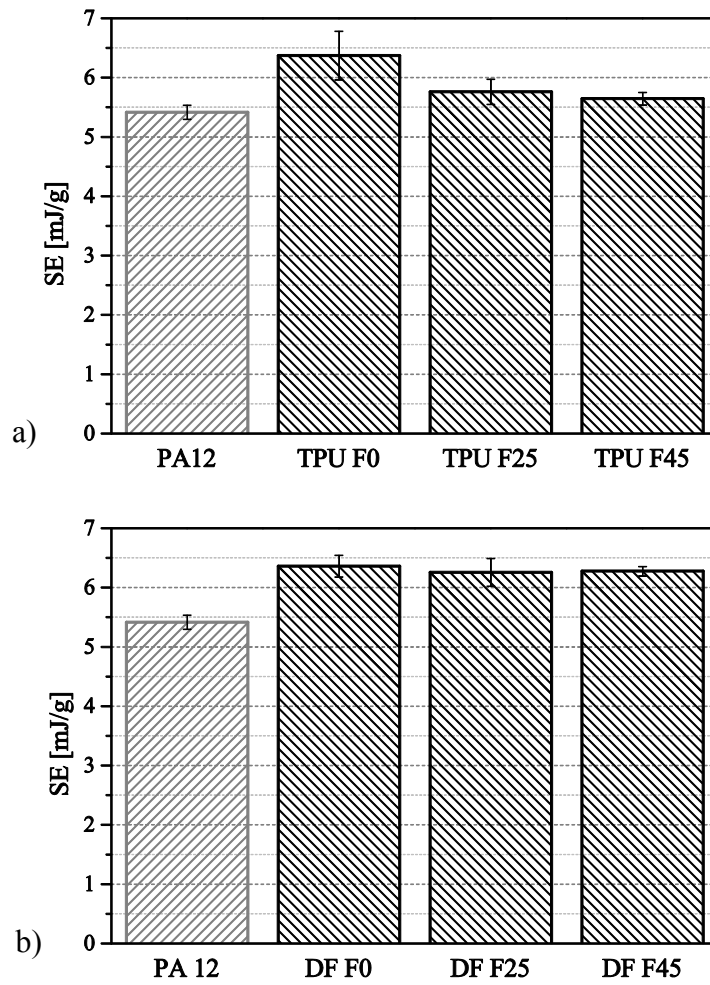


Figure 48: Specific Energy (SE) of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

This behaviour was also confirmed by the results for avalanche angle shown in Figure 49a. TPU F25 had a 12.51% lower and TPU F45 a 19.11% lower avalanche angle indicating enhanced flowability compared to TPU F0. Depicted by Figure 50, the materials that presented low flow efficiency also showed a rough bulk surface texture. The surface fractal value for TPU F25 was 17.7% lower and for TPU F45 was 23.91% lower than TPU F0. According to the results of the TPU SLS 4 fractions, the packing efficiency was higher for the PSDs that showed low SE, low avalanche angle and cohesion was lower (high BFE).

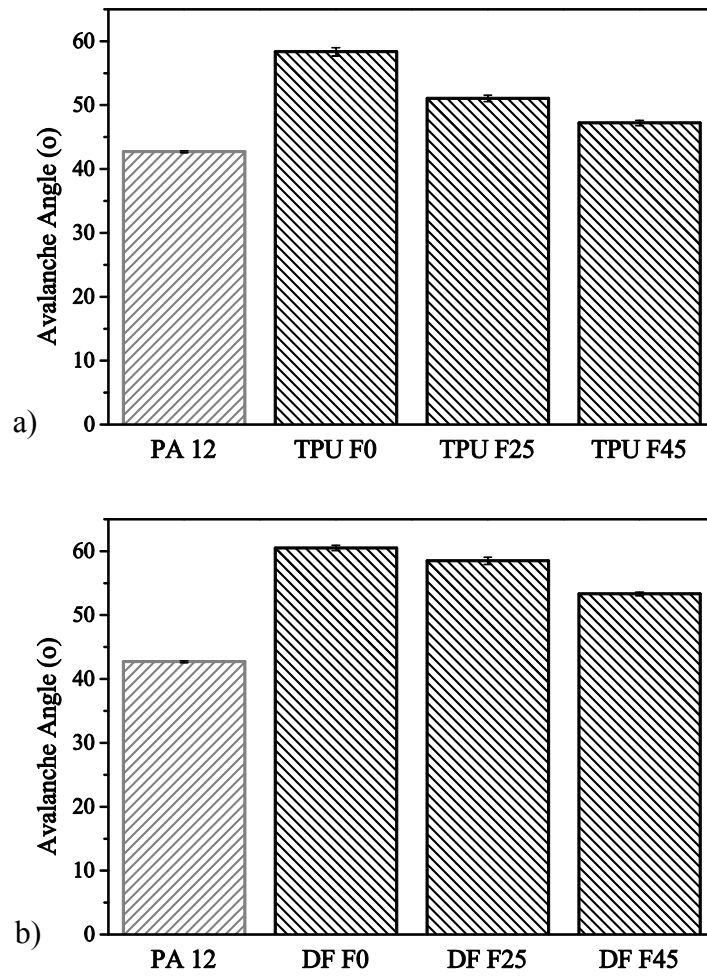


Figure 49: Avalanche Angle of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

The BFE values for DF in Figure 47b showed a similar trend with a decrease in fine particles ($DF\ F25 = DF\ F0 + 19.02\%$, $DF\ F45 = DF\ F0 + 30.7\%$). The SE value of DF F0 was 4.16% higher than F25 and within the standard deviation F25 and F45 did not show a significant difference. The avalanche angle values depicted in Figure 49 b showed a lower standard deviation with DF F25 showing a 3.31% and DF F45 a 11.9% lower avalanche angle compared to F0. Amongst the DF fractions, DF F0 did not flow as well as the other two fractions which did not present any significant difference in flowability (SE/avalanche angle). However, the cohesive behaviour (low BFE) of DF F0 was more intense than DF F25 whose cohesiveness was lower than DF F45. The surface fractal followed the trend of the packing efficiencies ($DF\ F0 = DF\ F25 - 2.53\%$, $DF\ F0$

= DF F45 + 11.6%). As depicted in Figure 50 powders with low packing densities created a rough bulk surface after rotation and deposition.

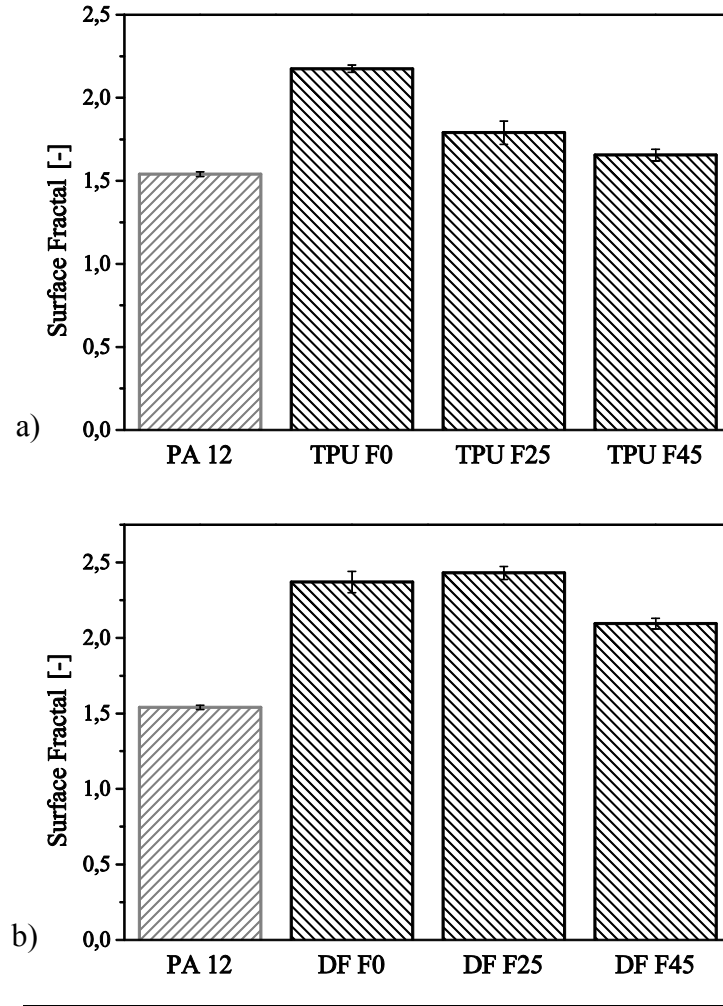


Figure 50: Surface Fractal of PA12 compared to a) TPU F0-F45 and b) DF F0-F45

As expected, the surface of the bulk was rougher for the DF fractions compared to TPU SLS 4.

5.5 Effect of varying Bulk Properties on Absorption and Thermal Conductivity

According to the equation Eq. 21 and the procedure described in section 4.2.10, the value for the specific heat capacity c_p , the bulk density (here in-situ LS density) as well as the thermal diffusivity are necessary input variables for the determination of the thermal conductivity of the powders observed. The results for the c_p values as well as the thermal diffusivity are shown in appendix A.6

and A.7 (Table 37 - Table 48). The values have been determined in steps of 20°C for a temperature interval of 20 – 120°C for the TPU SLS 4 fractions and between 20 – 160°C for the DF fractions. For each fraction (F0, F25, F45) two series of measurements have been performed to calculate the mean value. The lower and upper temperature limits of the intervals mentioned represented the range of varying processing temperatures (feed temperature, build chamber temperature). In the case of TPU F0, the c_p values showed a deviation from linearity, no data was determined above 120°C. For this reason, for the calculation of the thermal conductivity at 125°C the value of c_p was calculated on approximation of the value at 120°C. When comparing the c_p values it becomes obvious that they increase with temperature. What is noticeable is the increase of the heat capacity in dependence of decreasing fine particles within the powder fractions. This increase in c_p for the TPU SLS 4 fractions thereby is more significant. Besides the high c_p value of DF F0 all other c_p values of the TPU SLS 4 fractions are generally higher compared to the corresponding DF fractions. The values for c_p alongside the results for the thermal diffusivity that were used for the calculation of the thermal conductivity are shown in appendix A.6 and A.7 respectively. Besides the heat capacity in the corresponding tables (Table 43 to Table 48) of the appendix the values for the bulk densities applied as input variables are shown before and after the measurement. Due to the melting of the powder bulk they experience a densification. The bulk density before the analysis is taken from section 4.2.9 and approximately equals the in-situ bed density. The thermal conductivity was calculated for all fractions of the two materials at a feed-temperature of $55 \pm 0,5^\circ\text{C}$ (see Table 22) and at a build chamber temperature of $120 \pm 0.5^\circ\text{C}$ for TPU SLS 4 and $160 \pm 0.5^\circ\text{C}$ for DF respectively. Figure 51 a and Figure 52 represent the data for the thermal conductivity for the two materials powder fractions (F0 to F45) at the corresponding feed or build chamber temperature respectively. As a general remark, the results for the two materials (range of 0.202 – 2.380 W/mk) are in the expected range of thermal conductivity for polymers between 0.15 to 0.5 W/mk as shown in section 2.1.4. Within the fractions of each material it becomes obvious that thermal conductivity decreases with increasing temperature (feed vs. build chamber temperature). For the TPU SLS 4 fractions there is a maximum

decrease in thermal conductivity at feed compared to build temperature of approximately 19.33 %, whereas the maximum delta for the DF fractions equalled 42.95 %.

Another noticeable effect for the DF fraction is that their values of thermal conductivity vary in a narrower range in dependence of their particle size distributions compared to the TPU SLS 4 fractions. Thereby, the maximum deviation for the DF is 4.94 % while the difference between the minimum and maximum value of TPU SLS 4 is 13.95 %. The TPU SLS 4 shows a systematic trend of thermal conductivity in dependence of its fractions. With an increasing bulk density (decreasing amount of fine particles F0-F45 as depicted by Figure 51b for 55°C and Figure 53 a for 120°C) the thermal conductivity is also increasing. Within the standard deviations, though, this trend is merely significant for the TPU SLS 4 fractions (as e.g. shown in Figure 53a for build chamber temperatures) when considering the typical range of thermal conductivity of polymers ranging between 0.15 to 0.5 W/mk. This gets obvious as the thermal conductivity for the DF fractions increases in the order DF F25 to DF F45 to DF F0, while F45 has the highest packing density. Thereby, F0 represents the outlier value as it does have a lower CBD compared to DF F45, however it shows a higher thermal conductivity according to the results. In both cases, however, the effects can be attributed to the amount of fine particles in the corresponding bulk with reference to Figure 43a and b.

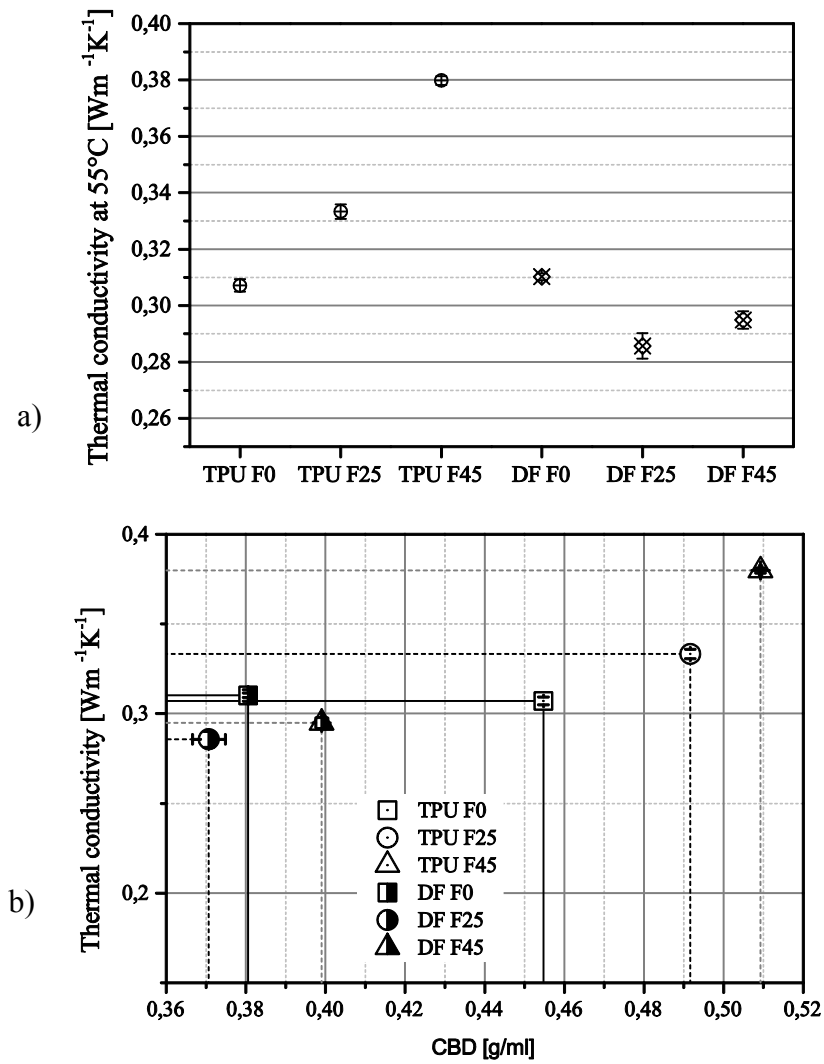


Figure 51: Results for thermal conductivity in a) dependence of PSD at 55°C for TPU SLS 4 and DF and b) dependence of CBD, both at 55°C for TPU SLS 4 and DF respectively

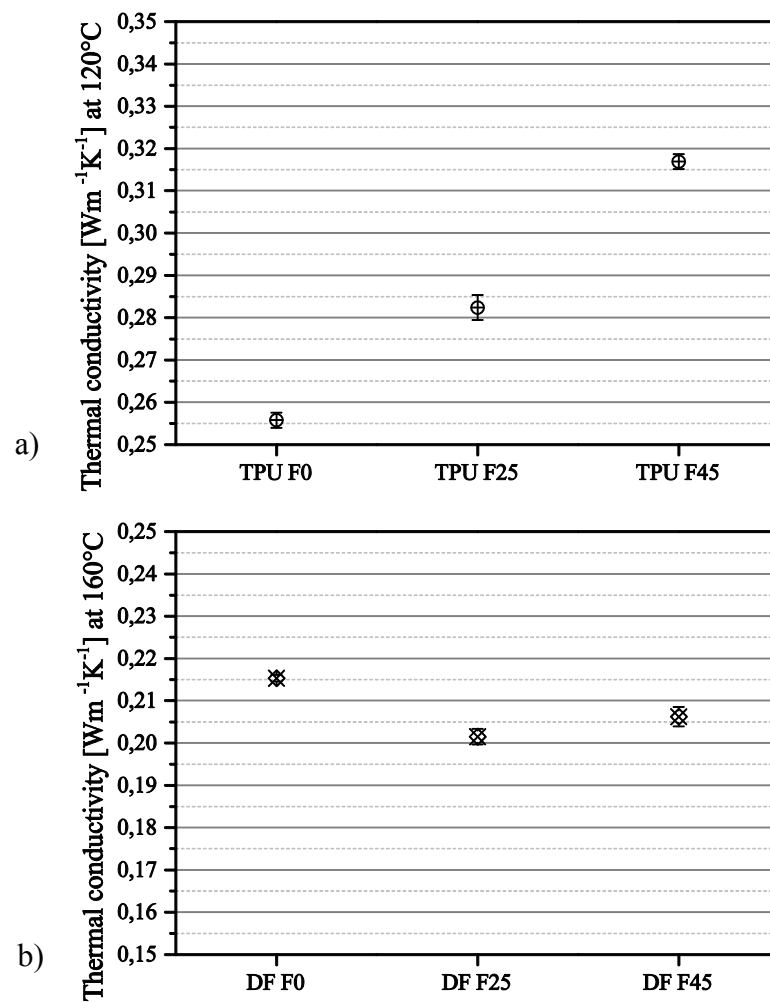


Figure 52: Results for thermal conductivity in dependence of PSD for a) TPU SLS 4 at 120°C and b) DF at 160°C

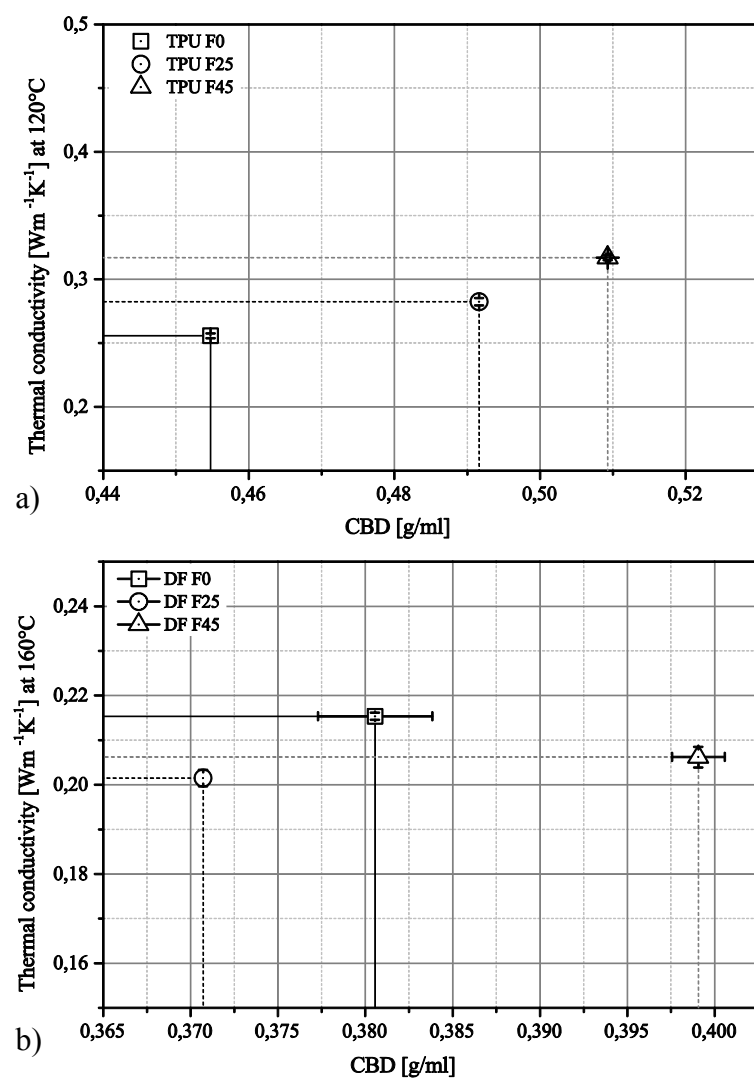


Figure 53: Thermal conductivity vs. CBD (FT-4 value) for the fractions of a) TPU SLS 4 at 120°C and b) DF at 160°C

5.6 Effect of in-situ Packing on Part Properties and Quality – Dependence on Powder Behaviour

Within section 5.4 the effects of varying PSD on the bulk behaviour such as packing density was described. In Figure 54, a comparison between the in-situ bulk density, determined on the basis of cubes that enclosed powder during the LS process (see section 4.2.9), and the laboratory scale density (CBD) detected with the powder rheometer is presented.

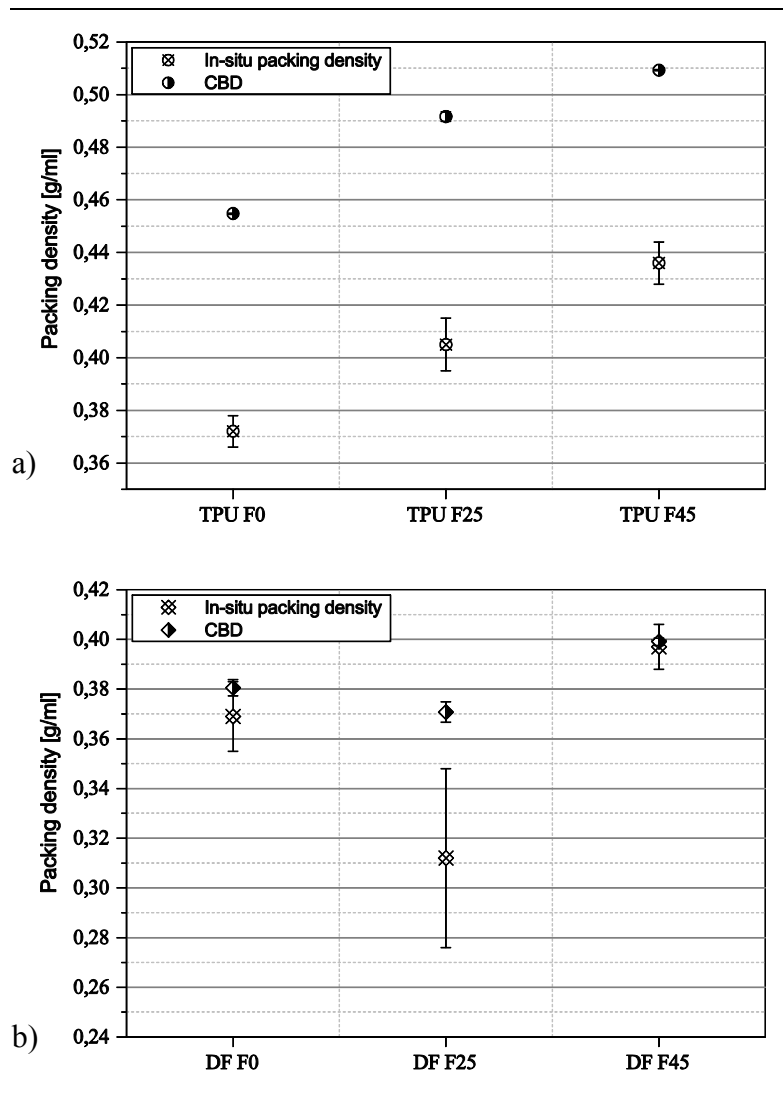


Figure 54 : Comparison of in-situ bulk density and laboratory scale density CBD for a) TPU F0-F45 and b) DF F0 - F45

It can be seen that the CBD measurements show a high repeatability compared to the results of the in-situ packing density. However, the mean values of the in-

situ densities for the TPU SLS 4 fractions in Figure 54a show a straight forward correlation to the CBD. When looking at the results of the corresponding DF fraction in Figure 54b it can be seen that, except for DF F25, the values for the in-situ density of DF and the CBD almost correspond within the standard deviation.

Besides the comparison shown above, this section presents the results of the influence of varying PSD on tensile properties as well as the part's quality in terms of density and surface roughness. For this reason only data of the two TPE materials was compared as described in section 4.2.9. The results for the tensile testing in terms of E-Modulus, UTS and EaB are shown in Figure 55, Figure 56 and Figure 57, respectively.

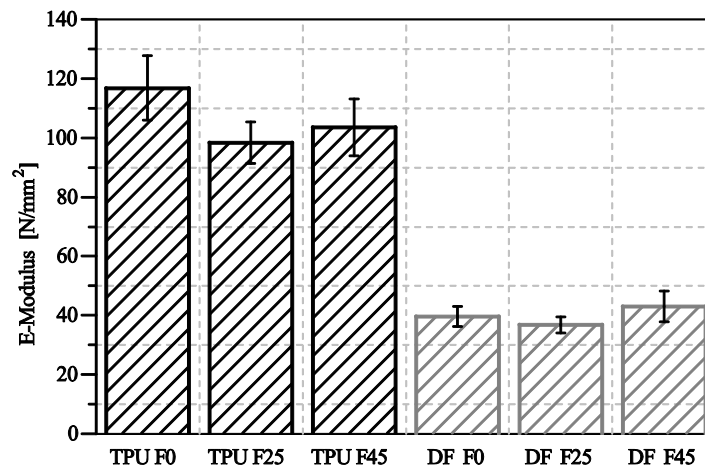


Figure 55: E-Modulus in dependence of PSD for TPU SLS 4 and DF fractions

The E-modulus for the TPU SLS 4 fractions did not show significant differences within the results' standard deviation, while the mean value for tensile strength of TPU F0 was 11.16% lower compared to TPU F25 and 11.41% lower compared to TPU F45. Within the standard deviation TPU F25 and TPU F45 did not show any difference in UTS. A more significant trend could be seen for the mean values of the %EAB (TPU F0 was 60.97% lower compared to TPU F25 and 66.23% lower compared to TPU F45). The change in flowability and packing did not show any influence in terms of shore hardness as shown in Figure 58, for either of the two materials and their corresponding fractions.

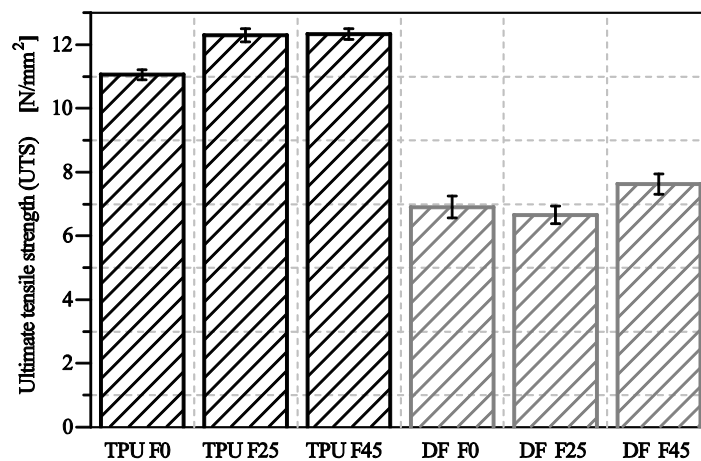


Figure 56: UTS in dependence of PSD for TPU SLS 4 and DF fractions

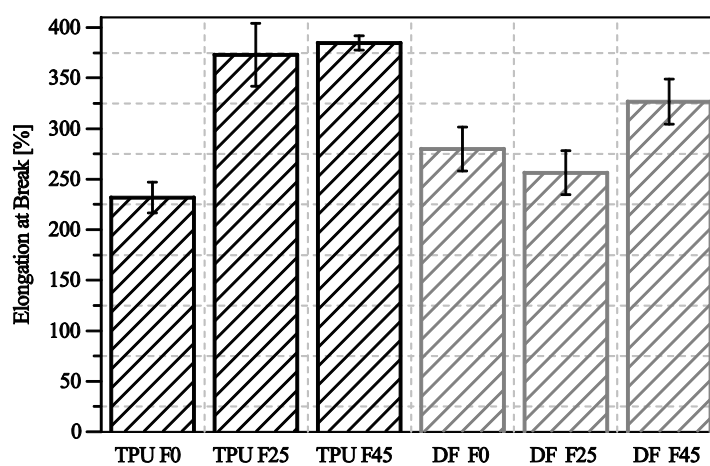


Figure 57: EaB in dependence of PSD for TPU SLS 4 and DF fractions

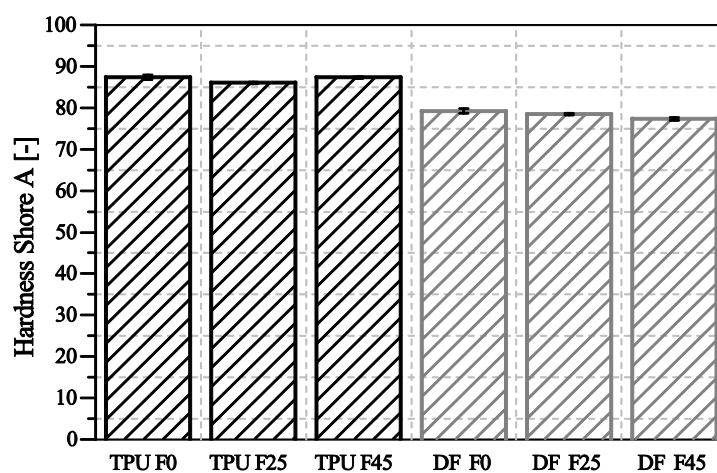


Figure 58: Hardness (Shore A) in dependence of PSD for TPU SLS 4 and DF fractions

In terms of surface roughness (see Figure 59) and the results' standard deviation, the only distinct difference observed was the higher roughness of TPU F0 compared to TPU F45. Parts manufactured with TPU F45 showed the lowest surface roughness followed by TPU F25 and TPU F0 with the highest surface roughness. The mean value for R_z of TPU F0 was 23.09% higher compared to TPU F25 and 34.76% higher compared to TPU F45. The mean values R_a and R_q followed the same trend as R_z where TPU F0 > TPU F25 > TPU F45.

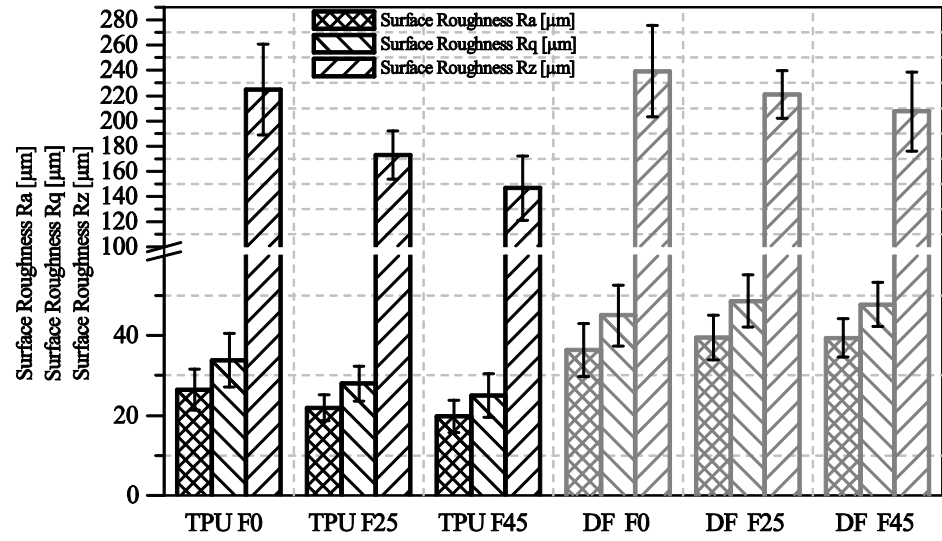


Figure 59: Surface roughness (R_a , R_q , R_z) in dependence of PSD for TPU SLS 4 and DF fractions

The porosity and the void volume of the parts manufactured by the different TPU SLS 4 fractions are shown in Figure 60. A straightforward correlation of the part's void volume and the part's porosity with the powders' packing and flow properties was observed. The part's porosity and the part's void volume both decreased with enhanced packing efficiency of the powders. As shown in Figure 61 the part's porosity for TPU F0 was 54.28% higher compared to TPU F25 and 54.75% higher compared to TPU F45. The part's void volume for TPU F0 was 45.39% higher compared to TPU F25 and 48.25% higher compared to TPU F45. The same trend could be observed for the flow efficiency as the part's porosity and the part's void volume both decreased as the flowability of the materials increased.

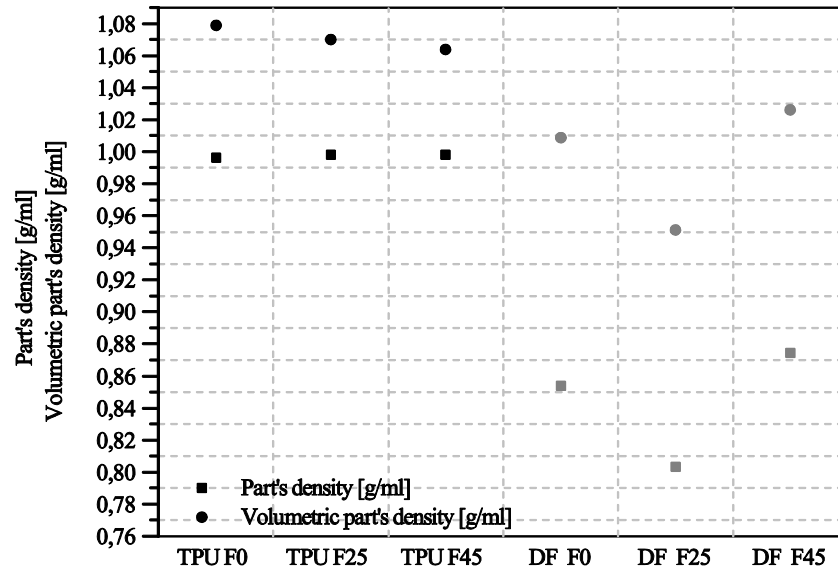


Figure 60: Part densities measured by CT in comparison to the calculated density by mass to volume ratio in dependence of PSD for TPU SLS 4 and DF fractions

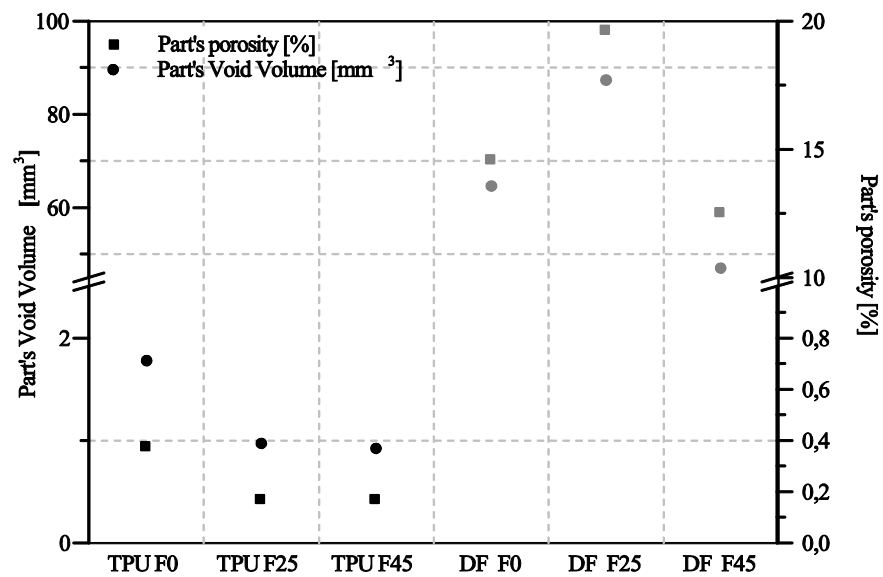


Figure 61: Part porosity and void volume measured by CT in dependence of PSD for TPU SLS 4 and DF fractions

The overall part density for the TPU SLS 4 fractions did not differ significantly. The part's porosity for DF F0 was 34.59% lower compared to DF F25 and 14.13% higher compared to DF F45. According to the CT results in Figure 61 the part's void volume for DF F0 was 35.18% lower compared to DF F25 and 27.28% higher compared to DF F45 that also had the highest flowability and packing density. The part density of the CT analysis for DF F0 was 5.75% higher

(5.92% higher calculated volumetrically) compared to DF F25 and 1.68% lower (2.41% lower calculated volumetrically) compared to DF F45.

5.7 Summary

Within the Pre-Process investigations the observed powders were optically evaluated with regards to their shape and surface morphology. Generally, the PA12 particles presented a smooth surface texture and a more spherical shape than the edgy and angular shaped particles of the TPU SLS 4 and the DF fractions resulting from their respective manufacturing processes. Being a precipitation product the PA12 has a narrow, controlled PSD and close to spherical shape, whereas the cryogenic ground TPE powders TPU SLS 4 and the DF result in a broad PSD with rather edgy particles with a rough surface morphology [299]. The fractions (F0, F25, F45) of TPU SLS 4 aligned more and more to the PSD of PA12 when reducing the amount of fine particles, whereas the PSD of DF remained comparatively broad and multimodal. The differences in moisture between the fractions of the same type of polymer didn't show significant variations when being exposed to the standard atmospheres over a controlled period of time. The comparison of the bulk behaviour of the three different powders in terms of packing and dynamic flow behaviour showed that the reduction of fine particles within the TPE powders allowed them to improve packing and flow efficiency. The effects of packing efficiency showed a good trend with thermal conductivity within the powder bulk alongside the part density or void volume and tensile properties. An increased powder bed density led to reduced bulk porosity. The TPU SLS 4, shows a direct proportionality between increasing PSD, the corresponding thermal conductivity and the effects on part qualities. The elastic modulus (E-modulus) did not show any change with varying PSDs within the measurements standard deviation. However, a significant enhancement of the ultimate tensile strength (UTS) and the elongation at break (%EaB) proportionally to increased packing and improved flowability of the powder bulk was shown. The surface roughness of the fabricated parts, even though they presented high standard deviations between the measurement points, showed a dependence on the powder bulk's density and surface quality with regards to the mean value of the results. A close packing of particles led to specimens with higher UTS and higher %EaB.

6 In-Process – Process-Material Interactions

6.1 Introduction

As discussed within section 2.1.4 finding the right build chamber temperatures is crucial for a stable processing of semi-crystalline polymers in LS such as PA12. In the literature, the isothermal crystallization of this type of polymer is well understood. In order to reveal the characteristic calorimetric properties of TPEs, the isothermal crystallization kinetics of TPU SLS 4 was investigated within an initial experiment in comparison to PA12 in a process adapted manner. Subsequently, three different TPEs (TPU SLS 4, DF, Desmosint) are investigated on the basis of the DOE introduced in 4.3 consisting of an overall energy approach taking into account important process and material properties. The resulting ultimate tensile strength and part crystallinity by means of X-ray diffraction is studied in dependence of this DOE in order to reveal the process requirements and specifics for TPEs in LS.

6.2 Initial Experiments to assess the in-Situ Heating Rates and Simulation of in-Situ Crystallization Kinetics

6.2.1 Thermography

The focus of the thermography analysis presented here, was on the analysis of the in-situ temperatures and their corresponding heating rates during laser exposure. The maximum temperatures occurring during the fill scan are shown in Figure 62 and Table 15. For the further discussion, the cooling rates were calculated from the data of the temperature-time-curve shown in Figure 63. What initially attracts attention looking at the graph is the extremely steep slope during exposure with the laser that leads to the extremely high heating rates by an average of 7184.0 ± 845.0 K/s and the rapid cooling down to the set bed temperature of 125°C with approximately 74 K/s.

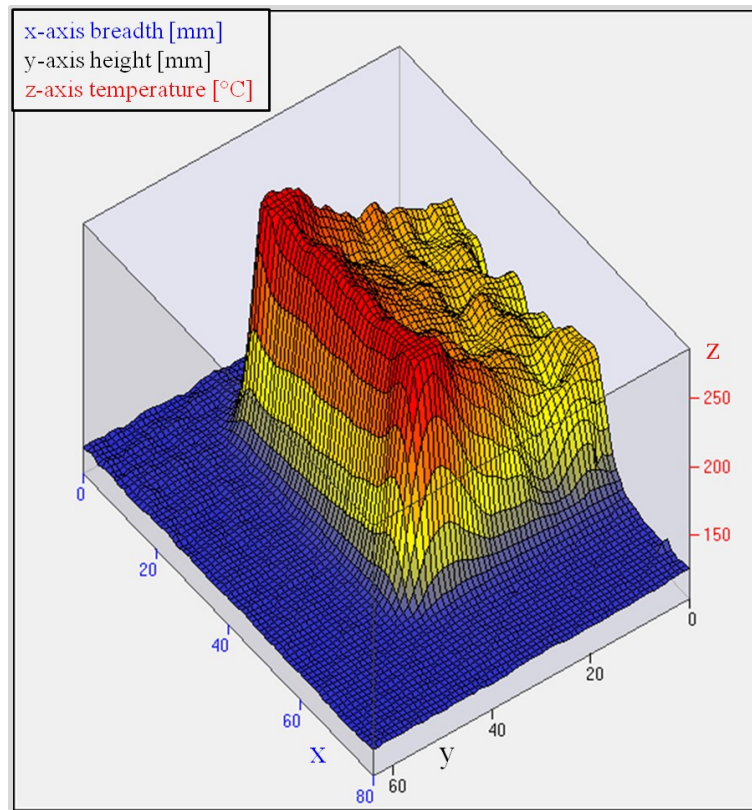


Figure 62: 3D representation of thermograph at the end of the fill scan

	Data point 1	Data point 2	Data point 3	Data point 4	Data point 5	Mean Value
Layer 1 [°C]	291.1	290.0	289.5	289.5	289.0	$289.8 \pm 0,8$
Layer 2 [°C]	291.6	290.6	290.2	289.8	290.0	290.4 ± 0.7
Layer 3 [°C]	291.1	289.9	289.5	289.8	288.9	289.6 ± 0.9
Total [°C]						290 ± 0.8

Table 15: Maximum surface temperatures of polymer melt during fill scan

Another observation that stands out is the high peak temperature during exposure of approximately 290°C. In taking a closer look at the peak, a gradual progressive increase of the temperature can be observed up to the maximum temperature. In addition it does not form a highly defined and sharp peak.

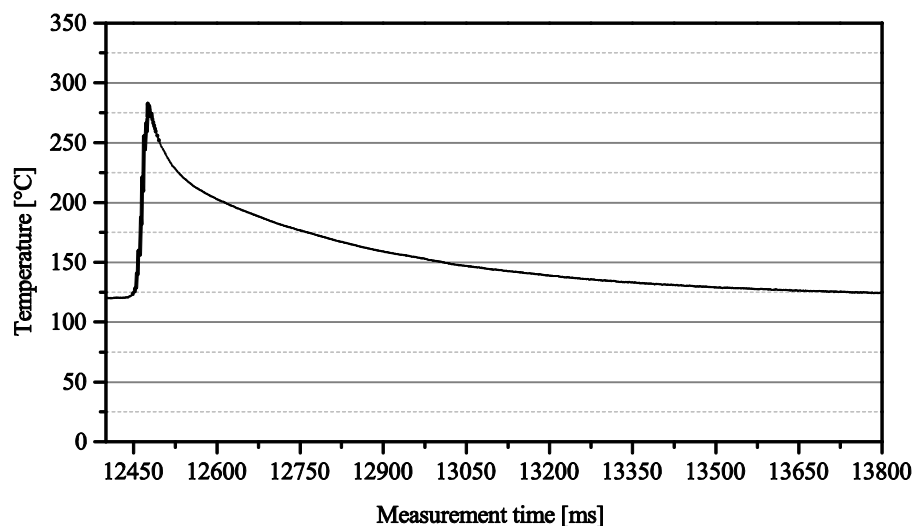


Figure 63: Temperature-Time-Curve of the consecutive processing steps - exposure with maximum temperature at the peak and cool down to build temperature for TPU SLS 4 [285]

The process kinetics detected with the IT serve as input for the FSC analysis in the following section.

6.2.2 Isothermal Crystallization of TPU SLS 4 compared with PA12 – Flash DSC

As a result of the heating and cooling dynamics observed throughout the IT measurements (Figure 63), the sensitivity towards different cooling rates for TPU SLS 4 and PA12 was investigated prior to the isothermal crystallization. In Figure 64 a) the polymers' dependency on increasing cooling rates is compared on basis of the subsequent FSC heating run after the melt was cooled down.

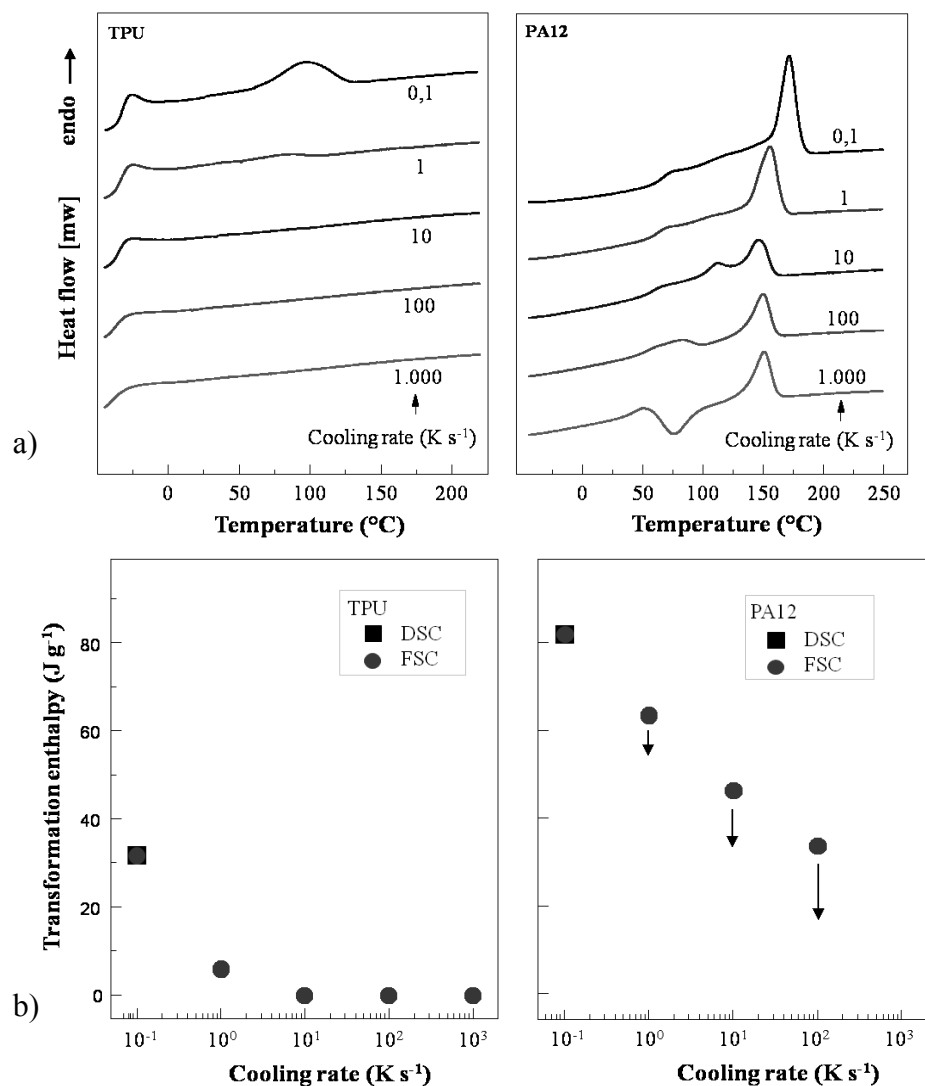


Figure 64: FSC heating runs after prior cooling of the melt with varying cooling rates between 0.1 and 1000 K/s for TPU SLS 4 (left) and PA12 (right) a) and transformation enthalpy determined from the previous crystallization at varying cooling rates for TPU SLS 4 (left) and PA12 (right) b); calibration was built in accordance with a DSC cooling run at a rate of 0.1 K/s (6 K/min⁻¹).

In the left part of Figure 64 a) the heating run (1000 K/s) subsequently to prior various cooling rates is shown for TPU SLS 4. It can be seen that at cooling rates higher than 10 K/s⁻¹ no crystallization takes place.

In the light grey bottom curve the heating run (1000 K/s) for PA12 which has been cooled down from molten state underneath the glass transition temperature prior to heating, is shown in the right part of Figure 64 a). It shows a glass transition below 50°C, followed by an exothermal cold crystallization at around 70°C. This peak is succeeded by an endo-thermal melting signal at around 150°C

that represents the enthalpy needed to melt the crystals that formed during prior cold crystallization. With decreasing cooling rates from around 600 K/s^{-1} the signal of the cold crystallization becomes smaller while the endo-thermal melting signal remains constant. Alongside the decreasing cooling rates the overall crystallinity of the PA12 increases. When evaluating the transformation enthalpies in the right part of Figure 64 b) it can be seen that the change in enthalpy in dependence of cooling rates follows a rather linear trend.

In order to determine the time and temperature dependent crystallization behaviour the relative fraction of crystal formation (relative crystallinity) was considered for TPU SLS 4 and PA12. The series of heating runs after the isothermal crystallization for TPU SLS 4 at different temperatures between 105°C and 125°C are shown in appendix A.4.1. The data from the time-and temperature resolved endothermic peak area in the analytical heating scan serves as an indicator of a previously formed crystalline phase and the corresponding enthalpy of phase transition is depicted in Figure 65. All curves show a sigmoidal course with decreasing crystallization rate and increasing measuring temperature. It can be noted that the crystallization starts after about 10 s in the case of an isothermal holding temperature of 105°C and after approximately 100 s at 125°C isothermal holding temperature.

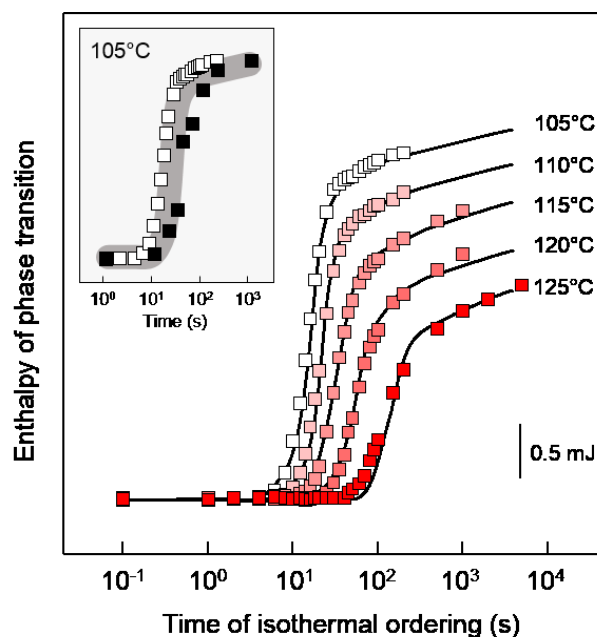


Figure 65: Isothermal ordering of TPU from the melt applying crystallization temperatures in the range from 105 °C to 125 °C. Inset shows comparison of FSC measurement after first heat of samples in virgin state (black filled symbols) and repeated usage on re-melt of one sample (white filled symbols, same data set as in the original graph).

From the data in Figure 65 it can be seen that the crystallization process slowed down with an increase of the isothermal holding temperatures. This correlates with a previous study where two holding temperatures (110°C and 125°C) were analysed in the lab of Mettler Toledo AG, Schwerzenbach, Switzerland, represented in A.4.2. While the crystallization process of the TPU SLS 4 within these measurements at 125°C was completed after approximately 200s, it took less than 100s for complete crystallization at 105°C. Derived from the observations on thermal stability following in section 7.2, another isothermal run for the TPU SLS 4 at 105°C with the maximum temperature of approximately 290°C during the DSC run (equal to the LS process maximum temperature during exposure) was performed as shown in Figure 66.

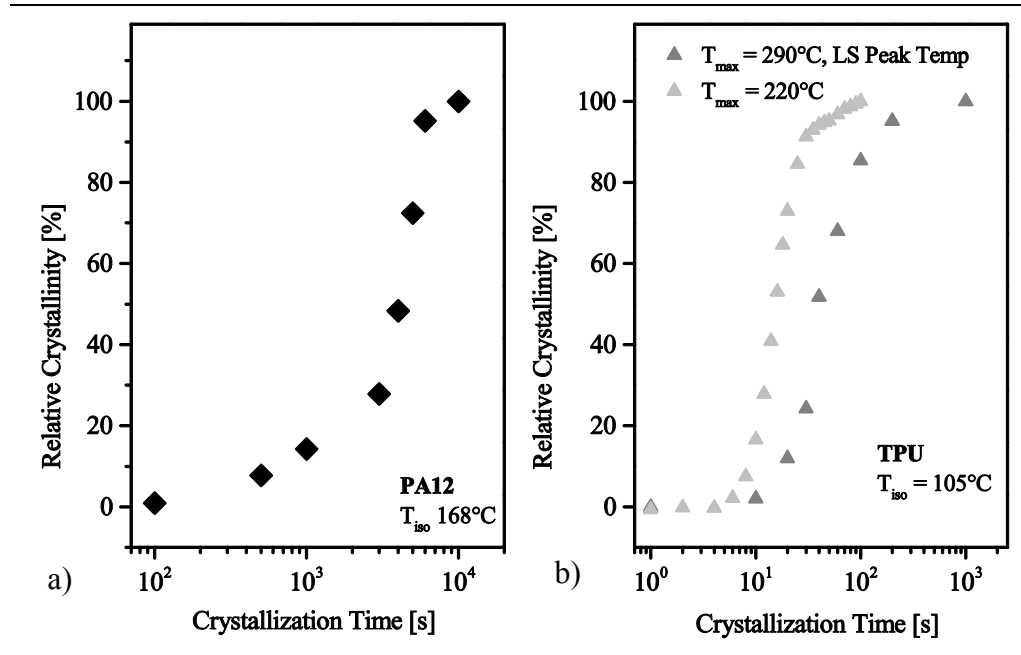


Figure 66: Relative crystallinity over crystallization time for a) PA12 at $T_{iso}=169^{\circ}\text{C}$ and b) TPU SLS 4 at $T_{iso}=105^{\circ}\text{C}$ for a maximum temperature in the FSC run of $T_{max} = 290^{\circ}\text{C}$ (equal to the peak temperature in the LS process) and $T_{max} = 220^{\circ}\text{C}$

The heating runs for PA12 after isothermal crystallization at 169°C in appendix A.4.3 show that heating with 1000 K/s again leads to cold crystallization and is followed by a melting peak at around 150°C at which the thereby formed crystals melt. After a holding time of 100 s at the isothermal temperature, an endothermal signal can be detected at around 180°C . It is proposed that this thermally more stable crystalline phase has formed during the isothermal crystallization. With an increasing crystallization time, the enthalpy of fusion for the peak at 180°C also increased as shown by the crystallization volume in dependence of holding time in Figure 66a. Thereby the transformation enthalpies detected in the FSC analysis have been related to the crystallization enthalpies from the DSC measurements of Rietzel in Figure 67 a).

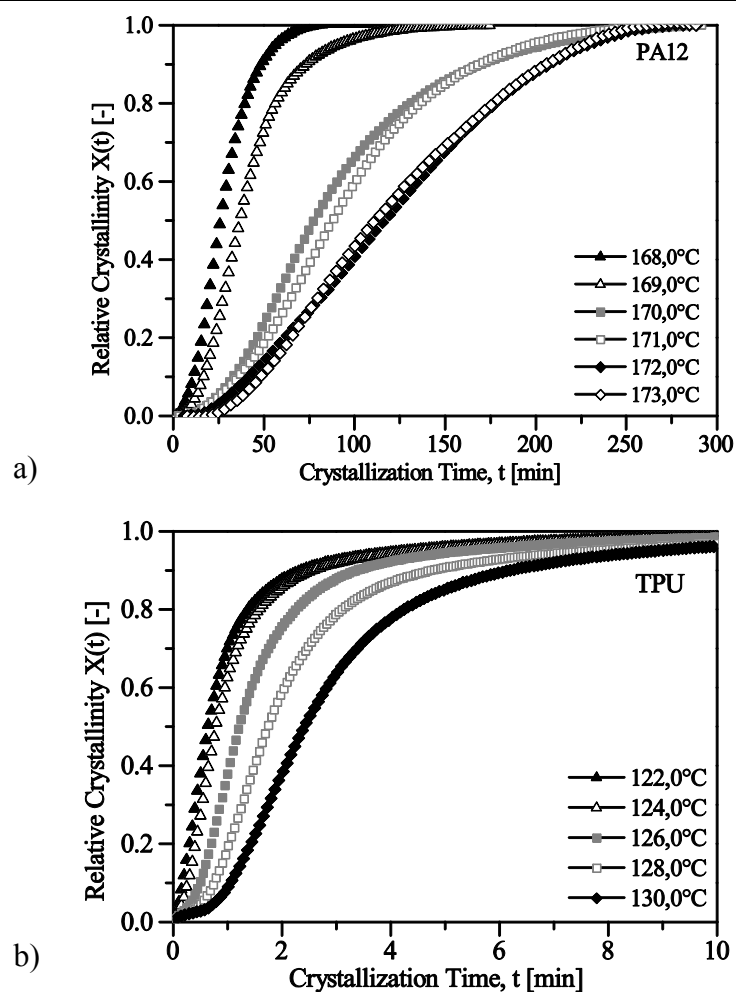


Figure 67: Relative fraction of crystal transformation in dependence of time for a) PA12 and b) measured in conventional DSC (heating at 20 K/s to $T_{\max}=T_{\text{pm}}+20$ K; cooling at 40 K/s⁻¹) [32]

Again the curves follow the sigmoidal course. The comparison with the results from Rietzel in Figure 67a show that the crystallization at $T_{\text{iso}}=169^{\circ}\text{C}$ seems to be slower in the process adapted FSC runs as it is reflected by the standard DSC analysis. In the DSC, a crystallization half-life of 37 min was determined while in the FSC it was 65 min.

For the TPU SLS 4 it was not possible to detect a complete exothermal peak during isothermal holding at lower temperature than 122°C in conventional DSC that would allow for calculation of the relative crystallinity. This is a result of the lower possible cooling rates in the conventional, at which the material already crystallizes during cool down from melt. When comparing the data from the FSC run for the TPU SLS 4 with the corresponding DSC run shown in Figure 67b it can be seen that the crystallization half time at an isothermal holding

temperature of 125°C is reached after approximately 60 s in the DSC and after approximately 90 s in the FSC.

6.2.3 Summary

By means of thermography the in-situ temperatures and corresponding heating rates while processing a TPU have been recorded and served as input for process adapted FSC as well as DSC measurements. In the first instance, the peak temperatures at the parameter combination of appendix A.1.2 were determined with the thermography camera. Subsequently, the two calorimetric methods have been applied in order to disclose the major differences in thermal behaviour and crystallization kinetics for the TPU SLS 4 in comparison to the most commonly investigated semi-crystalline PA12 under process adapted conditions. Noticeably, the crystallization of TPU is completed after approximately 200s even for the highest possible isothermal temperature (build chamber temperature), whereas the PA12 at its highest isothermal needs above 200 min for a complete conversion.

6.3 Influence of varying Build Temperature on Mechanical Properties

In the following section the results for the investigations on the mechanical properties dependent on build chamber temperature and the parameter combination of the DOE introduced in section 4.3.3 are presented.

The results are initially presented by means of UTS on the basis of tensile bars built in the XYZ-direction. The specimens built in this direction showed the lowest standard deviation, and hence allowed to significantly highlight the effects and magnitude of the parameter variations. The tables presenting the parameter combination for the DOE of all materials are shown in appendix A.8.3. In the following figures (Figure 68 to Figure 70) all results for UTS of the DOE and the corresponding materials are depicted.

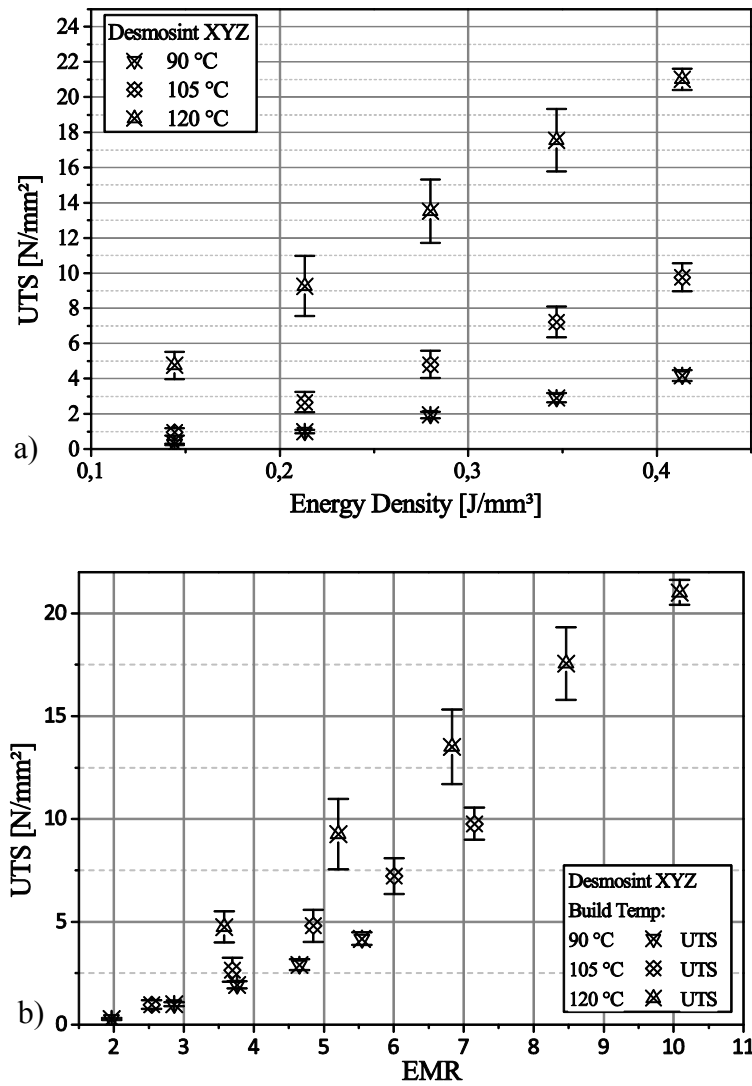


Figure 68: Tensile properties of Desmosint in XYZ-direction in dependence of build chamber temperature for a) UTS vs. energy density and b) UTS vs. EMR

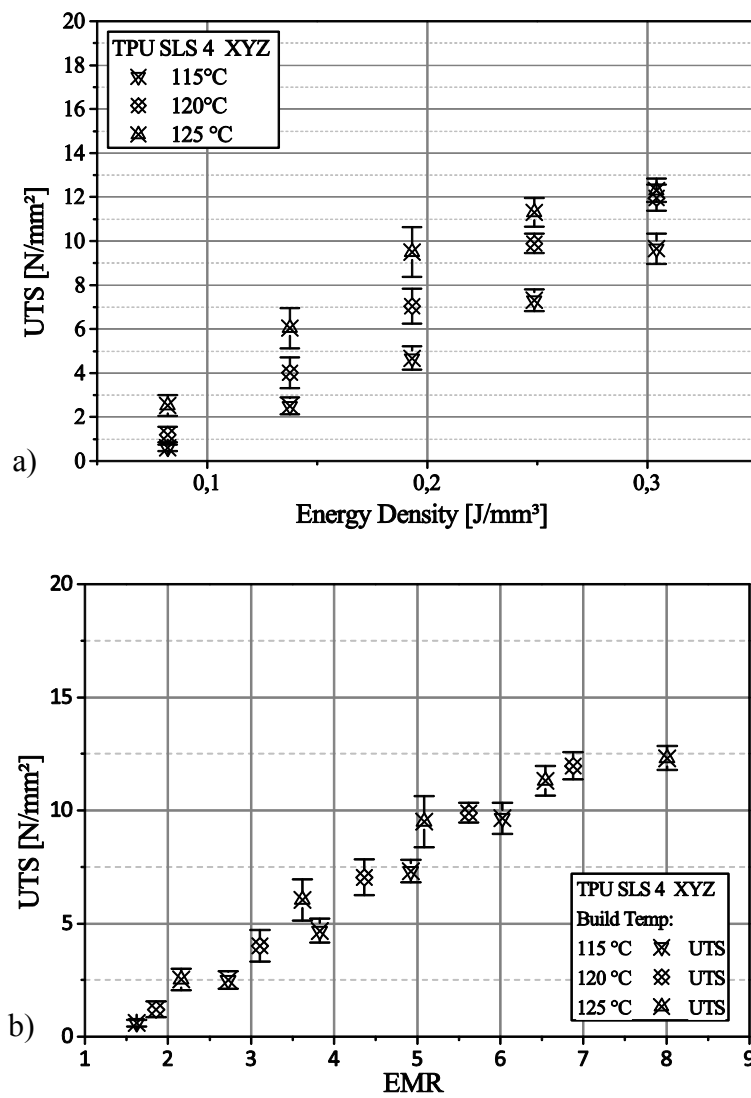


Figure 69: Tensile properties of TPU SLS 4 in XYZ-direction in dependence of build chamber temperature for a) UTS vs. energy density and b) UTS vs. EMR

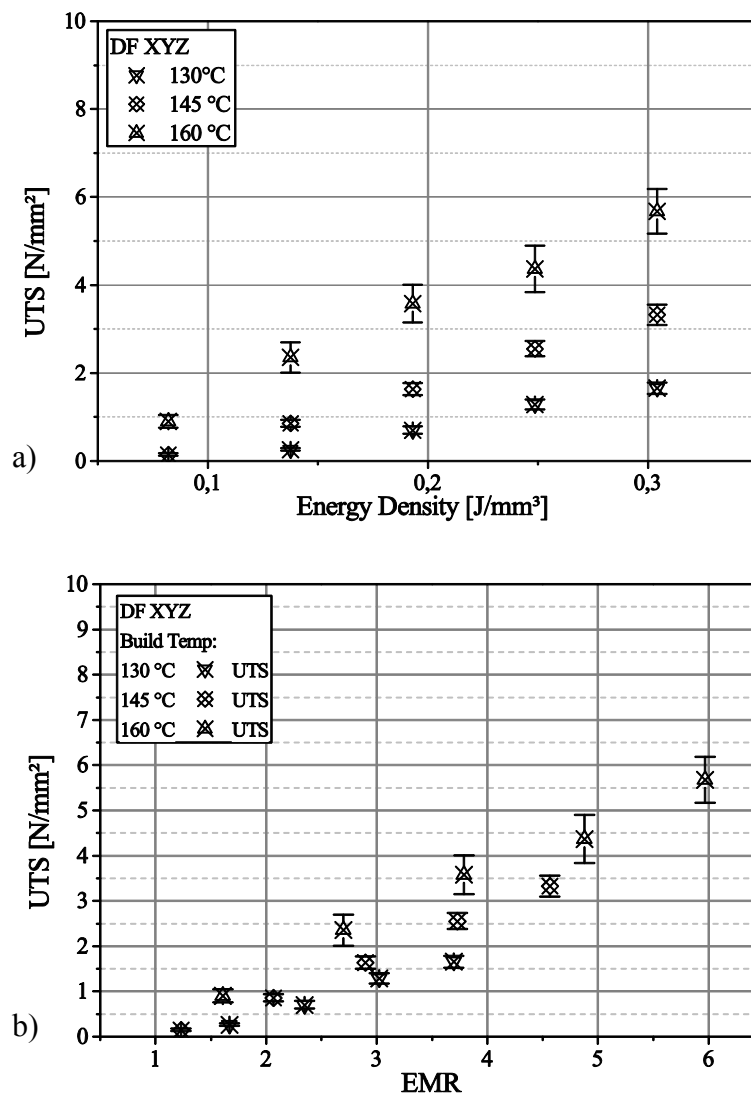


Figure 70: Tensile properties of DF in XYZ-direction in dependence of build chamber temperature for a) UTS vs. energy density and b) UTS vs. EMR

The results for Desmosint in Figure 68a clearly depict the influence of the build chamber temperature when looking at the results for UTS in an ascending order. It becomes obvious that with increasing temperature at comparable energy density, UTS increased by 143 % from 90°C to 105°C and by 159% from 105°C to 120°C. A similar trend for UTS dependence on temperature can be observed for the TPU SLS4 in Figure 69a showing an increased UTS of 38 % from 115°C to 120°C and 20% from 120°C up to 125°C. In experiment nr 1 for DF with the lowest energy density (0.08 N/mm²) at 130°C it was possible to sinter physical tensile bars, but in the tensile test no usable data was detected due to the low mechanical properties. However, when extrapolating from the higher values of

the parameter study, an UTS of 0.1 N/mm² can be theoretically achieved. Hence, mean values of 0.782 N/mm² for the lowest temperature can be determined. Comparing this to the mean values at the next higher temperature of 145°C (1.74 N/mm²) this equals an increase of 123 %. From 145°C to the maximum temperature of the DOE (160°C) an increase of 94% up to 3.38 N/mm² was observed.

Before addressing the results for UTS with changing EMR describing the overall energy approach, the effect of scan space on mechanical properties was observed and the results are shown in Figure 71 as well as in appendix A.8.4. The effect is described within literature, however this mainly applies to PA12 so far [300, 301], hence this effect will be indicated here within an additional study. The scan spacing was 0.15 mm which is considered the standard, as well as the two scan spacings of 0.1 mm and 0.2 mm. Performing the investigations at constant temperatures by means of the average temperature for the corresponding materials (Desmosint: 105°C, TPU SLS 4: 120°C, DF: 145°C) and adjusting hatch space within Eq. 3 and Eq. 5 of section 2.1.4, the volume energy density as well as the EMR for this experiments were considered constant.

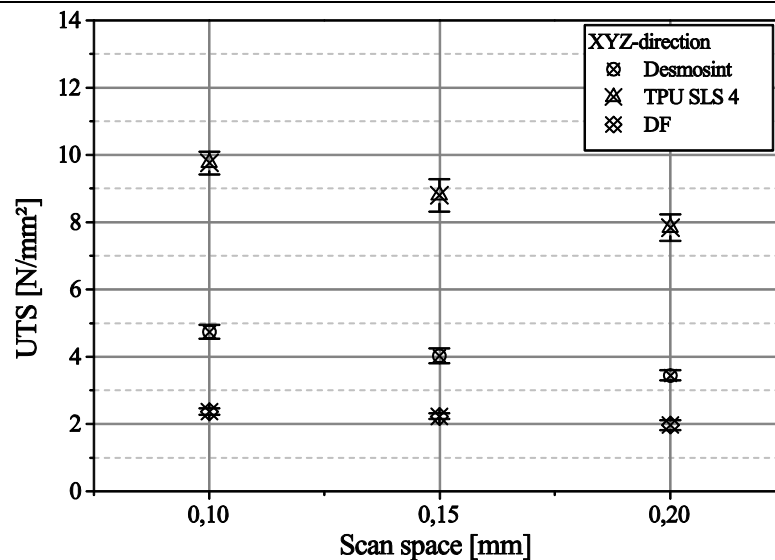


Figure 71: Influence of scan space at constant EMR on UTS for Desmosint, TPU SLS 4 and DF

As depicted by Figure 71, for the TPU SLS 4, an increase of scan space from 0.1 to 0.2 mm led to a decrease of UTS of 20% (1.92 N/mm^2). Similarly, the UTS of DF decreased by 17% to 1.97 N/mm^2 . The drop in UTS for Desmosint with 27% in UTS represents the most significant with a difference of 1.29 N/mm^2 . It can be noted that for all materials the best mechanical properties are generated at a scan space of 0.1 mm, which is related to the increased time of exposure of the material due to the overlap of the single lines of exposure (see section 2.1.4). This result however can't necessarily be made into a general conclusion, as different LS systems have varying laser beam diameters and over all different scan strategies.

6.4 Influence of varying Build Temperature on Hardness

In addition to the determination of tensile properties the influence of varying EMR on the shore hardness on the TPEs was studied. In Figure 72a – c, a graphical display of the results is given.

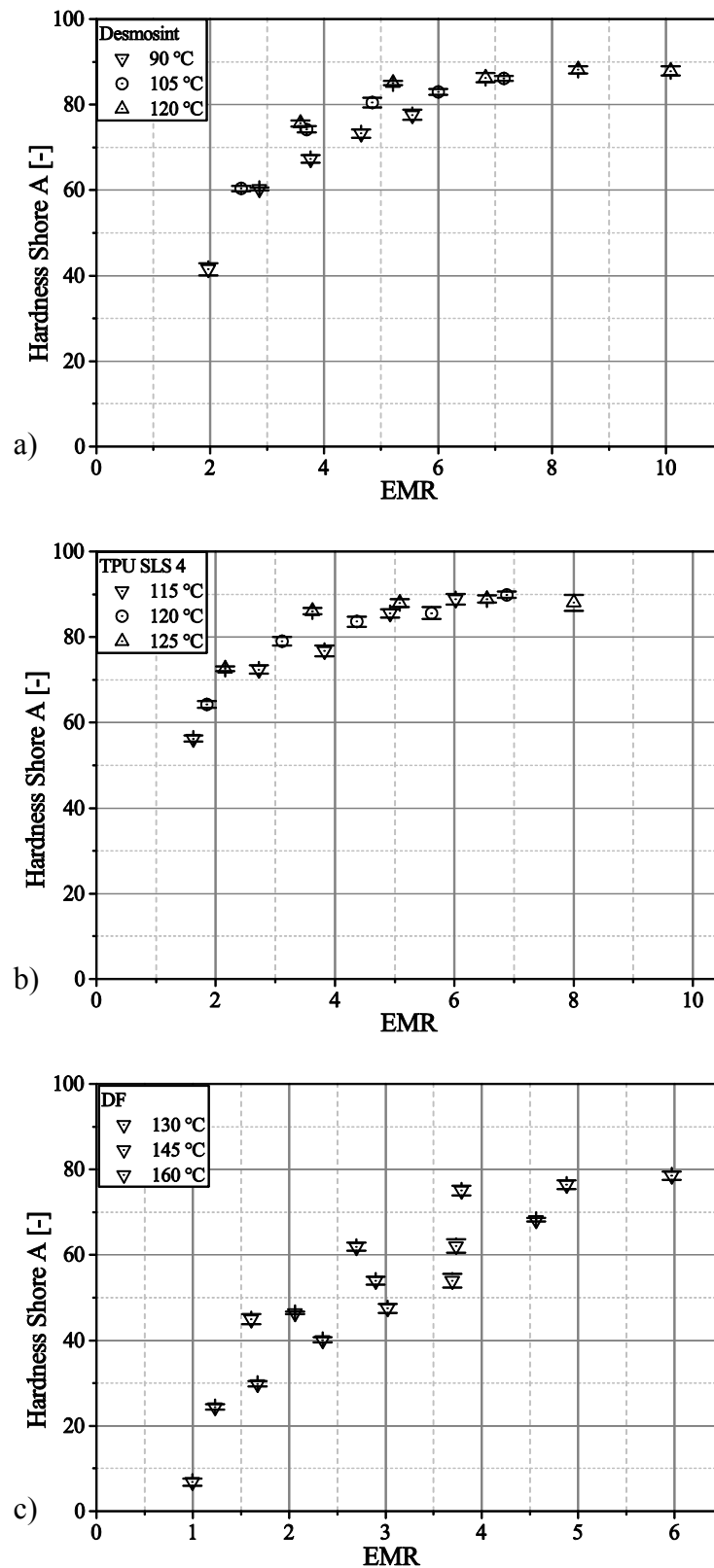


Figure 72: Shore hardness A in dependence of EMR for a) Desmosint, b) TPU SLS 4 and c) DF

The actual values with their corresponding parameters are shown in appendix A.8.5. On the basis of Figure 72a it can be seen that within the applied EMR for Desmosint a maximum range of 46.6 Shore A was achieved, reaching saturation at an EMR of around 6. Here a plateau at approximately 86 Shore A was detected that remained stagnant up to the maximum value of EMR. For TPU SLS 4 in Figure 72b it was found that the polymer was capable of reaching a hardness of Shore A between 56.26 up to 87.98 equalling a range of 33.62 Shore A. Here the plateau was reached at a maximum EMR of 5. On the basis of the gathered data for DF it was capable to cover a range of 71.68 Shore A to vary the shore hardness between min. and max. (see Figure 72c), although at the lowest hardness value no usable tensile properties hence no technically favourable part properties have been generated. The relevant value range therefore was chosen to begin at an EMR of 1.67 (first measurable tensile data) equalling a hardness of 29.84 Shore A. For DF the plateau for hardness is reached at an EMR of 5 similar to the TPU SLS 4.

6.5 Influence of varying Build Temperature on Crystallinity

As shown in the initial study of section 4.3.2, the crystallization of TPU SLS 4 was found to be complete relatively quickly when compared to PA12. After approximately 200 s the total crystallization volume for the TPU SLS 4 was reached and it was proposed that therefore the crystallization of the TPU SLS 4 might not have a major influence on the final parts crystallinity. In order to validate this hypothesis in the following X-ray measurements for all TPEs at different EMRs were conducted. The method was chosen in preference to DSC analysis in order to exclude artefacts of lacking contact between crucibles and test samples due to the partially high surface roughness of specimens. Table 16 and Figure 73 depict the results of the crystalline portion in the final parts for the three TPEs with build chamber temperature and the EMR applied.

Material	Sample Nr.	Build chamber Temperature [°C]	EMR	Degree of Crystallinity [±2 %]
Desmosint	Sample 1	90	3,76	1
	Sample 2	105	3,69	1
	Sample 3	120	5,58	1
	Reference	120	10,09	2
TPU SLS 4	Sample 1	115	6,02	19
	Sample 2	120	5,62	19
	Sample 3	125	5,08	20
	Reference	115	1,62	18
DF	Sample 1	130	2,35	22
	Sample 2	145	2,06	21
	Sample 3	160	1,62	21
	Reference	160	5,97	22

Table 16: Degree of crystallinity and parameters for specimens analysed in X-ray diffraction

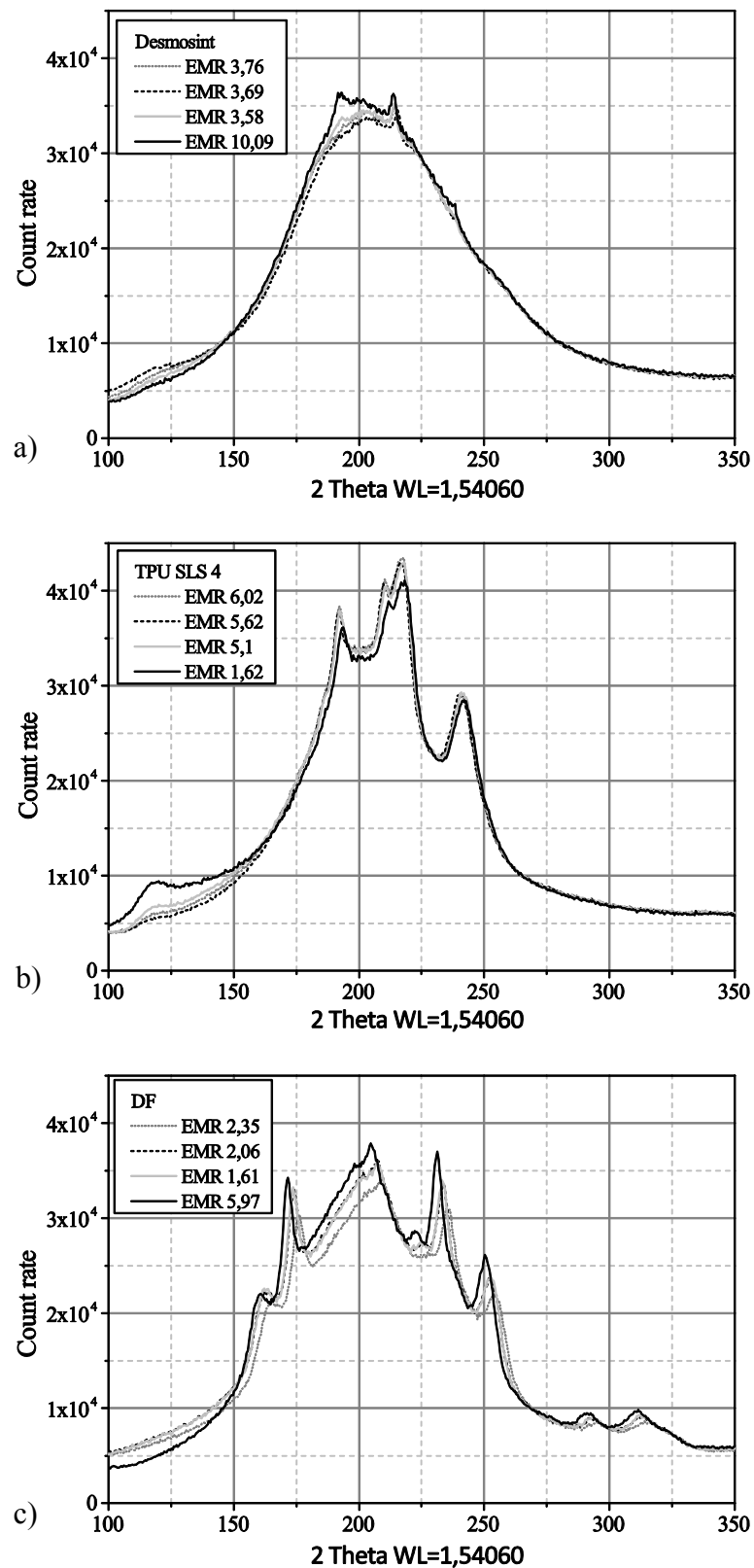


Figure 73: X-ray diffractogram of LS specimen at various EMRs for Desmosint, TPU SLS 4 and DF

For this relative comparison, a total of 4 samples for each material at a comparable EMR were used for the X-ray diffraction analysis. For a more precise referencing back to the processing parameters within a certain type of TPE a sample built at the highest EMR (highest build chamber temperature) was investigated. Due to the fact that the 100% crystallinity of the materials is not known, this sample represents the reference for upper extreme value of crystallinity. For the validation of the crystalline portion, the integral intensities of the “crystalline” reflections were determined and referenced with the background corrected sum component of the diffractogram [295]. The two TPU based materials, Desmosint and TPU SLS 4, thereby showed significantly different shares in crystallinity as it was expected after the DSC analysis on the basis of the powders (see appendix A.9). While the TPU SLS 4 shows a relatively high share in crystallinity at around 18 to 20 % ($\pm 2\%$), the Desmosint only contains a share of 1 to 2 % ($\pm 2\%$) that equals the measurements accuracy hence showing a quasi-amorphous character. DF shows a similar share in crystallinity at approximately 22 % ($\pm 2\%$).

6.6 Summary

In the first section of the In-Process investigations the influence of varying build temperature and energy densities on the UTS were investigated on basis of the EMR approach. For the materials observed it was shown that with increasing temperature at comparable energy density, UTS increased significantly. As depicted in Table 20, the mechanical properties of all observed materials showed a steeper rise in UTS with increasing build chamber temperature indicating that the relative effect of build chamber temperature was more significant than other parameters such as laser energy density. As a result of the increasing slope, it can be noted that the course of the energy insertion of the build chamber temperature follows a non-linear trend. The increase in UTS with increasing EMR reaches a maximum indicated by a plateau arising at the level of the maximum EMR. When investigating the effect of varying build temperature and energy densities on shore hardness it was shown that the maximum possible hardness of the TPEs observed developed at lower levels for EMR compared to the UTS. In the same context, potential effects on crystallinity of the specimens were studied in X-ray diffraction analysis. However, on the basis of the

numerical values, no significant influences of the processing parameters could be detected, supporting the hypothesis and the results of the initial investigations in section 4.3.2. The crystalline share is relatively low and crystallization is completed quickly when compared with PA12.

7 Post-Process – Ageing of TPEs in LS

7.1 Introduction

This chapter evaluates the ageing behaviour of TPU SLS 4, comparing it to its commercially available LS elastomeric material DF. The sensitivity, hence, the significance towards thermal degradation of TPU SLS 4 is initially investigated by fast scanning calorimetry. Consequently, by repeatedly processing the powders without refreshing with virgin material, 15 different ageing states of powder and 14 different ageing states of specimen are investigated. Following each ageing cycle, both the powders and the sintered parts are examined for chemical and physical ageing effects. The specimens' mechanical properties are studied by means of tensile testing, shore hardness and part density. The ageing effects on a macromolecular scale are discussed on the basis of melt volume rate, changes in the molecular weight are determined by HT-GPC supported by an extraction analysis of low molecular weight fraction as well as FTIR analysis in order to reveal potential chemical changes. For the identification of the powder particles' physical changes, particle size as well as their packing and flow efficiencies are investigated.

7.2 Initial Experiment on Thermal Stability

The results for all the heating segments from Table 13 in section 4.4.2 are represented in Figure 74 a). The melting peak at around 120°C represents the crystals that resulted from the cooling procedure of segment 5 from 180°C with 5 K/s. In cyclical increasing of the temperatures (+10 K) the melting peaks get larger but no significant change in the melting characteristics between T₁₈₀ (Seg. 6) and T₂₇₀ was observed. From the bold blue curve representing T₂₈₀ (Seg. 46) the peak areas were significantly larger.

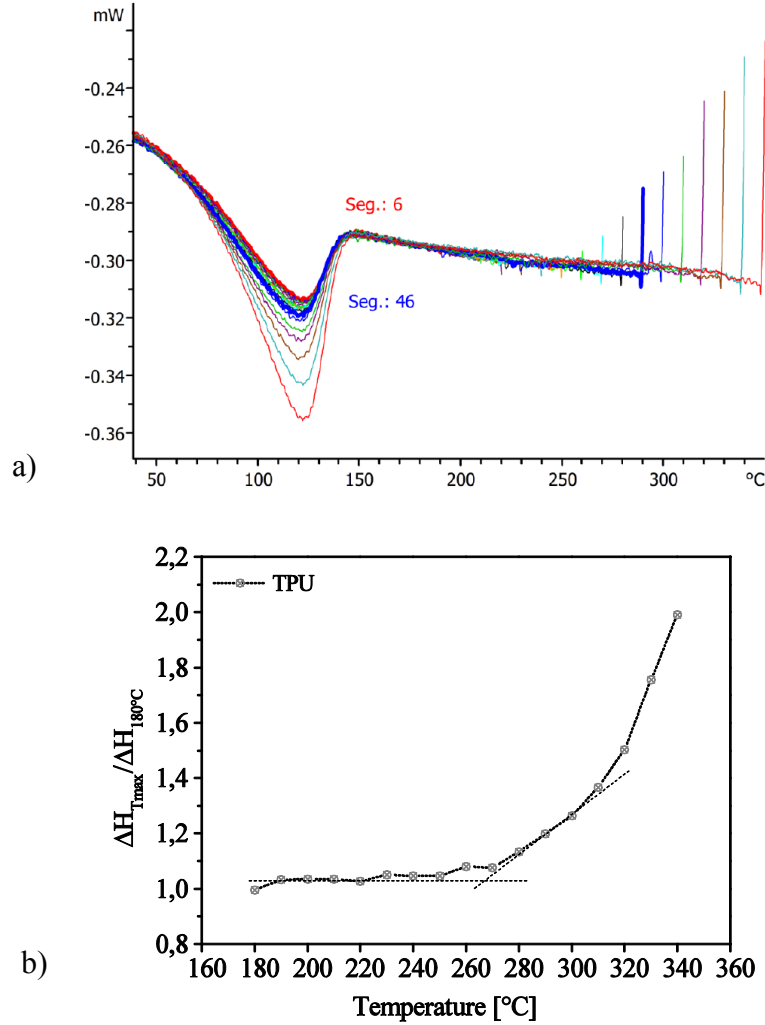


Figure 74: Melting curves after heating with 1000 K/s to $T_{max,i}$ a) and the relative enthalpy change of the crystallization process of TPU SLS 4 after 10 ms storage at T_{max} b)

As depicted in Figure 74 b) the ratio of the melting enthalpies after heating to $T_{max,i}$ related to the enthalpy after heating to T_{180} ($\Delta H_{T_{max}} / \Delta H_{180^\circ C}$) characterizes potential changes of the sample due to degradation [302]. It can be seen that the difference in the melting enthalpies between T_{180} and T_{270} was less than 10%. With increasing thermal loads the peak areas enlarge up to 200% at T_{340} .

7.2.1 Summary

The gathered data on in-process temperatures were used for the studies on thermal stability. It was shown that at a dwell time of 10 ms above 270 °C the TPU may likely be in the degradation range. FSC has proven to be a useful method for the analysis of thermal conversions by interrupting the

transformation by fast cooling and a subsequent determination of characteristics that consequently changed, such as reaction enthalpy in this example.

7.3 Mechanical Properties and Part Density

In Figure 75 and Figure 76 the tensile data for TPU SLS 4 and DF over all ageing stages is depicted. No data for TPU SLS 4 ageing state number 8 was collected due to a process breakdown presumably caused by a change in the powders PSD and therefore its bulk density that led to a ‘short feed’ within the process (see section 7.5). In general the TPU SLS 4 recorded higher tensile strength and stiffness compared to DF. The mean values of UTS and E-Modulus for both materials did not show a significant change over their ageing cycles. The TPU SLS 4 did show a slight decrease in UTS from 102 N/mm² to around 90 N/mm² while the DF showed a slight increase in UTS from 65 N/mm² to 75 N/mm². From ageing cycle eight the DF then decreased in UTS but levelled off at around 68 N/mm².

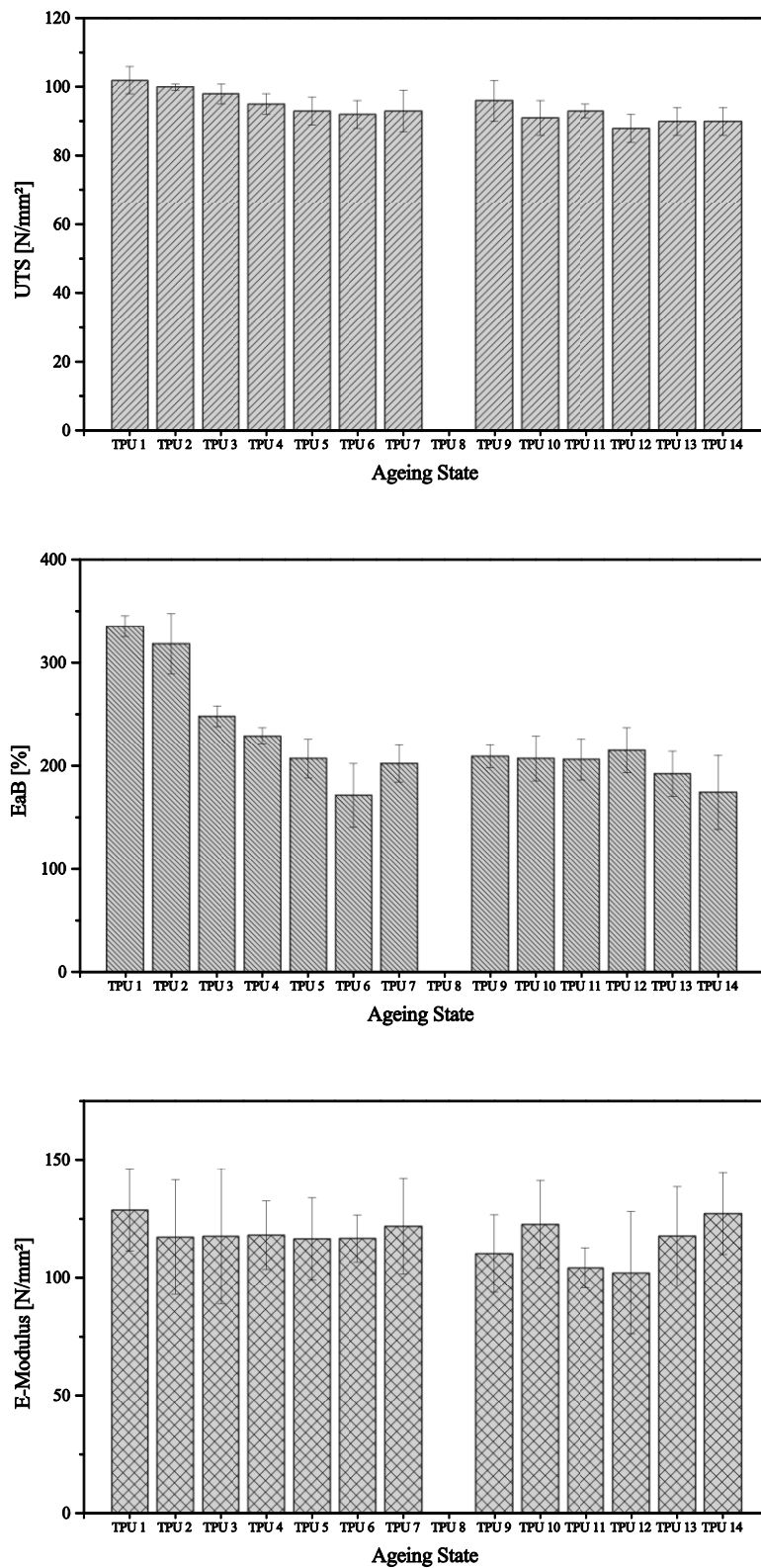


Figure 75: Results of tensile testing for TPU SLS 4 over all ageing states

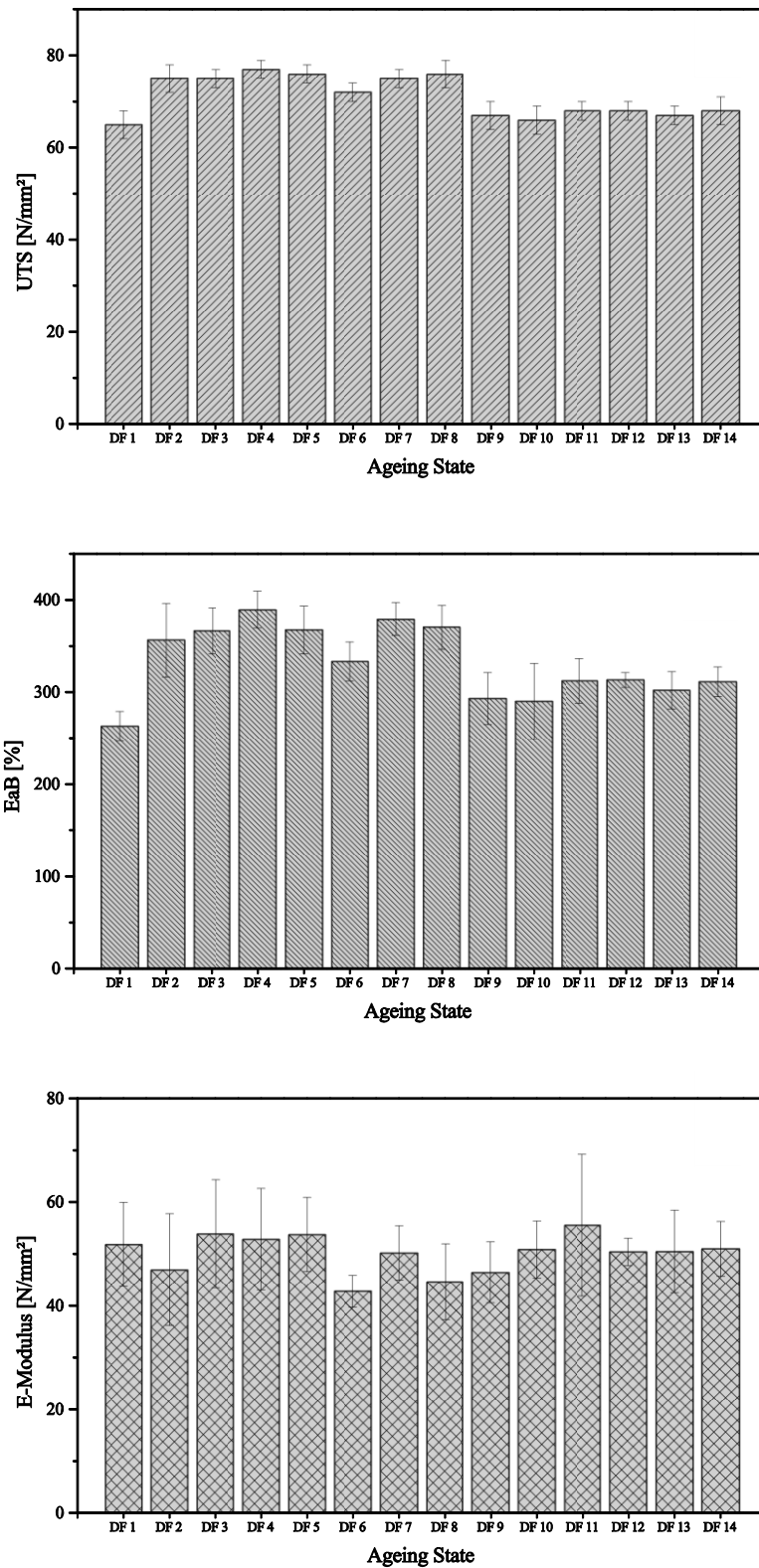


Figure 76: Results of tensile testing for DF over all ageing states

The stiffness of TPU SLS 4 with an E-Modulus of around $117 \pm 18 \text{ N/mm}^2$ was significantly higher compared to DF with a Modulus averaging $50 \pm 7 \text{ N/mm}^2$. When comparing the values for %EAB the results differ. While the TPU SLS 4 shows a higher %EAB at the first processing cycle at $335 \pm 10\%$ compared to DF with $263 \pm 16\%$, there is a reversed trend from cycle number two. From this ageing state on the TPU SLS 4 decreases significantly from around 335% to 170%EAB until ageing state number six to remain at this level until the 14th ageing state. The %EAB of DF increases from 263% to 389% coming from first to second processing cycle, descending to a %EaB of approximately 300% at cycle number 14. Table 17 and Table 18 depict the results of the CT analysis indicating that the TPU SLS 4 in general showed a part porosity that was significantly lower than DF. Both materials showed a reduction in porosity with progressing ageing cycles along with a decrease in molecular weight and even more clearly an increase in MVR.

Ageing State	DF - 1	DF - 7	DF - 14
Total Number of Pores	55772	55770	79286
min. Pore-Volume [μm^3]	2743.87	2743.96	2743.87
V_{50} [μm^3]	382×10^3	475×10^3	382×10^3
max. Pore-Volume [μm^3]	1.22×10^{11}	1.30×10^8	9.85×10^8
Part-Porosity [%]	13.24	4.26	6.50

Table 17: Pore-Analysis for DF Ageing States 1, 7 and 14, V50: mean Pore-Volume

Table 17 shows that DF did not vary significantly in number of pores coming from ageing state one to seven but showed an increase of around 30% at ageing state 14 compared to DF-7. In previously conducted studies on the effect of different particle size distributions on part density and tensile properties, applying the same processing parameters and the same DF powder as within this research, porosities of around 12.75% were recorded. Even for the preferable PSD with a reduced amount of fine particles leading to the highest packing density, the part porosity could only be decreased down to 11.15% in the virgin material state. Therefore, it can be assumed that this represents a typical porosity level for virgin DF parts even at favourable processing parameters and is the reason for often infiltrating the later parts in order to increase for example density

and shore hardness [255]. The overall part porosity within this study was the highest at DF-1 with 13.24% decreasing by 67.8% at the seventh ageing state and further increasing by 34.5% up to ageing state 14. The smallest pore size did not vary as the values were close to the resolution limit of the CT. The maximum pore size though does change with the biggest pore in DF-1 at $1.22 \times 10^{11} \mu\text{m}^3$ (second largest pore in DF-1 is $1.02 \times 10^8 \mu\text{m}^3$), 939 times larger than the biggest pore in DF-7. This largest pore in DF-1 is one open-pore system. The overall part porosity for DF investigated in this study was 14.6% and the max. pore-volume was $5.87 \times 10^{10} \mu\text{m}^3$ (second largest pore was $4.72 \times 10^7 \mu\text{m}^3$). From DF-1 to DF-14 that largest pore (Figure 77a) was downsized gradually with the ageing states.

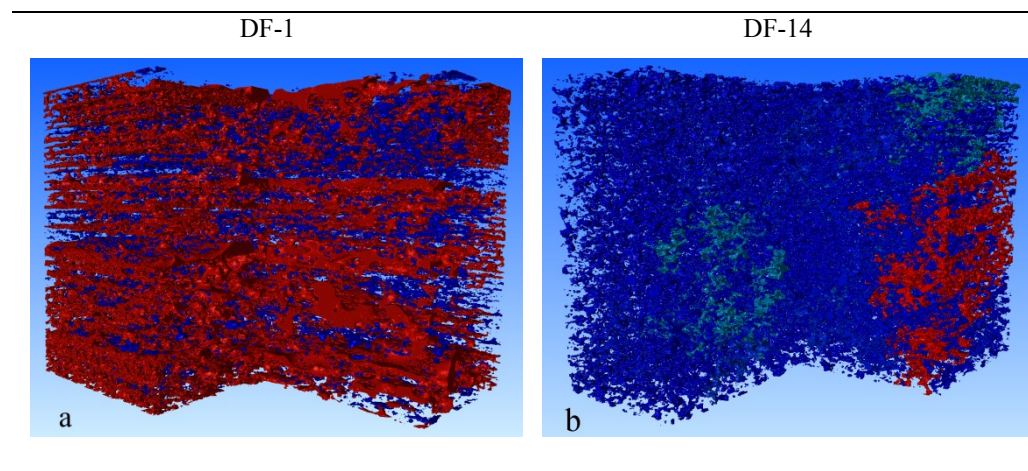


Figure 77: Pore analysis for a) DF 1 with single open pore network and b) DF-14 with reduced pore size

At ageing state 14 the maximum pore size increased again by $8.55 \times 10^8 \mu\text{m}$ compared to ageing state seven. Table 18 highlights the results for the pore analysis of TPU SLS 4.

Ageing State	TPU - 1	TPU - 7	TPU - 14
Total Number of Pores	123924	17218	37981
min. Pore-Volume [μm^3]	2743,96	2742,61	3374,70
V_{50} [μm^3]	423×10^2	596×10^2	861×10^2
max. Pore- Volume [μm^3]	906×10^4	267×10^4	170×10^4
Part-Porosity [%]	0.54	0.36	0.36

Table 18: Pore-Analysis for TPU SLS 4 Ageing States 1, 7 and 14, V_{50} : mean Pore-Volume

From TPU-1 with a total number of pores of 123924 this amount decreases by 86.1% to TPU-7 followed by an increase of 54.7% to TPU-14. From TPU-1 to TPU-7 the total number of pores did not change significantly while the max. pore-volume decreased by 70% and its mean pore-volume V_{50} increased by 29%. From TPU-7 to TPU-14 though, there is a slight increase of around $632 \mu\text{m}^3$ in the min. pore-volume alongside with an increase of V_{50} by 30% and a decrease in max pore-volume by 36%. The development of the maximum pore size shows a clear trend steadily decreasing. From TPU-1 to TPU-7 the maximum pore size is reduced by 71% and a total of 81.2% from TPU-1 to TPU-14. With this increase in the large pores the overall part porosity, which in general is already very low for TPU SLS 4, also shows a decrease of 0.18% from TPU-1 to TPU-7 to level off until the last ageing state.

7.4 Ageing on Macromolecular Scale

The stability of the melt properties of a LS polymer is an important criterion for reproducible part properties [303-306]. For the work presented here a practical method like the melt index tester introduced in section 4.4.5 was employed to measure a total of 15 different ageing samples for each TPE and correlate potential changes in molecular weight with the effect on the melt flow. The results are depicted in Figure 78 for TPU SLS 4 and Figure 79 for DF respectively.

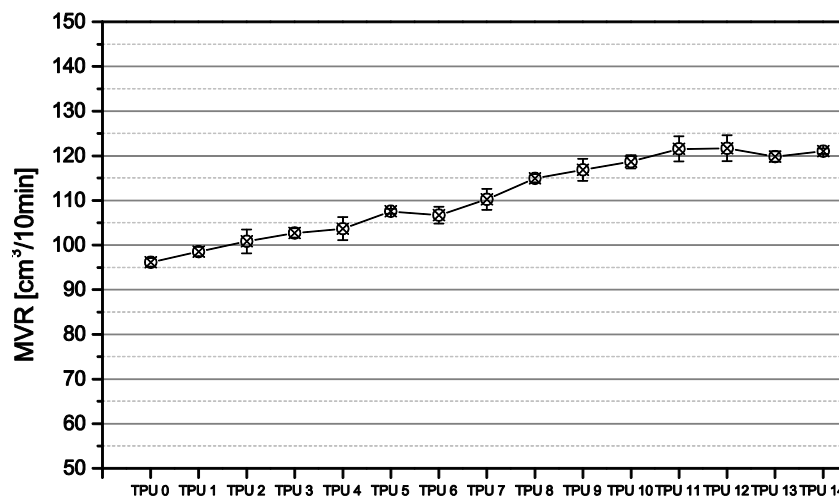


Figure 78: Melt Volume Rate of TPU SLS 4 over ageing states

For both, the TPU SLS 4 and the DF, an increase in melt volume rate can be detected with ongoing processing cycles representing an enhanced flow of the polymer melt.

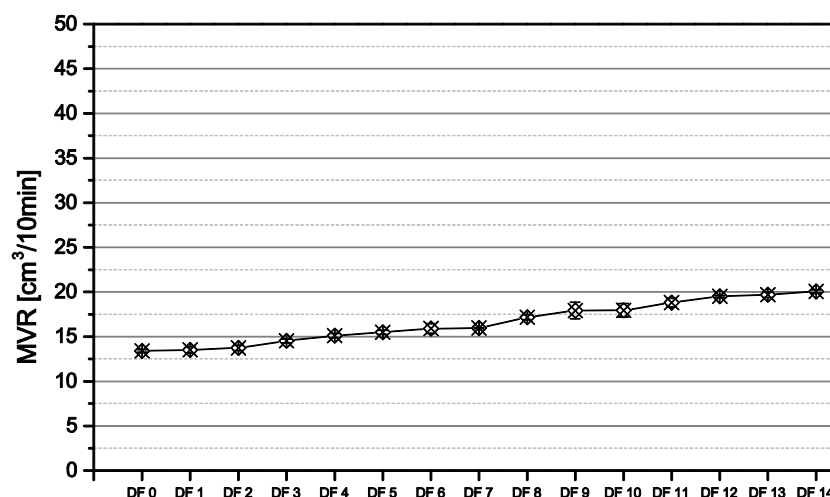


Figure 79: Melt Volume Rate of DF over ageing states

Coming from ageing state one, the TPU SLS 4 showed a MVR of approximately 96 cm³/10 min to steadily increase up to around 120 cm³/10 min at the 15th ageing state (+20% max. change in MVR ageing state one to 15). The DF came from 13 cm³/10 min reaching its highest value at the ageing state 15 at around 20 cm³/10 min (+33.3% max. change in MVR ageing state 1 to 15).

Deduced from the HT-GPC analysis, a statement on the absolute molar mass can be made. Hereafter, the TPU SLS 4 virgin material has a molecular mass at around 79.000 g/mol and the virgin DF a molecular mass of 90.000 g/mol. The weight average molecular weight Mw shows a reproducible trend of chain degradation for both materials see Table 19. Looking at the number average molecular weight Mn there also appears to be a decrease in the average value from ageing state one to 15 for the two polymers, though the trend is not systematic for the TPU SLS 4.

Ageing state	Mn [g/mol]	Mw [g/mol]	Ageing state	Mn [g/mol]	Mw [g/mol]
TPU 1	41854	79452	DF 1	65573	92131
TPU 7	36971	76082	DF 7	58124	79587
TPU 15	39509	73496	DF 15	47687	78128

Table 19: Results of HT-GPC analysis for TPU SLS 4 and DF of the ageing states 1, 7 and 15, reference in both cases was Polystyrene standard with $M_p = 98.000$ g/mol

The results of the extraction method in Figure 80 show that THF obviously is the solvent with higher solubilizing power compared to acetone.

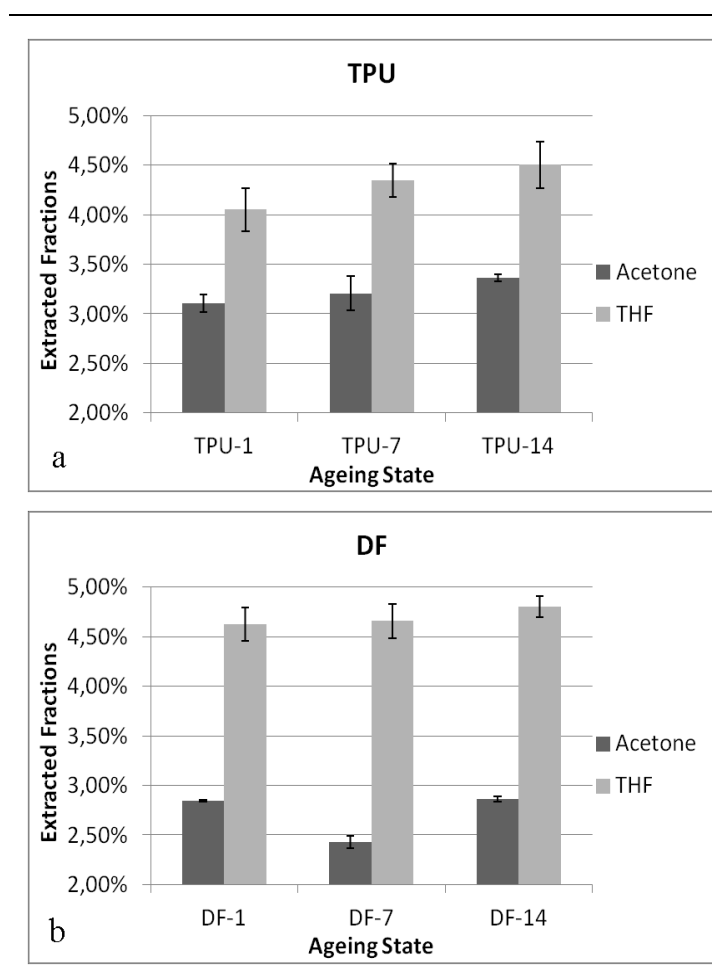


Figure 80: Results of extraction method showing the weight loss of the ageing states 1, 7 and 14 for (a) TPU SLS 4 and (b) DF

This becomes obvious, as the THF also dissolved oligomer fractions to a certain degree, as it created the higher percentage in weight loss. Both the TPU SLS 4 and the DF showed a slight increase in extractable low molecular weight fraction, although this increase was not significant within the standard deviation of the measurement.

Figure 81 and Figure 82 depict the results of the FTIR analysis in order to detect potential chemical changes of the macromolecules of both polymers due to the high processing temperatures.

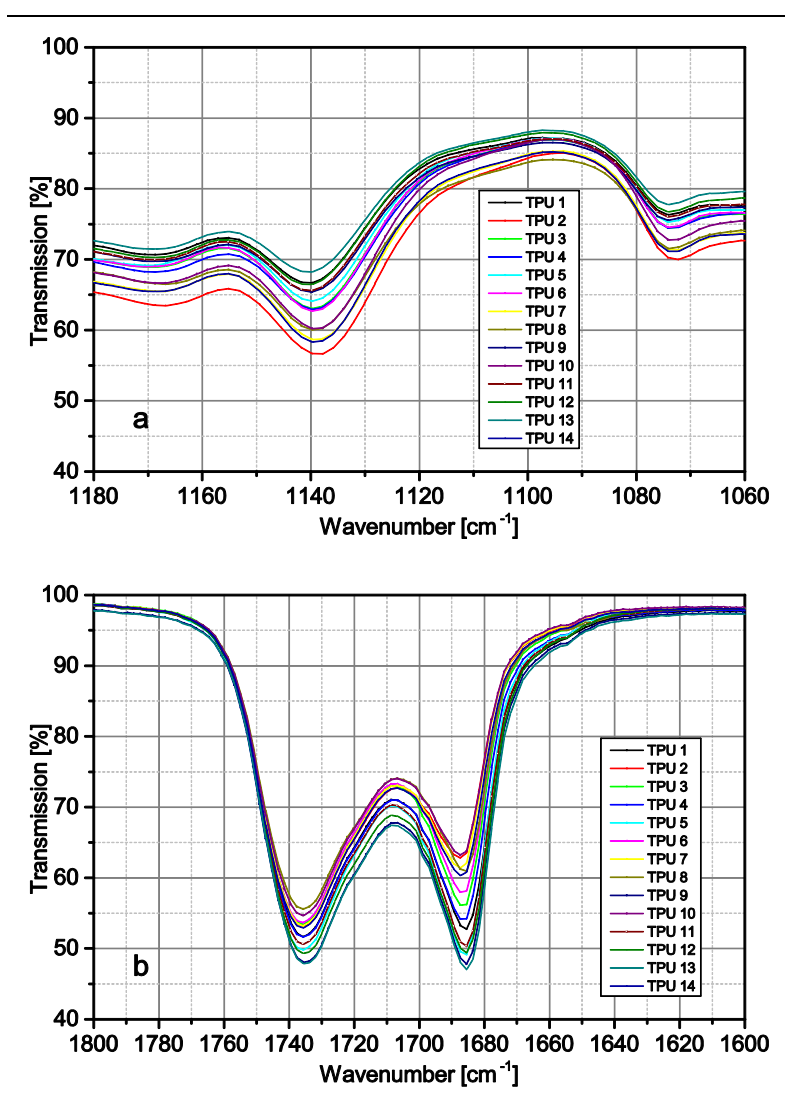


Figure 81: IR-spectrum of TPU SLS 4 ageing state 1 to 14, (a) Carbon-oxygen stretching vibration (wave number 1150 cm⁻¹ to 1040 cm⁻¹) and (b) the Urethane-bond (wave number around 1700 cm⁻¹)

Figure 81 indicates the IR-spectrum for TPU SLS 4 ageing states 1 to 14. In Figure 81a the characteristic range for the C-O bond stretching vibration (1150 – 1040 cm^{-1}) can be seen. Figure 81b shows the characteristic shoulder peak signal of the urethane bond between 1680 and 1750 cm^{-1} . Both sections in Figure 81 as well as the entire IR-spectrum of the TPU SLS 4, do not show shifts in their peaks in terms of changing wave numbers.

Figure 82 shows the results for the FTIR analysis of DF over its ageing states 1, 7 and 12. As the results for DF also did not show any systematic change over their ageing cycles they have only been tested up to ageing state 12.

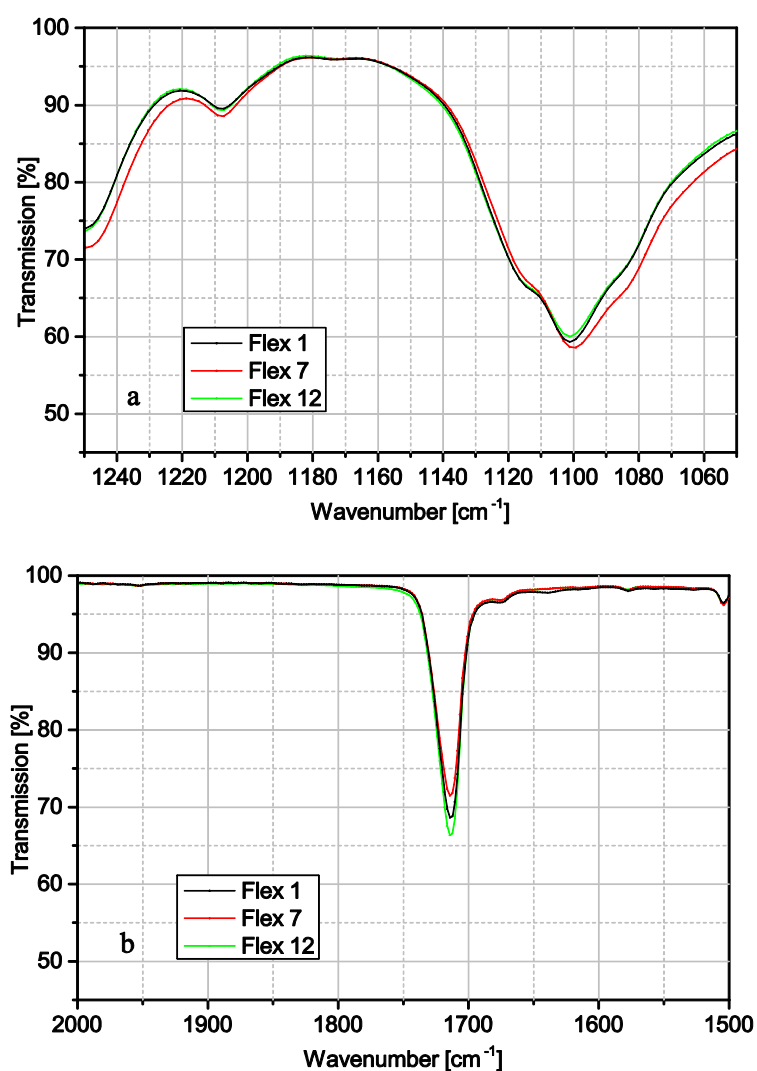


Figure 82: IR-spectrum of DF ageing state 1, 7 and 12, (a) Carbon-oxygen stretching vibration (wave number 1150 cm^{-1} to 1040 cm^{-1}) and (b) the Ester-bond (wave number around 1714 cm^{-1})

Again Figure 82a shows the characteristic range for the C-O bond stretching vibration (1150 – 1040 cm⁻¹), whereas Figure 82b depicts the single peak for the ester bond at around 1714 cm⁻¹. For both polymers no systematic change of the chemical bonds is present over their ageing states

7.5 Ageing on Powder Scale

The change in PSD for the two materials studied is depicted in Figure 83 over the ageing cycles one to 15, whereby ageing state one equals virgin powder and ageing state 15 equals powder that was processed 14 times. For reasons of clarity and as the trend over the different samples was the same, not all ageing states and their corresponding curves are shown. The most significant shift in PSD took place between the first and the seventh ageing state; this shift attenuated between states seven and 15 where no significant shifts could be observed after ageing state 11 for both TPEs.

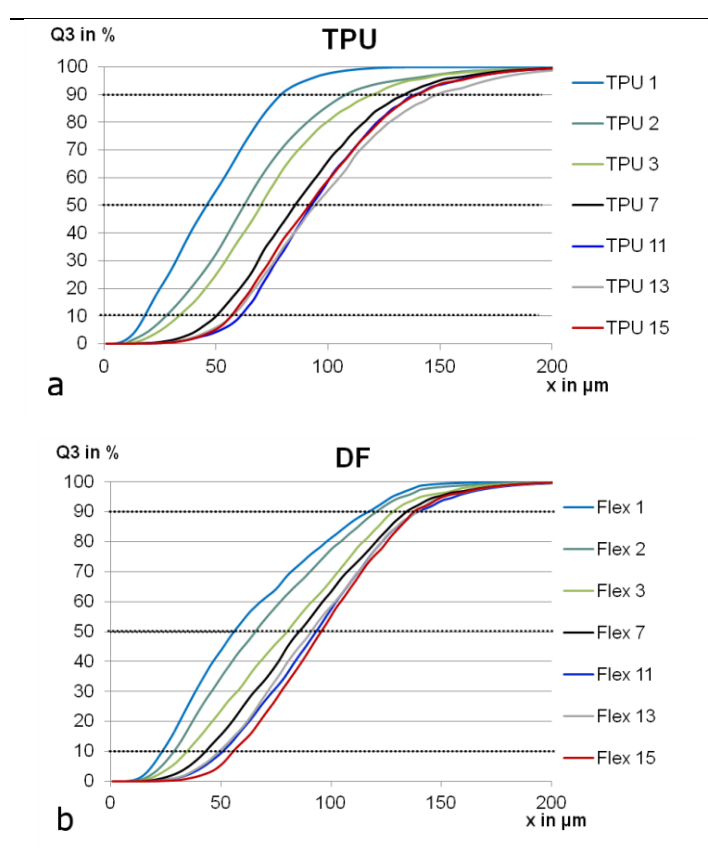


Figure 83: Cumulative particle size distribution based on volume for (a) TPU SLS 4 and (b) DF

The amount of small particles was reduced significantly while the share of large sized grains increased. Figure 84 shows the change in medium grain size (X_{50}) as well as the change in conditioned bulk density (CBD) over the ageing states one (virgin) to 15 for both powders. It can be seen that both materials showed a significant increase in the medium particle size that went hand in hand with a drop in CBD (for TPU SLS 4 approx. 30% from virgin to first ageing cycle).

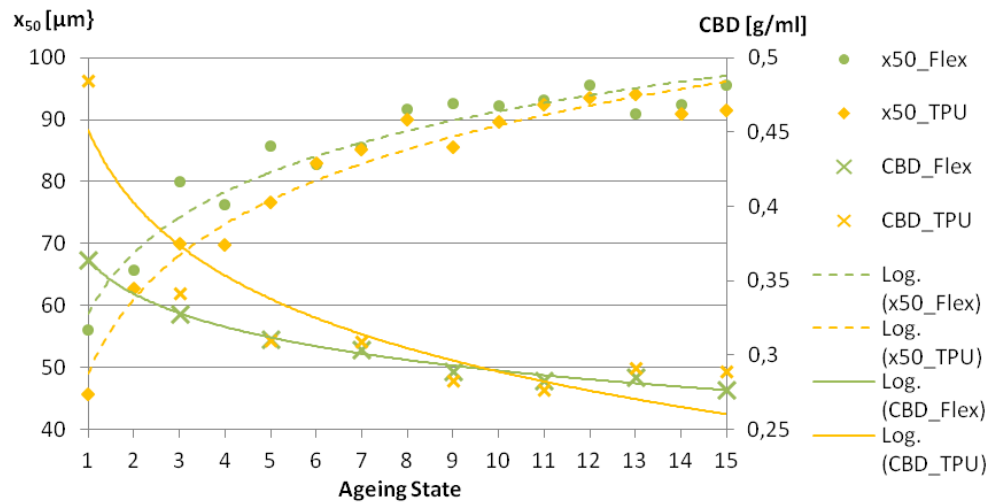


Figure 84: Correlation of change in medium grain size and conditioned bulk density

In general, the maximum change in CBD for the TPU SLS 4 was much higher than it was for the DF.

7.6 Summary

Within section 7.3 the effects of cyclical powder reuse without refreshing with virgin powder on tensile properties and part density were studied. Both the DF and TPU SLS 4 did not show a significant change over their ageing cycles in terms of UTS and E-Modulus. From ageing state one to ageing state six, however, the TPU SLS 4 showed a drop of almost 165% in EaB while the DF showed a slight increase of approximately 120% in EaB already from the first to the second ageing state. These values for TPU SLS 4 already indicated changes of the materials intrinsic properties due to potential degradation of the polymer chains as a result of chain scission. Analogous to the tensile properties presented in this studies, changes of the parts' densities were detected whereas both TPEs resulted in denser parts with a significant reduction of the volume of larger pores

with increasing ageing cycles as indicated by Table 17 and Table 18. Regarding the changes on the macro-molecular scale, the HT-GPC showed slight decreases in the average molecular weight, M_w , and the average molecular number, M_n , indicating chain degradation. In the scope of the extraction method no significant change of the low molecular weight fraction in the polymers was observed. The FTIR results depicted in Figure 81 and Figure 82 did not reveal any systematic chemical changes of the macromolecules of both polymers.

On a bulk scale both TPE powders showed an increase in medium grain size leading to a decrease in bulk density. This was already indicated in Figure 83, as with increasing processing cycles the amount of fine particles significantly decreased while the change in medium grain size levelled off at a certain point.

8 Discussion

8.1 Introduction

This chapter presents a discussion of the experimental results presented in the previous chapters. The discussion is divided into three main parts, and starts with a discussion of the Pre-Process observations covering the effect of varying bulk properties on the powder's static and dynamic flow properties as well as the effects on process and part quality by means of in-situ packing, thermal conductivity along with the resulting tensile properties and part densities. This is followed by a discussion of the In-Process findings on the characteristic calorimetric properties of TPU in comparison to PA12, by investigating their isothermal crystallization kinetics. In addition the results of the DOE introduced in section 4.3.3 on ultimate tensile strength and part crystallinity are discussed. Finally, the results of the Post-Process studies investigating potential chemical and physical ageing effects of the materials are being discussed. Thereby, the ageing on powder scale are discussed on the basis of their packing and flow behaviour. The effects of thermal loads on the materials are discussed on basis of melt volume rate, changes in the molecular weight determined by HT-GPC supported by an extraction analysis of low molecular weight fraction as well as FTIR analysis in order to reveal potential chemical changes. The effects of repeated processing on the specimens' mechanical properties are discussed on basis tensile properties, shore hardness and part density.

8.2 Pre-Process

The results of the initial investigation on the quantification of powder shape in section 5.2 helped to derive reliable and sensitive shape indices. While the Conv did not allow for clear differentiation of the varying particle shapes, the results of the b/l showed that PA2200 was on the same level as TPU SLS 4. This, however, differs significantly from the assessment of SEM analysis showing that the PA2200 as a precipitation product has the more spherical particle shape and especially the smoother surface texture compared to the edgy and almost fibrous surface of the cryogenically ground TPU SLS 4. Consequently, the b/l ratio might not be sensitive enough in order to allow for

precise differentiation. From a hierarchical order (least round to roundest particles) the Symm and SPHT values matched the optical SEM-assessment. In relative terms, the SPHT value allows for a more distinct differentiation between the different shapes when compared to the Symm as its results varied in a very narrow range. Therefore, derived from this initial experiment the SPHT is going to be applied for the further quantification of particle shape throughout the relevant parts of this thesis.

The fractions (F0, F25, F45) of TPU SLS 4 aligned more and more to the PSD of PA12 when reducing the amount of fine particles, whereas the PSD of DF remained comparatively broad including multiple peaks (multimodality) with rather large particles between 0-157 μm . As a result, these powders were expected to have different behaviour regarding packing and flowability, especially caused by their multimodal distributions. According to Yang *et al.* [307] and Amado *et al.* [28], commercially available powders showing good flowability consist of spherical particles with a narrow distribution in particle size around $D_{50} = 60 \mu\text{m}$ and a volumetrically low amount of fine particles at around $10 \mu\text{m}$. TPU F25 and F45 showed a D_{50} of 52.2 and 62.8 μm , respectively. These powders not only consist of a low amount of fine particles but their bulk and flow behaviour also presents similarities with PA12 [249]. For TPU F25 and F45, the reduced fine fraction lead to particles with a less rough surface and clear edges that presumably are preferable for increased packing efficiency and contact areas between the adjacent particles. The DF fraction remained rather jagged and more angular containing “crater-like” areas. This surface constitution might hinder the formation of high contact areas, thus packing efficiencies of the particles within a bulk. Proportionally to the reduction of fine particles, the SPHT of the TPU fractions aligned to the SPHT values of PA12 presumably enhancing their flowability as well as their packing density. The DF fractions did not show an improvement in SPHT with the reduction of fine particles with an average SPHT of DF F0 that was 0.84% lower than the SPHT of DF F25 and DF F45 which showed the same value. As a result, the difference in shape was insignificant and therefore no major differences in powder behaviour could be expected nor can it be associated with shape.

According to Seville *et al.* [188] the capillary forces are the dominating forces in moisturized powders causing moisture bridges inside the bulk material that inhibit their flow properties. At the same time, in some cases it was reported that moisture didn't act as a factor which decreased a powder's packing or flow efficiency but behaved as a lubricant enhancing the flowability and creating a rather tight bulk density [185]. For this reason, the moisture content of the powders observed was studied within section 5.3 with the aim to validate the effects of the conditioning and whether significant changes could be observed in dependence of PSDs. However, differences in moisture content between the fractions of the same type of polymer didn't show significant variations when being exposed to the standard atmospheres over a controlled period of time. Therefore, changes in powder performances could be derived directly to the effects of PSD and shape of the particles within a certain material.

In section 5.4 the results of the influence of different PSDs on the bulk and flow behaviour of the observed powders are presented. Referring to the state of the art in section 2.3, a high tendency towards consolidation of a bulk material indicates that the particles do not pack well if they are not forced by external factors such as tapping. A material may not pack well if it is just poured inside a container but can have a higher packed density after tapping. Other materials pack well even though no tapping has been applied. For all materials investigated in this section, tapping increased the packing efficiency, whereas a small delta between the poured and tapped density is characteristic for powders that flow well as a result of comparatively low cohesiveness [249]. The increased contact area of the TPU F45 particles combined with weight forces, in turn increasing with particle size, result in more efficient packing [188]. The relatively spherical and round shapes of PA12 particles compared to cryogenically ground ones create voids between them decreasing the packed density, compared to the edgy shape of TPU SLS 4 particles at their given particle size distribution and surface characteristics [27]. However, looking at the results for the DF fractions in comparison with PA12 depicted in Figure 44b it becomes obvious that for none of the fractions the packing efficiency of PA12 is reached. PA12 has a 24.45% higher poured density compared to DF F0, 24.97% higher than DF F25 and 16.01% higher than DF F45. A similar scenario was given for the tapped

condition, at which the best packing efficiency was determined for DF F45 reaching the bulk density level of PA12. Powders that present a high level of consolidation after tapping, are, as previously mentioned, considered not to pack efficiently if no external forces (gravity, forces due to powder handling) are applied to them such as manual tapping [156, 308]. Other materials pack in tightly, even though no tapping has been applied acting as an exogenous force [309]. For all the materials observed in this study, manual tapping increased the packing efficiency. Particles approaching the shape of a sphere appear to pack in tighter structures than particles with non-spherical shapes [219]. The closer the average SPHT (see Table 14) of a particulate system gets to the value of 1 (perfect sphere), the higher its mass density and consequently the packing efficiency of this powder bulk becomes [310]. With reference to this, angular and edgy shaped grains show rather random particle formulations within a bulk structure resulting in inter-particle bridges and internal friction forces as a result of the rough irregular surface texture of the particles as it was observed for DF particles [311]. Therefore, as the average particle SPHT value of a powder bulk increases, the void volume decreases at the same time reducing the porosity degree which essentially leads to a higher packing density [161]. The CBD values are in accordance with the results on the manual tapping studies. Especially the tapped density values showed a good correlation with the user-independent FT-4 results on CBD.

The comparison of the bulk behaviour of the observed powders in terms of dynamic flow behaviour showed that the reduction of fine particles within the TPE powders allowed them to not only improve packing but also flow efficiency as a result of decreased cohesiveness. This is shown by the results for BFE (Figure 47) and SE (Figure 48) in section 5.4. On basis of the BFE results it can be stated for the DF fractions, that powders that packed well were less cohesive and vice versa. The multi-modal PSDs of the DF fractions also failed to create a smooth powder bulk surface. As a result of the hindered packing efficiency the DF F25 showed the worst bulk surface texture followed by DF F0 and DF F45. For the TPU SLS 4 fractions, the fine particles obstructed the flow of the materials due to their size and irregular/edgy shape, whereas large particles increased the powders' flowability as they presented less irregularities on their

surface texture, an increased mass and SPHT of the single grains. As depicted in Figure 50 powders with low packing densities created a rough bulk surface. Thereby, the DF fractions created the rougher bulk surfaces compared to the TPU fractions. This is due to their angular shape, the relatively large particles (up to and above 150 μm , see Figure 43) contained in the overall bulk as well as the high disparity in particle sizes. Particle shape and surface morphology have a major impact on the flow characteristics of a powder bulk material [203]. Angular and irregular shapes of particles are connected to poor flowability due to their natural orientation to interlock with each other [187]. In addition, they tend to increase adhesive bonds, thus the powder particles resist free flow [157]. On account of this, mechanical interlocking of grains leads to the formation of caking, arches and voids inside the bulk leading to higher cohesive behaviour and shear stresses [153]. On the other hand, particles with close to spherical shape and smooth surface texture present higher flow efficiency compared to irregular and edgy shaped particles with rough surface morphologies that show a higher tendency to hook and twist together than the particles with more spherical and rounder shapes as well as with smoother surfaces [198, 312]. In the same way, particle size and PSD are two characteristics that play a significant role on a powder's flowability [199]. As described in section 2.3.2, fine particles fundamentally present a more cohesive behaviour than coarse particles do [313]. In principle, this behaviour can be attributed to the air drag force present on the motion of the particles during the handling of the bulk, which is much higher for fine particles [314]. In addition to the previously mentioned, Zou *et al.* [315] showed that the cohesive character of a powder is reduced as the average particle size of the PSD is increased. In addition to their studies, Lumay *et al.* [157] proved that powder flowability, indeed, decreases as a consequence of the average particle size's reduction. Hobbel *et al.* [164] reported that the lower the consolidation index of a particulate material is, the less important the inter-particle forces become and particle size becomes the dominant influencing factor. Again to be emphasized is the fact that the flowability of near spherical particles with smooth surface is higher than the flowability of particles with edgy and elongated or cylindrical shapes [156]. Similarly, Chan *et al.* [316] showed that irregular and angular shaped grains tend to mechanically interlock that in

turn leads to higher inter-particle friction and resistance towards particle flow. These particles are adhered together creating strong formations and mechanically interlock enhancing the overall cohesive character of the material [317]. According to Mullarney *et al.* [318] and Jallo *et al.* [159] small particles ($<20\text{ }\mu\text{m}$) are found to have a relatively large specific surface area, resulting in high extent of adherence to surfaces and cohesiveness between the contacting particles. They found that applying a shear stress to larger grain sizes ($>100\text{ }\mu\text{m}$) forces the particles to slide past each other more easily as they display decreased adhesive and cohesive behaviour. The reason for this notable difference is the overruling of the adhesive and cohesive inter-particle forces (originating from electrostatic, capillary or van der Waals interactions) by the forces arising from external systems such as the weight force [319]. Only when these external forces obstructing powder flow are weakened, the powder's flowability can be significantly enhanced, as shown by [320]. As shown in this study and flow efficiency and bulk behaviour (packing) of LS powders are closely related to inter-particle forces, a fact that is also supported by Castellanos *et al.* [139, 321]. In most cases, the powders exhibiting an efficient packing, show also a high flowability [322]. Consequently, cohesion and particles adhesion fundamentally influence the bulk and packing characteristics as well as the flowability.

The effects of packing efficiency studied throughout section 5.5 showed a good trend with thermal conductivity within the powder bulks. Besides the high c_p value of DF F0 all other c_p values of the TPU SLS 4 fractions are generally higher compared to the corresponding DF fractions. Consequently, this means that for the TPU SLS 4 fractions with a reduced amount of fine particles (TPU F25 and TPU F45) more energy is needed in order to increase temperature in the powder bulk compared to the DF fractions. For all fractions of both materials a decrease of thermal conductivity was observed. According to Crolla *et al.* [323] this can be attributed to the semi-crystalline character of the two polymers. According to the authors, the solids expand with temperature due to an increase in the distance between the molecules alongside a decline of the molecules short-range order.

On account of this, for the TPU SLS 4 fractions there is a maximum decrease in thermal conductivity at feed compared to build temperature of approximately 19.33 %, whereas the maximum delta for the DF fractions equalled 42.95 %. This high delta for DF however, might be linked to the higher temperature deviation between feed and build chamber. At the same time, the decrease in thermal conductivity represents a positive effect for the LS process as described in section 2.1.4. While the higher thermal conductivity in the feed might cause the feed powder to be thoroughly heated, the decreased thermal conductivity in the build chamber ensures that the energy inserted by the laser leads to increased depth of melted layer and a more homogenous formation of the melt pool. Likewise, the thermal loads of the surrounding powder are expected to be decreased at a decreased thermal conductivity, especially as the observed TPEs are processed within their softening range (see section 2.4.2, Figure 26) [27].

A systematic trend of thermal conductivity in dependence of its fractions is only present for the TPU fractions as depicted by e.g. Figure 53 for build chamber temperatures. For the TPU SLS 4, the reduction of really fine particles that enhanced packing efficiency was higher compared to DF and led to a lower standard deviation in their CBD. The DF powders were found to have multi-modal peaks over all different fractions leading to less reproducible bulk behaviour as described in section 4.2.8. In addition, the deviations for the bulk density especially for DF F0 also might cause a higher error during measuring the input values for the calculation of thermal conductivity such as c_p . Hence for the DF fraction no reliable nor systematic trend for thermal conductivity can be observed.

Alongside the trends on packing and thermal conductivity in dependence of varying PSD, the part density or void volume and tensile properties showed a direct correlation as shown in section 5.6. In Figure 52, a comparison between the in-situ bulk density, determined on the basis of cubes that enclosed powder during the LS process (see section 4.2.8), and the laboratory scale density (CBD) detected with the powder rheometer is presented. The CBD measurements show a high repeatability as they apply reproducible conditioning cycles as well as a confined vessel. The higher deviations for the in-situ density on the other hand,

are a result of variation over the four cubes that were measured as well as inaccuracies resulting from taking the powder out. It is not guaranteed that for every cube the same amount of powder (e.g. due to powder that sticks to inner walls) is taken out for the subsequent weighing of the solid. However, the mean values of the in-situ densities for the TPU SLS 4 fractions in Figure 54a show a straight forward correlation to the CBD. As a general remark, the higher densities in the CBD result from the previously mentioned conditioning cycle that applies external forces to the powder bulk and therefore compresses the powder to a higher degree as compared to the powder application in the LS process [249, 255]. The results for the DF fractions in Figure 54b show that, except for DF F25, the values for the in-situ density of DF and the CBD almost correspond within the standard deviation. This might be due to the fact that the DF is not as compressible nor as free flowing, hence not as sensitive towards externally applied forces. DF F25 again showed the reproducible results that correlate with the performance shown in section 5.4. However, similar to the results for TPU SLS 4, the trend for the densities of in-situ and CBD are the same.

In Figure 55, Figure 56 and Figure 57, respectively the results for the tensile testing in terms of E-Modulus, UTS and EaB are shown. Generally it can be noticed that enhanced flow behaviour and packing efficiencies led to better part properties whether in terms of tensile properties, surface roughness or the density of the parts manufactured. The enhanced flowability and packing did not show any influence in terms of shore hardness as shown in Figure 58, for either of the two materials and their corresponding fractions. Considering the results on surface roughness it stands out that the higher the proportion of large particles and the narrower the PSDs were the smoother was the surface of the sintered parts according to the average numbers. Another factor could be the smoother surface of the TPU SLS 4 particles as more fine grains were separated from the PSD, although the caking of larger particles on the specimen's surface during processing was expected to lead to higher roughness values. However, relating this effect back to the results for the thermal conductivity in section 5.5, it can be reasonably assumed that less particles stick to the melt surface during exposure and later cooling as the heat is transferred more easily into the adjacent

powder bed [27]. Another factor that is favoured by the better thermal conduction is that the larger particles for TPU F45 do not melt as fast as fine particles as evidenced for TPU F0 due to higher mass consumption. By considering only the mean values without the standard deviations, a correlation between the surface fractal value obtained by the flowability test of the RPA section 5.4 and the surface roughness R_z of the manufactured parts could be identified. The surface quality of the bulk had a direct influence on the surface roughness R_z of the fabricated part although the method applied did not help to differentiate more distinctively. It is however important to consider surface roughness as it was found to have a direct influence on the parts' mechanical properties as found by Kühnlein *et al.* [65]. By building parts at different orientation in a mask-sintering process and also applying different finish scenarios such as milling on the surface of the specimens they found that with enhanced surface quality the EaB of the parts was increasing. They concluded that this was due to the reduced notch effect initiated by the surface roughness and the layer-wise production of the parts. Apart from surface roughness, reduced flowability and loose packing of the powders led to parts which had higher porosity than the parts manufactured by powders with an enhanced flowability and a lower cohesion value. Similar to the surface roughness, the porosity could be linked to the mechanical properties of the parts as the material density is a crucial factor influencing the fatigue life of SLS parts as shown by Van Hooreweder *et al.* [324]. The lower the density, the more inclusion within the parts and the higher the chance of crack initiation. This corresponds with the results for density and mechanical properties of TPU SLS4. As shown in Figure 61 the part's porosity for TPU F0 was 54.28% higher compared to TPU F25 and 54.75% higher compared to TPU F45. The mechanical properties followed the same trend while the mean value for tensile strength of TPU F0 was 11.16% lower compared to TPU F25 and 11.41% lower compared to TPU F45. A similar tendency could be seen for the mean values of the %EAB (TPU F0 was 60.97% lower compared to TPU F25 and 66.23% lower compared to TPU F45) The part's void volume for TPU F0 was 45.39% higher compared to TPU F25 and 48.25% higher compared to TPU F45.

As the TPU SLS 4 has a relatively low melt viscosity due to its low molecular mass (approx. 79,000 g/mol) it was able to generate smooth and dense melt films in the LS process, generally leading to higher densities with small pores compared to DF as shown in Figure 61. Higher particle contact areas in combination with low viscosity that in turn favours particle coalescence and the resulting enhanced thermal conductivity might also help to form denser structures [46, 196, 306]. The differences in the part's density were therefore more to be found on the microscopic scale by means of pores and their volume that did not significantly affect the overall density. This also applied for the volumetric density of the components (calculated arithmetically through the mass to volume ratio) that did not seem to be influenced by the packing and flow efficiencies of the powders.

The parts manufactured from the DF fractions exhibited differences in the mechanical properties, the density and the surface quality as well. The interpretation of these differences identified more correlations between the powder behaviour and the part properties. As the melt viscosity and the molecular weight of the DF (approx. 90,000 g/mol) are significantly higher compared to the TPU SLS 4, it was more dependent on efficient packing, thus increased contact areas between the particles enabling the particles to increase neck growth during sintering.

Again the shore hardness was not highly influenced by the density of the specimens and did not provide sufficient correlation with changing PSDs and their corresponding powder behaviour. The tensile strength for DF F0 was 3.68% higher compared to DF F25 and 10.47% lower compared to DF F45. Again the E-modulus and %EAB did not show significant differences with varying fractions within the results' standard deviation. The mean values for surface roughness did indicate a trend that is not significant though.

Amongst the DF fractions, all tensile properties of the fabricated parts were improved with enhanced packing and flow efficiencies of the powder bulk. In only comparing the mean values without the standard deviations, a trend could be identified between the surface fractal value obtained by the flowability test of the RPA and the mean value of the surface roughness R_z of the manufactured parts. The surface quality of the bulk had a direct influence on the surface

roughness R_z of the fabricated parts. There was a straight forward correlation of the part's void volume and the part's porosity in comparison to the bulk properties also for the DF fractions. The part's porosity and the part's void volume were both decreased as the packing density of the materials is increased. For the DF fractions, the part's density (both the calculated density with the mass to volume ratio and the CT analysis) showed high dependence on the packing and flow efficiencies of the un-sintered powder. As mentioned before, for the DF the improved part properties might be more related to efficient packing, leading to an overall lower porosity in the powder bulk favouring higher particle contact and in turn neck growth during exposure. The higher part density thereby reduces the risk of crack initiation as described above, resulting in improved tensile properties [65, 324, 325].

8.3 In-Process

In section 6.2 the in-situ temperatures have been studied by means of thermography as basis for the simulation of process adapted isothermal crystallization. The duration of the heating and the cooling process of the generated layer (Figure 63) down to ambient build chamber temperature takes less than 2 seconds. The high heating rate results from the large delta between powder bed temperatures (build chamber temperature) and the high melting temperatures that are reached during exposure at the high energy density introduced throughout section A.1.2. The gradual progressive increase of the temperature seen in the peak of the temperature-time-curve is resulting from the line by line pattern at which the laser focus approaches the camera's field of view [283]. According to Wegner *et al.* [283, 285] the formation of the peak described in section 6.2.1 is resulting from the fact the detector is reaching its upper limit of the measuring range at this temperature not being able to detect higher radiation intensities anymore. That in turn means that the actual peak temperatures might possibly even get close to 300°C [285, 326]. At this high level of peak temperatures it is known from previously conducted TGA measurements and from studies carried out by Vasquez [13] on thermal stability on TPU based polymers that these materials almost reach their degradation point. Prior to the studies on isothermal crystallization, the sensitivity towards different cooling rates for TPU SLS 4 and PA12 (see Figure 64). As the amount of the

heat flows for the cold crystallization and the melting peak are almost equal the sample can be considered to be amorphous after being cooled at 1000 K/s^{-1} . A higher heating rate might allow for the analysis of crystallization of the quasi-amorphous PA12 due to suppressed cold crystallization and reorganization but would demand significantly smaller sample sizes. As with decreasing cooling rates from around 600 K/s^{-1} the signal of the cold crystallization becomes smaller while the endo-thermal melting signal remains constant, it can be assumed that crystallization can take place when cooling the melt down at rates lower than 500 K/s^{-1} . The corresponding transformation enthalpies in the left graph of Figure 64 b) more clearly shows that the crystalline phase of the TPU decreases exponentially with increasing cooling rate. In this representation a cooling rate of between $3 - 10 \text{ K/s}^{-1}$ is sufficient to reach supercooling leading to fully amorphous material. This indicates that crystallization for the TPU is suppressed during the high cooling rates within LS. However, for PA12 uncertainties exist for cooling rates above 1 K/s^{-1} as it comes to superimposition of reorganization and crystallization.

Figure 65 shows the isothermal ordering of TPU from the melt applying crystallization temperatures in the range from 105°C to 125°C . It is worth noting that the beginning as well as the degree of crystal formation from the melt is hindered at higher temperatures, because of increased polymer chain mobility as a general remark. Thus, the ultimate crystallinity decreases alongside an increase of the isothermal crystallization temperature, which is concluded from the levels of equilibrium that are approached over annealing time [282, 327]. The results on the process-adapted isothermal crystallization of TPU performed in the FSC are shown in Figure 66a. It is interesting to observe that an effect of enhanced crystallization due to the potential chain degradation after heating to a higher temperature was observed during the isothermal crystallization. This gave additional cause to study the thermal stability in the FSC within section 4.4.2.

The comparison with the results from conventional DSC runs shown in Figure 67a indicate that the crystallization at $T_{\text{iso}}=169^\circ\text{C}$ seems to be slower in the process adapted FSC runs as it is reflected by the standard DSC analysis. In the DSC, a crystallization half-life of 37 min was determined while in the FSC it was 65 min. The fact that up to 100 s of isothermal dwell time within the FSC

run almost no crystallization occurred might indicate that a sub-cooled amorphous phase forms due to the process adapted cooling rates and heating rates. This sub-cooled phase might start to crystallize later in the process probably forming smaller crystals between the larger spherulites that emerged during the slow iso-thermal crystallization. The difference in crystallization half time between FSC and DSC analysis for the TPU corresponds with the results determined for PA12 and might be caused by the thermal inertia (overshooting during cool down from melt at 40K/min for PA12 or 20K/min for TPU) of the higher sample mass within the DSC analysis. Due to this hypothermia the crystallization might be favoured and more quickly completed compared to the FSC.

The results of the effects of varying build temperatures can be divided into three parts. At first, the results from section 6.3 showing the effect on tensile properties are going to be discussed. In order to reach the highest UTS it takes a high energy insertion with the laser at the highest build chamber temperature. By the example of Desmosint this means an energy density of 0.41 J/mm^3 at a build chamber temperature of 120°C leading to a maximum UTS of 21.01 N/mm^2 . The increase of the mechanical properties with EMR therefore is in good approximation following a linear trend. The remaining deviations at different build chamber temperatures might be due to the changing ratio between energy insertion by the laser and the heater tray. On the other hand, the EMR approach is not considering optical effects such as transmission and absorption of the material or effects of thermal conduction that might change in dependence of temperature.

The mechanical properties of all observed materials show a steeper rise in UTS with build chamber temperature as depicted by Table 20 indicating that the relative effect of build chamber temperature is more significant than other parameters. As a result of the increasing slope, it can be noted that the course of the energy insertion of the build chamber temperature is not linear. Compared to the other polymers, for the TPU SLS 4 the relatively small change slope is related to the range of varying temperatures that is only possible in a relatively small processing range of 10°C . Especially for the TPU SLS 4, the effect of energy insertion on the quasi-linear trend of UTS with EMR reaches a maximum at

which no increase in UTS can be achieved with a further increase in energy as there is a plateau arising at the level of the maximum EMR. In further increasing the EMR it presumably comes to thermal degradation of the polymer as described in literature [13] and additionally supported by the results of the initial Post-process experiments throughout section 7.2. Starr *et al.* also observed this effect for PA based polymers at higher EMR levels [58].

Material	Build chamber temp. [°C]	Slope
Desmosint	90	15.04
	105	33.85
	120	45.19
TPU SLS 4	115	41.56
	120	49.4
	125	52.26
DF	130	8.96
	145	14.45
	160	19.82

Table 20: Slope of UTS in dependence of build chamber temperature

The development of the observed plateau thereby has to be related to the overall energy relation as the possible degradation might not be solely related to the energy insertion by the laser. This gets more obvious when looking at the lower build chamber temperatures at constant energy density as depicted by Figure 69b, where the plateau for TPU SLS 4 is reached at the highest EMR (125°C; 0,31 J/mm³ at 23 W laser power). In case the degradation would only be caused during the exposure by the laser beam, it is assumed that the effects of thermal loads would also be identifiable at the same energy density at lower temperatures e.g. at 120°C already. However, this is not the case as the course of the curve is still linear with a slope of 49.4 at this stage. For Desmosint and DF this plateau could not be detected but it is expected that on basis of the similar material behaviour and the effects described in literature that they might be analogous [58].

The second investigation studied the effects of build temperature on Shore Hardness within section 6.4. Taking a closer look at the values for the Shore Hardness in combination with the UTS in Figure 85a – c it can be noted that the

maximum shore hardness is not reached at the maximum values for UTS with respect to the applied parameter combinations. Especially on thorough examination of TPU SLS 4 the maximum possible shore hardness developed at an EMR of 5, whereas the UTS keeps increasing up to an EMR of around 8 representing the upper limit of the investigated range. Desmosint and DF in principle show a similar behaviour although the values for its shore hardness deviate a lot more compared to the TPU SLS 4. This might be due to effects of surface roughness and part porosity of DF (see section 5.6) which are relatively high for this material. However, the graphs show that the maximum possible values for hardness are reached at lower energy densities as compared to the tensile properties; hence Shore Hardness A does not solely help to derive a statement on maximum mechanical capabilities of the TPEs.

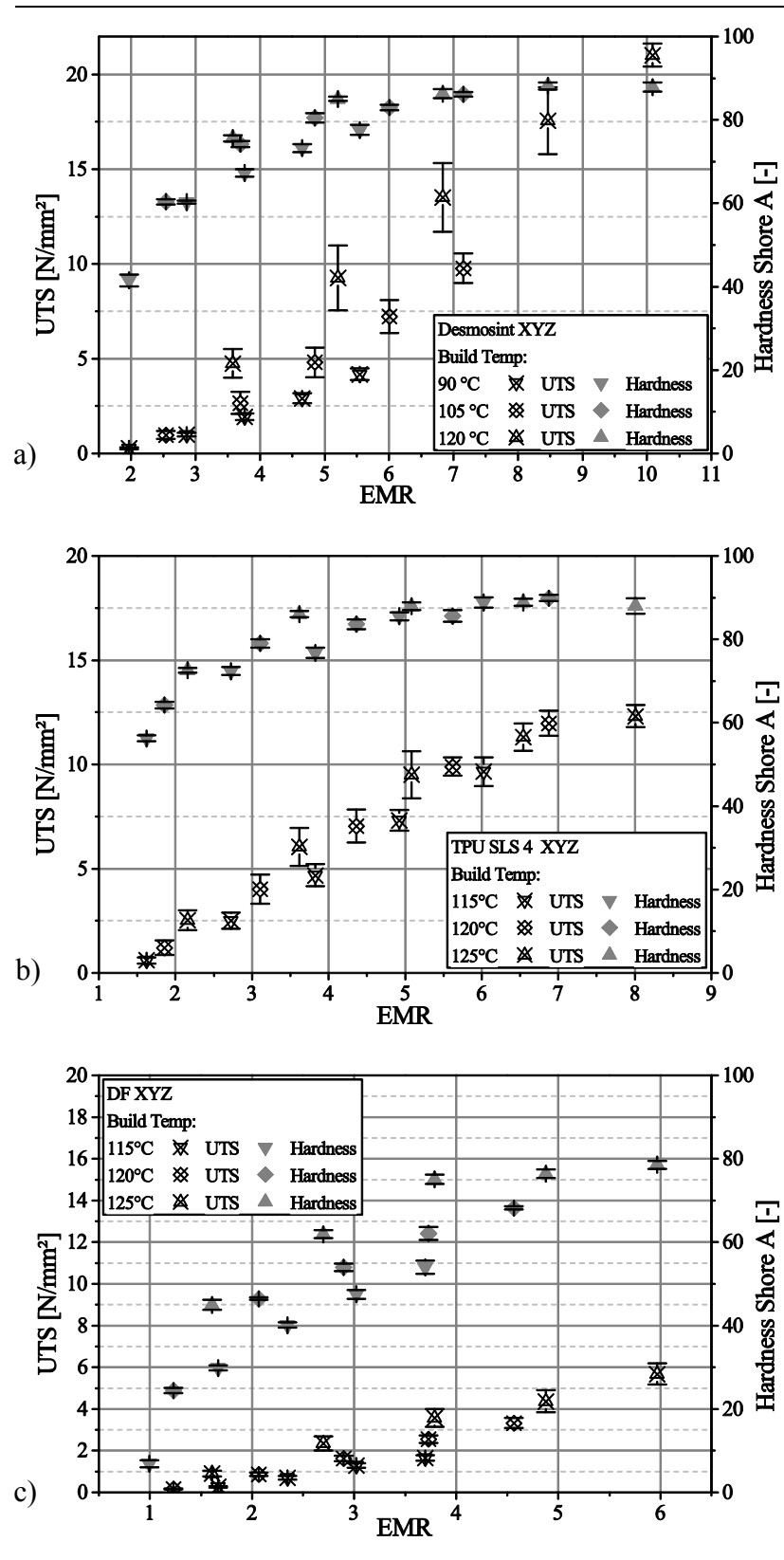


Figure 85: Shore Hardness A and UTS in dependence of EMR for a) Desmosint, b) TPU SLS 4 and c) DF

The third part of the investigations considered the effects of varying processing temperatures on the crystallinity of the specimens as presented in section 6.5.

When taking a closer look at Figure 73a – c, it can be concluded that on the basis of the numerical values no significant influences of the processing parameters could be detected. However, for DF and its different parameter combinations (from EMR of 2.35 to 5.97) shown in Figure 73c shifts in the reflex positions within the crystalline structural share can be observed. Such shifts in reflex positions towards smaller diffraction angles indicate increased distances between lattice plains of different crystalline shares [295]. Overall, the results helped to make a distinct differentiation between the different TPEs and indicated that no significant effects on the degree of crystallinity within a certain polymer could be detected despite small shifts in reflection positions for the DF samples.

8.4 Post-Process

In section 7.2 the sensitivity towards thermal degradation of TPU SLS 4 was initially investigated by fast scanning calorimetry. The increase in melting enthalpy indicates that the ability to crystallize was enhanced due to chain degradation. Hence, heating the material up to temperatures above 270°C or longer than 10 ms could lead to the beginning of chain degradation. The enhanced ability to crystallize after the consecutive heating runs due to possible chain degradation increased more rapidly when exceeding temperatures above 290°C – 300°C. These results correlate with the observation of fuming during the parameter study in section A.1.2 for higher energy densities. Based on the outcome of this initial experiment the ageing behaviour will be further investigated in the course of chapter 7. In accordance with the Post-Process objectives the ageing behaviour was investigated on basis of mechanical properties and part density, the materials ageing on macro-molecular scale as well as on powder scale. The results are going to be discussed hereinafter.

During the tensile testing of DF, a clear delamination of the single layers was observed in the tensile test specimens representing weak and inhomogeneous layer bonding. Such weak bonding seemed to cause the breakage in single layers rather than in the entire cross section of the tensile specimen and is likely to reduce the polymers original capabilities even more. However, neither material

seemed to be significantly affected by the repeated processing and the thermal load in terms of their stiffness and UTS.

The results of the CT analysis indicated that the TPU SLS 4 in general showed a part porosity that was significantly lower than DF. This connected to the level of viscosity which is significantly lower (-12% in average molecular weight in ageing state one, see Table 19 for TPU SLS 4) favouring particle coalescence [328] during the exposure of the material as previously discussed in section 8.2. Similarly, the reduction in porosity for both materials with progressing ageing cycles along with a decrease in molecular weight, is connected to enhanced particle coalescence. In addition, the formation of a homogenous melt layer leading to lower porosity is favoured by the viscous flow due to enhanced mobility of the polymers' macro molecules. The pore size of DF-14 increased again by $8.55 \times 10^8 \mu\text{m}$ compared to ageing state seven. It is assumed to be an artefact of the powder application process or issues within the temperature control of the LS-system, as the pore did not generate systematically over the whole part rather than on one side of the part (see Figure 77b).

For the study of the ageing behaviour on macro-molecular scale the MVR and changes in the molecular weight were investigated. In order to interpret the results the right way, it is important that one does not correlate the values for MVR between the two different polymers. The tendency of a polymer to change the MVR due to thermal loading in LS, though, allows a statement on how sensitive a certain material reacts on these stresses. Over all its ageing states, DF did not level off as the TPU SLS 4 did from ageing state 12 and therefore might show a further increase in the MVR likely to affect the test bars EaB undergoing additional processing cycles. The results of the HT-GPC show that there is slight chain degradation present for both polymers with increasing processing cycles [120]. Although polycondensation (principle reaction for DF) and polyaddition (principle reaction for TPU SLS 4) are different reactions, the mechanism of both types is similar, being the step reaction mechanism. Therefore, a chain scission will be the primary degradation mechanism with a random chain scission in the segments, representing the weakest "linkages". As the drop in viscosity (MVR) was significant compared to the changes in molecular weight, the extraction method was applied as a practical and especially quick method to

detect whether the unexpected effect of depolymerisation from the end of the chains occurs. Therefore, within the accuracy of the investigation, no significant change of the low molecular weight fraction in the polymers was found. This indicates that the increase in viscosity was not necessarily caused by low molecular components that might act as a plasticizer within the polymer chains. This observation is in accordance with the step mechanism these types of polymers result from. Polyadducts like polyurethane and polycondensates like polyesters do not typically degrade from the chain ends but randomly break the macromolecule, most likely the ester links [76, 91]. The probability for a scission close to the end of the polymer chain is low, so the increase of the fraction of oligomeres in the polymer matrix can generally be expected to be low, too. The reduction of melt viscosity, indicated by the increased MVR in Figure 78 and Figure 79 can therefore be attributed to the overall reduction of the mean chain length of the polymers due to randomly occurring chain scission. According to the results from the extraction method, both the TPU SLS 4 and the DF showed a slight increase in extractable low molecular weight fraction. However, this increase was not significant within the standard deviation of the measurement. Therefore, within the accuracy of the investigation, no significant change of the low molecular weight fraction in the polymers was found. This indicates that the increase in viscosity was not necessarily caused by low molecular components that might act as a plasticizer within the polymer chains. This observation is in accordance with the step mechanism these types of polymers result from. Polyadducts like polyurethane and polycondensates like polyesters do not typically degrade from the chain ends but randomly break the macromolecule, most likely the ester links [76, 91]. The probability for a scission close to the end of the polymer chain is low, so the increase of the fraction of oligomeres in the polymer matrix can generally be expected to be low, too. The reduction of melt viscosity, indicated by the increased MVR in Figure 78 and Figure 79 can therefore be attributed to the overall reduction of the mean chain length of the polymers due to randomly occurring chain scission.

FTIR analysis was applied in order to detect potential chemical changes of the macromolecules of both polymers due to the high processing temperatures. Ester-based thermoplastic elastomers in general show enhanced resistance to

oxidation, whereas, ether-based TPEs are more resistant towards hydrolysis while showing more pronounced oxidative reactions when exposed to thermal loads in atmospheric oxygen [105, 118, 119]. The thermal weak point in TPUs is the hard segment of the macromolecules, the polyurethane bond [121, 122]. As the LS process works under inert conditions (nitrogen flooded build chamber), oxidation is not expected to dominate potential degradation effects. In Figure 81a the characteristic range for the C-O bond stretching vibration (1150 – 1040 cm⁻¹) can be seen. Effects of oxidation would potentially affect this bond [329, 330]. Figure 81b shows the characteristic shoulder peak signal of the urethane bond between 1680 and 1750 cm⁻¹ which for the ester-based TPUs which for the ester-based TPUs is likely to be affected by hydrolysis [331-333]. The small shifts in transmission relative to the corresponding signals for the ageing states do not allow any conclusions about chemical changes due to oxidation or thermal cracking and might rather be associated with the specific sample preparation (density of sample and pressure during sampling). In addition, the changes are not systematic in correlation to the ageing steps 1 to 14. In Figure 82 the results for the FTIR analysis of DF over its ageing states are depicted. As before, Figure 82a shows the characteristic range for the C-O bond stretching vibration (1150 – 1040 cm⁻¹) potentially affected by oxidation, whereas Figure 82b depicts the single peak for the ester bond at around 1714 cm⁻¹ which might show a shift in its wave number due to thermal cracking. The fact that no systematic change of the chemical bonds is present for both polymers over their ageing states indicates that no new molecular structures or bonds emerge, so that in accordance to the IR-analysis and its measuring accuracy no chemical changes of the materials observed were detected.

Looking at the ageing effects on powder scale it can be seen that the amount of small particles was reduced significantly while the share of large sized grains increased. Thermoplastic elastomers have a lower softening temperature than semi-crystalline polymers do, leading to the effect that they show a higher tendency to build out agglomerates in the LS process compared to semi-crystalline polymers [68, 76]. Thereby smaller particles start tacking at the larger ones and lead to a change in PSD also affecting the powders' behaviour in terms of flowability and bulk density [63, 158]. All samples have been taken from a

previously sieved and tumbled bulk before being passed through a chute riffler ensuring representative samples. Therefore, the shifts in PSD for the two materials shown in Figure 83 can be related back to agglomeration that took place throughout the processing cycles as smaller particles adhered to larger ones. This effect is also represented by Figure 84 showing the correlation of change in medium grain size (X50) and the change in conditioned bulk density (CBD). As described in section 7.3 this drop in CBD and therefore the real bulk density inside the feeds of the LS-system, presumably led to a short feed for the TPU SLS 4 build cycle eight. While the feeders still supplied a constant volume of powder (they were feeding a fixed distance in the z-direction) for the next layer to be applied, this reduction in powder density brought forth a reduced mass that was not sufficient to cover the whole build chamber. This has to be considered for a stable processing of LS powders.

8.5 Summary

An increased powder bed density led to reduced bulk porosity and increased contact areas between adjacent particles that in turn enhanced thermal conductivity and particle coalescence, consequently the sintered density of the specimen. The TPU SLS 4, showed a direct proportionality between increasing PSD, the corresponding thermal conductivity and the effects on part qualities. The elastic modulus (E-modulus) did not show any change with varying PSDs within the measurements standard deviation. However, a significant enhancement of the ultimate tensile strength (UTS) and the elongation at break (%EaB) due to increased packing and improved flowability of the powder bulk was shown. The surface roughness of the fabricated parts, even though they presented high standard deviations between the measurement points, showed a dependence on the powder bulk's density and surface quality with regards to the mean value of the results. For the observed LS powders, independent of its particles' average shape, the most influencing factor on the mechanical properties was the packing density of the bulk material. A close packing of particles led to specimens with higher UTS and higher %EaB. Thus, the different powder properties, their effects on bulk behaviour as well as process and parts have to be considered when designing new materials for LS.

The results of the initial investigations on isothermal crystallization proved that there is no quasi-isothermal or two-phase mix-zone applicable for TPE laser sintering. This is due to the fact that there is an overlap of melting and crystallization peaks that does not allow for an isothermal processing window (see Figure 86). However, the TPEs were still stable upon processing at various build temperatures within the non-isothermal range.

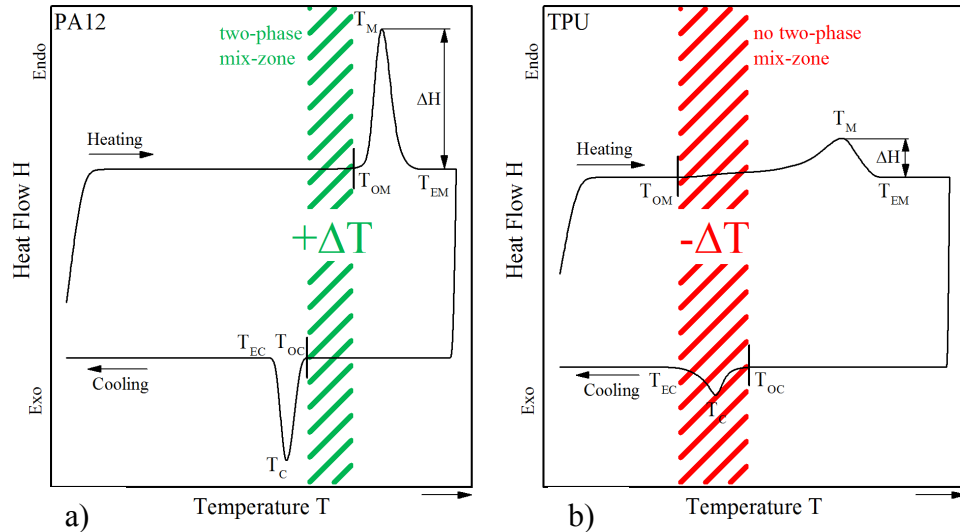


Figure 86: Schematic comparison of DSC run and the delta between onset of melting and onset of crystallization of a) PA12 and b) TPU, adapted from [32]

According to the state of the art, the EMR approach represents the most comprehensive model to describe and predict part properties in relation to processing and material input values. For the first time this model has been applied for TPE-based polymers within this study in terms of varying build chamber temperatures. Despite the mentioned inaccuracies of the EMR approach, not considering optical effects or, for example, thermal conductivity in dependence of PSDs or temperature, a good prediction of the mechanical properties in dependence of the parameter variations of the DOE was achieved. In the first section of the In-Process investigations the influence of varying build temperature and energy densities on the UTS were investigated on basis of the EMR approach. For the materials observed it was shown that with increasing temperature at comparable energy density, UTS increased significantly. As depicted in Table 20, the mechanical properties of all observed materials showed a steeper rise in UTS with increasing build chamber temperature indicating that

the relative effect of build chamber temperature was more significant than other parameters such as laser energy density. As a result of the increasing slope, it can be noted that the course of the energy insertion of the build chamber temperature follows a non-linear trend. The increase in UTS with increasing EMR reaches a maximum indicated by a plateau arising at the level of the maximum EMR. At this plateau the necking behaviour of the powder during exposure might reach its optimum and the polymers presumably would degrade in further increasing the EMR as it was observed by the effect of fuming within preliminary studies shown in appendix A.1.2. When investigating the effect of varying build temperature and energy densities on shore hardness it was shown that the maximum possible hardness of the TPEs observed developed at lower levels for EMR compared to the UTS. This was especially the case for TPU SLS 4. For example, the hardness of TPU SLS 4 levelled off at approximately 60% of the maximum EMR applied, whereas the tensile properties in terms of UTS kept increasing over the remaining 40% of EMR as shown in Figure 87.

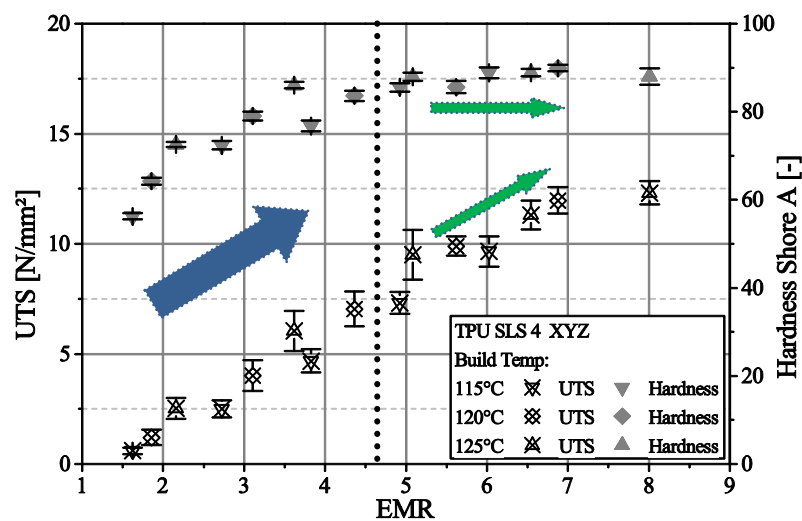


Figure 87: Shore Hardness A and UTS in dependence of EMR for TPU SLS 4. The blue arrow marks the range of adjustable UTS alongside adjustable Shore hardness; the green arrows highlight potential increase of UTS at constant Shore hardness

This leads to the assumption that the mechanical properties can still be increased after the parts reach optimum density levels, thus are demanding for higher energy densities and especially higher build chamber temperatures that allow for enhanced sintering as well as favoured entanglement amongst the polymer layers. In the same context, potential effects on crystallinity of the specimens were studied in X-ray diffraction analysis. However, on the basis of the

numerical values, no significant influences of the processing parameters could be detected, supporting the hypothesis and the results of the initial investigations in section 4.3.2. The crystalline share is relatively low and crystallization is completed very fast when compared with PA12.

Within section 7.3, the effects of cyclical powder reuse without refreshing with virgin powder on tensile properties and part density were studied. Both the DF and TPU SLS 4 did not show a significant change over their ageing cycles in terms of UTS and E-Modulus. From ageing state one to ageing state six, however, TPU SLS 4 showed a drop of almost 165% in EaB while DF showed a slight increase of approximately 120% in EaB already from the first to the second ageing state. These values for TPU SLS 4 already indicated changes of the materials intrinsic properties due to potential degradation of the polymer chains as a result of chain scission. In a vice versa manner this is also known from PA12 ageing studies on tensile properties, where an increase in EaB is described in literature due to chain degradation and cross linking. The TPEs also show an opposite trend in terms of part density when compared with PA12. Analogous to the tensile properties presented in these studies, changes in the parts' densities were detected whereas both TPEs resulted in denser parts with a significant reduction of the volume of larger pores with increasing ageing cycles as indicated by Table 16 and Table 17 [21, 23, 136]. These results also represent an opposite trend when compared with PA12 which was found to exhibit the highest part density in the virgin powder state [21].

When linking the findings on the part properties with the results from section 7.4 on the ageing on macromolecular scale, it can be seen that the enhanced melt-flow of the TPEs has an influence on part density. It was shown that with increasing processing cycles, slight changes in molecular weight are present, indicating chain scission due to thermal stresses. This effect could be the reason for the enhanced flowability of the polymer melt and the reduced elongation at break that were observed. Other than for PA12 which is known to exhibit an increase in melt volume rate alongside a higher average molecular weight with heat exposure time, the effects on part density for the TPEs can be attributed to an overall reduction in molecular weight (see Table 18) [112, 136]. The FTIR

results depicted in Figure 80 and Figure 81 did not reveal any systematic chemical changes of the macromolecules of both polymers.

On a bulk scale both TPE powders showed an increase in medium grain size leading to a decrease in bulk density. Due to the lower softening range, TPEs show a higher tendency to build out agglomerates (especially fine particles adhering to larger ones, see Figure 82) even at relatively low processing temperatures when compared to typical semi-crystalline polymers such as PA12 [32, 68, 76]. This was already indicated in section 7.5, as with increasing processing cycles the amount of fine particles significantly decreased while the change in medium grain size levelled off at a certain point. In accordance with the results from 5.5 the significant decrease in bulk density as a result of changing PSD was expected to also affect the density of the sintered parts. However, the increased viscosity shown in the MVR results seems to be dominating this effect. It enables the parts to build out higher densities due to enhanced particle coalescence and formation of homogenous melt films, hence is a dominant material property to be considered within material design. On the bulk scale, though, a drop in bulk density, as present for the TPU SLS 4, has to be considered to guarantee a stable process especially for materials that have a strong tendency to agglomerate.

9 Conclusions and Future Work

Throughout the previous chapters the objectives and the results have been discussed. This chapter gives final conclusions of the study and recommends future research activities based on the outcome of this work.

9.1 Conclusions

The qualitatively and quantitatively gathered data within this study revealed the dominating process-material interactions as well as process-part property interactions for the successful processing of TPEs in LS. The results could serve as input for the design of new materials, processing strategies as well as for future simulations or model-like derivations of the LS processing chain for TPEs. Consequently, the introduced methods could serve as potential tools for product design and quality assurance. In the following the conclusions for Pre-, In- and Post-Process are presented.

9.1.1 Pre Process

The principle interactions and effects on powder scale as well as process and parts were revealed. Well establishes methods such as the HR as well as novel analysis methods in the field of LS powder characterisation, the RPA and FT-4, have been applied. The aim was to build important correlations in order to validate their significance and transferability on the LS process. The comparison of the bulk behaviour of three different powders in terms of packing and dynamic flow behaviour showed that the reduction of fine particles within the TPE powders allowed them to improve packing and flow efficiency as a result of decreased cohesiveness. TPU SLS 4 thereby aligned more and more to the powder performance of the benchmark material PA12. The FT-4 powder rheometer thereby showed the most straightforward correlation with in-situ packing and flow properties. Due to its user-independent and highly repeatable measurement procedures it represents a valuable method to study the materials static and dynamic bulk properties. This method could allow to facilitate material selection and constitutes a valuable tool for quality assurance. For the observed TPE powders, independent of its particles' average shape, the most valuable influencing factor on the mechanical properties was the packing density of the

bulk material. Overall, the gathered data on powder, process and part scale could serve as valuable input as well as validation for simulations on powder application and packing behaviour in LS and future material design.

9.1.2 In-Process

The specific processing characteristics of TPEs in LS have been disclosed in the scope of an overall energy approach in order to study the dependence of tensile properties on material and process parameters. The EMR approach, not considering optical effects or, for example, thermal conductivity in dependence of PSDs or temperature, allowed a good prediction of the mechanical properties in dependence of the parameter variations applied within the DOE. The relative effect of build chamber temperature on UTS was found to be more significant than other parameters such as laser energy density. The effect of varying build temperature and energy densities on shore hardness showed, that the maximum possible hardness of the TPEs developed at lower levels for EMR compared to the UTS. The input of material characterization data and the correlations between achievable mechanical properties as well as the shore hardness revealed interesting knowledge for the design of part property profiles and allows for derivation of appropriate machine parameters.

9.1.3 Post-Process

An approach for the quantification of ageing behaviour of LS polymers was introduced. Thereby, the physical and chemical ageing behaviour of DF and the newly developed TPU SLS 4 were investigated. In the scope of an initial FSC experiment it was shown for the TPU SLS 4 that at a dwell time of 10 ms above 270°C the TPU may likely be in the degradation range. Derived from the thermography results in section 6.2 the in-situ temperature is approximately even 20-30°C higher in the actual LS process, hence increases the probability of thermal stresses. Overall, the TPE materials showed good performance in terms of powder life and their reuse representing a promising type of polymer for LS. However, alongside a reduction in the molecular weight an average drop in EaB of 140% was determined for the highest ageing state of the two TPEs, indicating changes of the materials intrinsic properties due to potential degradation of the polymer chains. This constitutes the exact opposite degradation behaviour as it

is described for PA12. The approach introduced in this study allows for comprehensive investigation of degradation behaviour of LS powder and constitutes a valuable tool for material design and quality assurance. The technique of stability estimation by crystallization analysis (see section 7.2) by FSC is a very promising tool for the characterisation of a stable sintering region. As a supplement to thermogravimetric analysis (TGA), which is only sensitive to degradation related to mass loss at relatively low heating rates, it measures the influence of decomposition on crystallization kinetics at in-situ kinetics. Consequently, it gives process adapted understanding on the short time thermal stability of semi-crystalline polymers, a property that is essential for fast polymer processing such as LS. In addition it only requires very low sample masses, hence is an efficient tool for an early stage in material design.

9.2 Recommendations for Future Work

This work with its comprehensive approach, taking into account the whole LS processing chain, has opened up opportunities for future studies in various directions. In the following some recommendations to extend the knowledge beyond that performed in this work are given.

9.2.1 Pre-Process

Research on Comminution/Milling Process for Narrow PSDs

Cryogenic grinding at the current state of the art often leads to very broad PSDs for LS powders. Especially for the TPE-based polymers no precipitation process allowing for control of PSD as for the PA12 is applicable or developed so far. In order to achieve favourable powder performance these bulk powders' PSDs have to be adjusted subsequently to grinding by, for example, an air classification process as applied in this PhD study. Depending on the polymer, such a process could potentially be a emulsion separation in a suitable liquid or an extrusion process in which the material is fed into a nozzle for e.g. spray drying or the generation of droplets working with turbulences as proposed by Rietzel *et al.* [299]. A secondary effect potentially achieved by applying these processes could be an optimized shape and surface morphology of the manufactured powders

enhancing flow and packing performance of the powders as well as improved surface quality of the parts manufactured.

Another approach, increasing the efficiency of material reuse for the ground powders, could be a particle return system with e.g. a cyclone. Subsequently to the grinding process, the very fine powders could be lead back to an extruder under conditions where the polymer does not degrade and therefore the resulting granules can be led into grinding process again. This would increase overall efficiency and economics of these types of polymers that show very good properties in terms of powder life already.

Simulation of Powder Performance and In-Situ Powder Behaviour

The generated data on powder interaction as well as the interconnection with part properties should be used for validation of the LS process simulations.

Initial results have been gathered throughout the course of the PhD investigations in collaboration with the Leeds Institute of Particle Science & Engineering at the University of Leeds. In building digital libraries for particle shapes based on X-ray scans of the actual powders and the use of that data to undertake simulations of particle packing also under process conditions, could be a powerful tool for material development and design of powder properties before going into expensive manufacturing processes of the same. In a second step, these simulations could be combined with effects of heat transfer by, for example, conduction and convection as well as sintering behaviour in terms of neck growth.

9.2.2 In-Process

Simulation of LS Process in Fast Scanning Calorimetry

Derived from the observations of the initial experiments in section 4.3.2, FSC proved to be a powerful tool to simulate the in-situ kinetics (peak temperatures at melting, as well as heating/cooling and subsequent isothermal crystallization) of the LS process as it allows for adaption of the real heating and cooling conditions. Studies on, for example, the effects of the polymer melt crystallization before (layer delay time) as well as after powder application prior to possible isothermal crystallization can be performed. Theoretically, the whole processing steps (pre-heating – exposure – cool down to ambient build

temperature – layer delay time as well as the slow cool down in the powder bed after completion of the build) and its potential influence on the material processing and the resulting part properties could potentially be studied in FSC. However, the database is not sufficient in order to allow for quantitative correlations yet and it is therefore a recommended field of research for future work.

Further Research on the Effects of Fuming

At very high levels of energy introduction during LS it was observed within the PhD studies, that fuming occurred during laser exposure. Analysing the gases could lead to a better understanding of the degradation phenomenon the polymer might experience and how they potentially affect the process and quality of parts.

9.2.3 Post-Process

Refining the significance of EMR approach and Stable Sintering Region with FSC thermal stability

The model of stable sintering region was introduced by Vasquez in combining the EMR of Starr *et al.* [58] with TGA measurements to indicate the max. boundary of energy introduction before a certain polymer degrades [13, 334].

The TGA studies were based on the assumption that heating dynamics in the TGA device were comparable to the thermodynamics the polymer experiences during LS. Based on high resolution thermography, the results of the PhD investigation presented in this thesis proved that the heating rates are depending on the polymer several 100 times higher than the possible heating rates within TGA analysis. A first indication that the predicted degradation point of the stable sintering region detected with TGA is not sufficient, is that the mechanical properties were still increasing after exceeding the critical point of energy introduction. The comparatively low heating rates during the TGA might cause a premature decomposition of the analysed sample compared to the kinetics it experiences during exposure with the laser. In addition, TGA only detects degradation effects that are involved with a reduction in mass or the formation of gas. However, molecular changes such as de-polymerisation or cross-linking, both sensitively affecting the crystallization kinetics of a polymer, can't be detected in TGA. Hence, the significance of the model of stable sintering region

could be refined in using FSC for the analysis of actual thermal stability under LS processing conditions. A promising approach to study thermal stability of SLS powders under process adapted conditions was introduced in section 4.4.2 using FSC method.

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Appendices

A.1 Preliminary Investigations and Material Characterization

Alongside the major findings of the literature review discussed in section 2.4, the preliminary investigations introduced in this section of the appendix served to confirm the approach applied and to build the substantial basis for the principle objectives of this thesis.

As only little data exists that could be built upon, the investigations were essential in order to assess the principle and most important process-material interactions and specifics for the TPEs observed. In addition, to disclose the differences of TPE-based to the typical semi-crystalline LS polymers such as PA12 and their processing characteristics that are well understood and documented in literature today, the intention was to derive and enable suitable analysis methods for the main experiments that follow in chapter 4.

A.1.1 Pre-Process Investigations

Powder Performance with Modified Particle Size Distribution – Aims and Theory

The task of this section's investigations was to indicate potential changes in the powder performance arising from modifications of the particle size distribution within a certain powder batch. As described throughout section 2.3 there is a strong connection between particle characteristics such as shape and size distribution and the bulk behaviour. Of major interest here was the packing of powders that in turn is strongly dependent on the particle size distribution (PSD). In this regard, an optimum PSD of the observed bulk in terms of packing does not necessarily favour good flow characteristics (see section 2.3 and 0). Therefore, an initial experiment with two of the observed materials and their modifications was conducted with the aim of detecting the effect of varying PSD on powder flow and packing density.

Materials

The material observed was the experimental TPU SLS 4. In terms of powder performance this section considered PA2200 as a benchmark LS material [28], known for stable processing and repeatable properties of the manufactured components in terms of mechanical capability and surface roughness [6]. All powders were used in their virgin state. Moreover, the TPU SLS 4 powder samples were modified in terms of particle size distribution before testing in order to detect the effects of different size distribution on the packing and flow characteristics. Therefore the original batch has been divided into three different particle size fractions (F0, F25 and F45) by applying an air classification process. The resulting PSDs are shown in Figure 88. The fraction F0 therefore refers to the standard distribution out of the manufacturing process; F25 and F45, respectively, indicate that most of the fine particles below 25 μm or 45 μm are sifted out.

Methodology and Analysis

Conditioning and Sampling

For the conditioning of LS powders no quantitative data is available in current literature and there are no standardized scenarios within industry describing their conditioning. Therefore, in the scope of a previous study conducted by Freudenberg Forschungsdienste SE & Co. KG (FFD) by order of BMW, the TPE-based powders' flowability was investigated in dependence of moisture content. Thereby, the powders especially the TPU SLS 4 showed a tendency towards electrostatic charges due to tribo-electrical effects in a dried condition. It was found that at their equilibrium moisture (between 0.3-0.4 %) they showed the best performance [242]. On account of this and in order to achieve similar and homogenous exposure towards environmental humidity, the powders were conditioned prior to the investigations for approximately 15 ± 1 hours in a stable environment of the standard atmospheres for conditioning and testing of polymers as described by DIN EN ISO291 [243] and ISO 23529 [244]. As described above, every powder sample that was taken out of the powder reservoirs was selected using a powder sample splitter to ensure that the powder samples were representative of the entire powder bulk in terms of PSD [238].

Quantification of Powder Performance – Hausner Ratio

For a quick determination of the powders' packing and flow behaviour, the Hausner ratio (HR) test was performed according to ASTM D7 481 standard [246] with the manual tapping of a powder sample as amongst others described by Liu *et al.* [247]. It is defined by the ratio between the poured and tapped bulk densities (see Eq. 22) and therefore is a measure for the powders flowability [248].

$$\text{Hausner Ratio (HR)} = \frac{\text{bulk volume}}{\text{tapped volume}} = \frac{\rho_{\text{tapped}}}{\rho_{\text{poured}}} = \frac{V_{\text{poured}}}{V_{\text{tapped}}} \quad \text{Eq. 22}$$

$HR < 1.25$ high powder flowability

$1.25 < HR < 1.4$ decreased powder flowability

$HR > 1.4$ cohesive powder

ρ_{poured}	poured density of powder sample
ρ_{tapped}	tapped density of powder sample
V_{poured}	poured volume of powder sample
V_{tapped}	tapped volume of powder sample

As the HR is highly dependent on the user due to the manual tapping of the powder samples, three runs were completed for this technique in order to increase its statistical significance. The vessel that was used for the measurements was a 100 ml polymer vessel. The filling of the powder was performed without any mechanical stress applied from a defined height into a funnel on top of the vessel. The Hausner ratio is rather a relative method to compare materials as their values can vary depending on the methodology used. However, a round robin test performed by the Association of German Engineers (VDI) additive manufacturing working group showed that this method can be conducted with a low repeatability standard deviation [335]. Hence, in this stage it was a useful method to get a simple and quick indication for changing packing and flowability of the different powder fractions.

Results and Discussion

The resulting PSDs of the air classification process for the fractioning of the original TPU SLS 4 bulk are presented in Figure 88. TPU F0 showed a multimodal peak with approximately 90% of the particles between 5-100 μm . The more fine particles that were separated from the original bulk F0, the narrower the corresponding PSD became, thus, aligned more and more to the PSD of the PA2200 with a mean particle size of around 50-60 μm [6]. For TPU F25, 90% of the particles ranged between 25-100 μm , while for the TPU F45 90% of the particle population ranged between 45-100 μm representing the narrowest PSD.

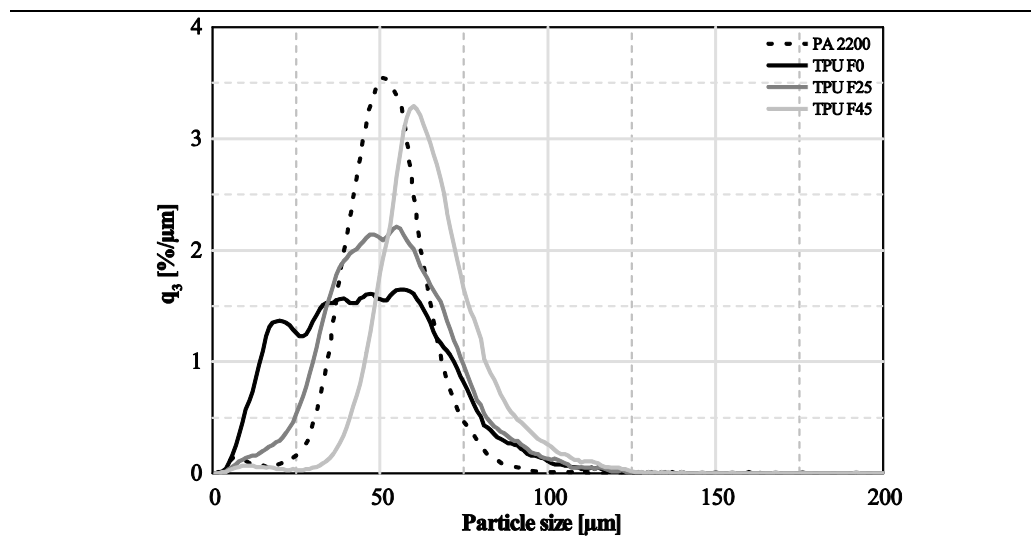


Figure 88: Particle Size Distributions for TPU fractions in comparison to PA2200

For all TPU fractions 10% of particles lay between 100-120 μm and therefore had a higher amount of larger particles compared to the PA2200 as shown in Figure 88. These three fractions of the TPU built the basis for the Hausner Ratio measurements and the results are depicted in Figure 89.

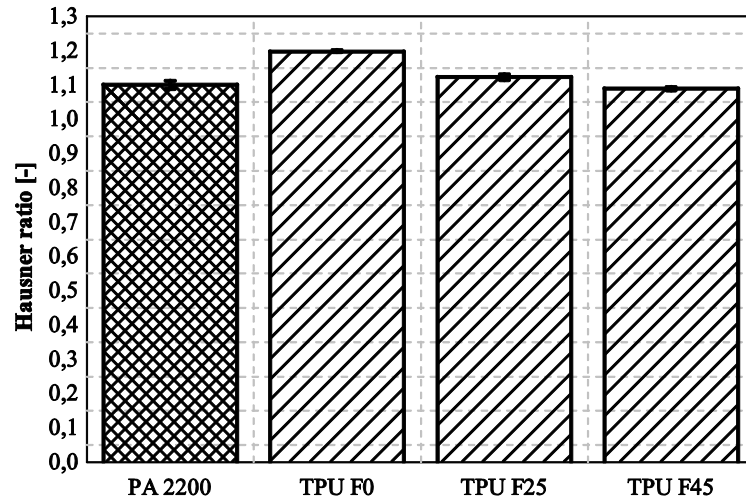


Figure 89: Hausner Ratio of PA2200 compared to the TPU fractions

The results show that the HR is 8.91% higher for TPU F0 ($HR = 1.198$), 2.05% higher for TPU F25 ($HR = 1.123$) and 0.97% lower for TPU F45 ($HR = 1.09$) when compared to PA 2200 ($HR = 1.01$) in ambient conditions. According to the definition of the HR, all powders showed high flowability with the TPU F45 reaching the level of the PA2200 with an HR at around 1.1 with low standard deviation. Hence, it is expected that the different fractions of the TPU SLS4 show different or even improved processability and effects conducive on part quality as the decreasing HR value also indicates more efficient packing behaviour that in turn might have a positive influence on part density.

A.1.2 In-Process Investigations

Parameter Study – Aims and Theory

It is known that properties of parts built in LS change depending on the processing parameters (see section 2.1.4). The focus of this study was to provide a parameter setup to achieve favourable tensile properties. This parameter setup builds the basis for the later Pre-Process observations and is kept constant throughout them. In general the mechanical properties of parts produced in LS are increasing proportionally to the energy density applied. Nevertheless, this only applies to a certain extent as at some point the polymer reaches its degradation temperature [9, 336].

Materials

The LS powder used for the parameter study was the TPU SLS 4 exclusively supplied and developed for the LS process within a project between BMW AG and Freudenberg Forschungsdienste SE & Co. KG. The TPU SLS 4 is an aliphatic, ester-based (building the soft segment) block copolymer (polyurethane building the hard segment) without ether linkages.

Methodology and Analysis

LS system and production of test samples

A SinterStation[®] 2500 plus (3D Systems, Rock Hill, USA) was used for the manufacturing of tensile test specimen. Type S2 tensile test specimen were produced according to DIN 53504:2009-10 (as specified by the International Standard ISO 37:2005) [239]. The tensile samples were produced in the XYZ-direction according to ASTM F2921-11e3 ensuring a flat build that did not require a large amount of powder [1]. As before the powders for all builds were processed at equilibrium moisture between 0.2–0.3 % to ensure comparable starting conditions. The layer thickness within this study was set constant to 100 µm for all experiments and the parameters laser power and hatch space have been varied in order to reach different energy densities. A cross-scan strategy was used to build the parts and in order to get comparable results they were all built with the same layer delay time in order to reduce the influencing factors during the build. At the lowest level of the test build flat crosses were built in order to detect the correct temperature of the build chamber without curling or uncontrolled melting. Temperatures that were too low or inhomogeneous temperature distribution within the build chamber could be detected and adjusted within this stage of the build before the actual parts were produced. During the study, it was found that a temperature of 125°C assured stable processing and was therefore set constant in order to find favourable scan parameters. As the favourable mechanical properties of the DuraForm[®] Flex (3D Systems), that was to be compared to the TPU in subsequent investigations, reached its favourable mechanical properties at comparable energy density levels (between 0.25 and 0.3 J/mm³, see Figure 70), the TPU was used to find the best possible parameter

set-up that both materials share. The favourable build chamber temperature for the DuraForm[®] Flex (3D Systems) was found at 160°C.

Nr.	Parameter Setup		
	Energy Density [J/mm ³]	Scan Space [mm]	Laser Power [W]
1	0,05	0,10	2,50
2	0,05	0,15	3,75
3	0,05	0,20	5,00
4	0,15	0,010	7,50
5	0,15	0,15	11,25
6	0,15	0,20	15,00
7	0,20	0,15	15,00
8	0,30	0,10	15,00
9	0,30	0,15	22,50

Table 21: Parameter setup for parameter study showing the values in the order of Energy Density, Scan Space and Laser Powder – green area denotes parameter set that lead to best possible mechanical properties.

Table 21 shows the laser exposure parameters investigated in order to find the parameter set leading to the best possible tensile properties with the materials examined.

Mechanical Properties

The assessment of the mechanical properties was obtained by means of tensile testing. All tensile tests were performed in a controlled environment, at 20°C and 50% relative humidity (RH) detecting Young's modulus, ultimate tensile strength (UTS) and percentage elongation at break (%EAB). The testing machine used was a Zwick Z020 (Zwick GmbH & Co. KG, Ulm, Germany) equipped with a 1 kN load cell, an optical extensometer, and a testing speed of 200 mm/min (DIN 53504:2009-10). For each of the parameter set, five S2 tensile bars were tested at ambient conditions and the average value was used for comparison.

Results and Discussion

The parameter combination nr. 8 in Table 21 applied for the TPU tensile bars generated an average modulus of around 97 N/mm², an average tensile strength

of around 10 N/mm^2 and the highest elongation at break at approximately 285 %. As pointed out in Figure 90, at this parameter setup formation of white fumes (also see Figure 91) emerged due to the relatively high energy density that was applied.

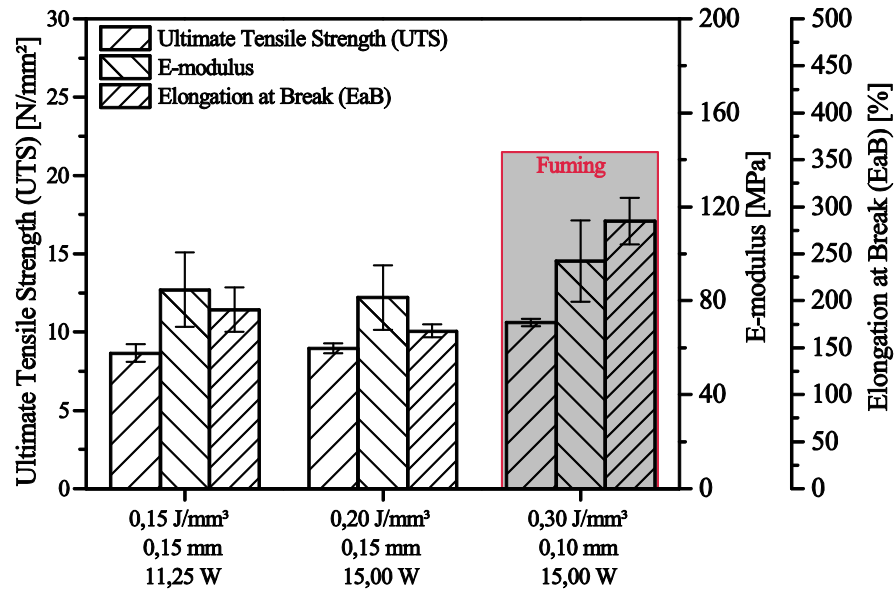


Figure 90: Tensile properties using three different parameter sets

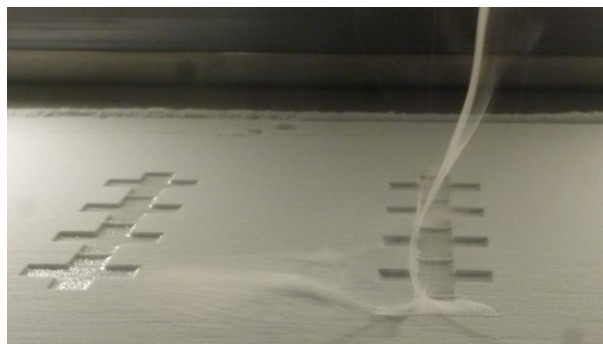


Figure 91: Formation of white fume occurring at highest energy density level (setup nr. 9 shown in Table 21)

This might indicate that at this energy density additives or monomers may be vapourised out of the polymer powder bed due to thermal degradation. Based on the lack of knowledge about the mechanism, the impact of fuming and the

probability that it might affect the process, a parameter combination between setup number 7 and 8 (highlighted by the green lines in Table 21) with an energy density of 0,025 J/mm²- 0,15mm - 18,75W), was used for the further investigations.

Parameter description	Parameter value	
	TPU	DF
Left and right feed heater set point	55°C	55°C
Part heater set point	125°C	160°C
Powder layer thickness	0.1 mm	0.1 mm
Left and right feed distance	0.38 mm	0.38 mm
Fill laser power	18.75 W	18.75 W
Fill scan count	1	1
Outline laser power	5 W	5 W
Outline scan count	1	1
Slicer fill scan spacing	0.15 mm	0.15 mm
Scan speed	5 m/sec	5 m/sec

Table 22: LS parameters used for the production of the TPU and DF test specimens

As a result of this preliminary experiment the parameter set shown in Table 22 can be derived for the DuraForm[®] Flex and the TPU and are consequently used for some of the subsequent investigations.

Investigation on the effects of Part Positioning and Build Temperature – Aims and Theory

Within laser sintering it is known that temperature differences that exist in various regions of the build platform can lead to different shrinkage as well as mechanical properties of the parts manufactured. This effect was found to be even more pronounced for materials with a relatively small processing window [6, 41]. In order to exclude and reduce the number of influential factors on processing and part properties it is beneficial to reach a homogenous temperature distribution on the platform. Hence, within this study the areas of the build chamber generating comparable mechanical properties were aimed to be

detected. On account of this, the system was upgraded with a multi-zone (8-zone) heating system as well as an advanced temperature control device reducing the variations of temperature over the build platform to guarantee a good starting point. Subsequently, the effects of varying build chamber temperature on mechanical properties are going to be investigated within the areas that were found to have the most homogenous temperature distribution. This is supposed to give a first indication on the possible range that TPE-based polymers can be processed in, applying build temperatures even below their crystallization temperature.

Material

The material used for the investigations was a commercial ester-based TPU grade (DESMOSINT[®] X92A-1, Lehmann&Voss&Co., Hamburg). This material will be referred to from now on as “Desmosint”.

The investigation of this TPU grade makes sense in particular, as it provides another TPE-based reference (TPU) that equals the experimental TPU SLS 4 from a chemical perspective, while showing a significantly lower degree in crystallinity and different melting characteristics manifested by a broader melting peak (onset of melting approximately 30 K lower compared to TPU SLS 4 at a comparable melting peak temperature at around 150 – 155°C). It therefore provides a useful additional reference in order to gather information on the processing specifics in dependence on material properties.

Methodology and Analysis

LS System and Production of Test Samples

A DTM SinterStation[®] 2500 plus was upgraded with an UNIHEAT multi-zone heating system and an ATC (advanced temperature control) by LSS (LSS Laser-Sinter-Service GmbH, Holzwickede) for the investigations on effects of build chamber temperatures in order to guarantee a more homogenous temperature distribution over the build platform. Type S2 tensile test specimens were fabricated according to DIN 53504:2009-10 (2009) and International Standard ISO 37:2005 (2005) in XYZ-direction according to ASTM F2921-11e3 (2011) in order to assure a flat build not demanding for a high amount of powder. The

specific build jobs and parameters for the two experiments on part positioning and build temperature are going to be introduced in the following.

Part Positioning

Tensile specimens were built at constant parameters over the effective build area in the DTM 2500 plus with the heater upgrade introduced in section 4.3.3. The parameter combination in Table 23 was used:

Parameter description	Parameter value (Desmosint)
Left and right feed heater set point	55°C
Part heater set point	80°C
Powder layer thickness	0.1 mm
Left and right feed distance	0.38 mm
Fill laser power	20 W
Fill scan count	1
Outline laser power	5 W
Outline scan count	1
Slicer fill scan spacing	0.15 mm
Scan speed	5080 mm/sec

Table 23: Machine parameters used for the production of the Desmosint test specimens for the verification of temperature distribution

Figure 92 shows the positioning of the tensile specimens distributed over the build platform for the screening of the possible temperature gradient.

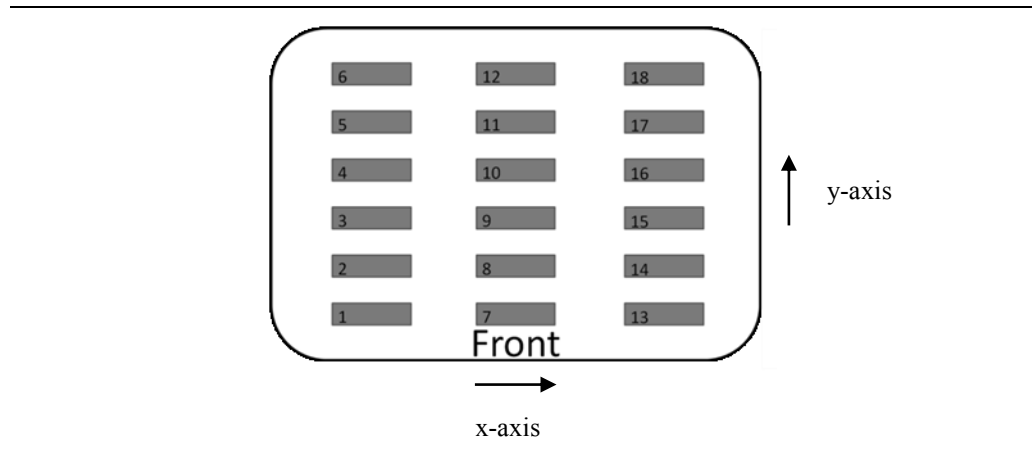


Figure 92: Positioning of specimens for screening of temperature distribution within the build chamber

The tensile properties were subsequently correlated with their corresponding position on the build platform.

Build Temperature

The optimum build temperatures for the TPU SLS 4 and the DF were introduced above within the scope of the parameter study. Thereby, the lower limit was determined by the temperature at which curling occurred as the temperature got too close to the crystallization point of the polymers and vice versa for the upper limit, where melting or glazing of the material occurred due to temperatures close to their melting point. For verification of the hypothesis that there is a crucial and measurable influence of varying build chamber temperatures, exceeding the range of a quasi-isothermal processing window, tensile specimens made of Desmosint were built at constant volume energy density in XYZ-direction. Therefore, the same machine parameters as for the previous study were applied and solely the build chamber temperature (part heater set point) was varied as shown in Table 24.

Laser Power [W]	Layer thickness [mm]	Scan speed [mm/s]	Slicer fill scan spacing [mm]	Part heater set point [°C]
20	0.1	5080	0.15	80, 85, 90; 100; 110; 115, 120; 125

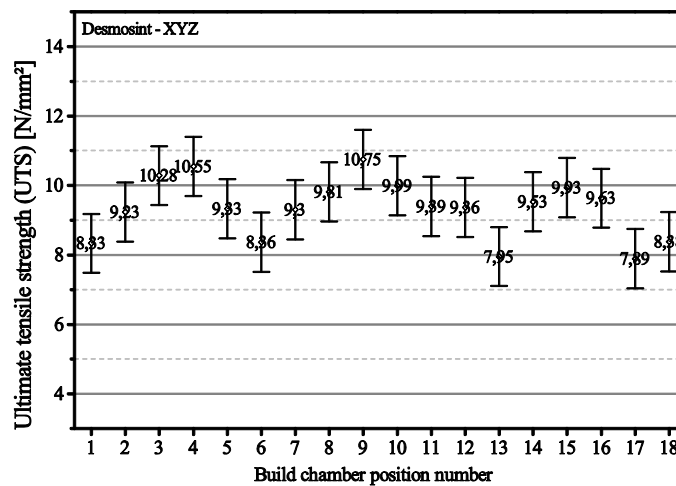
Table 24: Machine parameters used for the production of the Desmosint test specimens for the verification of influence of varying build chamber temperature

The UTS of the manufactured specimen was compared in a final step in order to verify the magnitude of the varying build chamber temperature.

Results and Discussion

Part Positioning

The comparison of the mean values for UTS (Figure 93) in dependence of the build chamber position shows that there is a maximum difference of 2.85 N/mm² (26 %) at a standard deviation of 0.85 N/mm².



Standard deviation [N/mm ²]	$\Delta_{\max}$ UTS [N/mm ²]	$\Delta_{\max}$ UTS [%]
0.85	2.85	26

Figure 93: Ultimate tensile strength (UTS) of Desmosint in dependence of build chamber position of test specimens (cf. Figure 92)

The tensile specimens placed in the corner areas of the build platform (position 1, 6, 13, 18) showed an approximately 20 % lower mean value for UTS (8.26 N/mm²) compared to the mean value of the parts positioned rather in the middle of the platform with the highest UTS (position 3, 4, 9, 10). This correlates with the literature, where the effect of part positioning on properties like density and tensile properties is well described and the corner areas typically were found to be potential cold spots leading to decreased density or mechanical properties respectively [6, 36, 337, 338]. Although the statistical significance of this investigation might not be sufficient in order to describe the effects of build chamber position on mechanical properties representative for the whole build height, it was supposed to give an indication on potential cold or hot spots. Although the maximum deviations in numerical terms were still low compared with other materials observed within the literature [6, 339], it was shown that the corner spots of the build platform should not be used for the investigations on build chamber temperatures. These spots supposedly represent colder areas with a rather inhomogeneous temperature distribution compared to the other positions and represent a factor of uncertainty for the studies on effects of varying build temperature. The results of this screening test on the basis of the current machine setup were taken into account in the subsequent investigations and parts were placed rather in the middle (build chamber position 3,4,7,8,9,10,11,12,14,15,16) of the build chamber.

Build Temperature

For the verification of the effects of varying build chamber temperature, tensile specimens in xyz-direction with Desomsint were manufactured within the areas showing the lowest deviation in mechanical properties. A total temperature range of 30 K was examined initially but at temperatures below 90°C no utilisable mechanical properties could be recorded. On the other hand, at temperatures above 120°C the material started to get soft and began to melt, a phenomenon often called the glazing temperature [283]. The results in terms of UTS vs. percentage EaB for the useful tensile bars are presented in Figure 94 and Table 25.

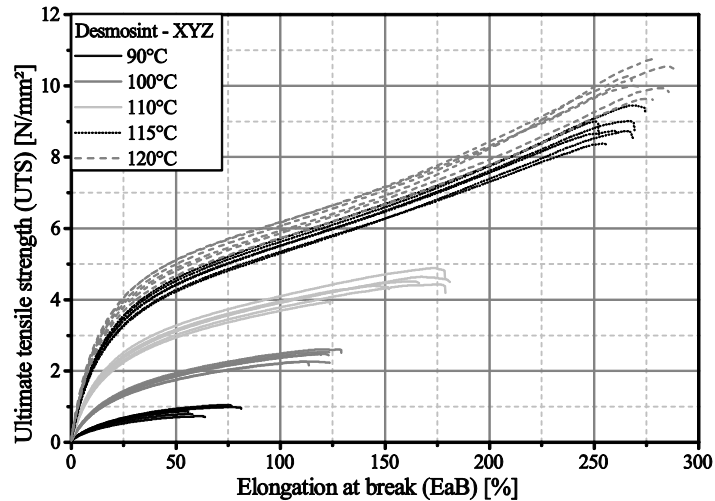


Figure 94: Ultimate tensile strength (UTS) vs. Elongation at break (EaB) of Desmosint in dependence of build chamber temperature

Build chamber temperature [°C]	UTS max [N/mm ²]	Standard deviation [N/mm ²]	Increase of UTS [N/mm ²]	Increase of UTS [%]
90°C	0.91	0.15	-	-
100°C	2.44	0.14	1.53	166
110°C	4.47	0.32	2.03	83
115°C	8.88	0.35	4.41	99
120°C	10.19	0.41	1.31	15

Table 25: Ultimate tensile strength (UTS) of Desmosint in dependence of build chamber temperature

The UTS thereby showed a clear non-linear dependence on build chamber temperature as the increase in UTS of 3.56 N/mm² between the leap from 90°C up to 110°C is significantly lower compared to the subsequent leap between 110°C and 120°C showing an increase in UTS of 5.72 N/mm². Thereby, the maximum increase in temperature of 25 % from 90°C to 120 °C lead to a total increase in of UTS of approximately 90 %.

Summary

The preliminary investigations were performed in order to reveal important interactions within the Pre-, In- and Post-Processing steps. In addition, they were

aimed to support the preliminary hypotheses that there is no quasi-isothermal LS for TPEs (see Figure 26) due to their specific thermal properties as well as their crystallization kinetics. Compared with PA12, however, they own a broad range of possible processing temperatures in which part properties can be adjusted.

The implications of the data gathered from these initial studies alongside the understanding of the current state of the art throughout chapter 2, helped to derive the principle hypothesis and research objectives following in chapter 3. In the sections below the outcome of the preliminary investigations is summarised.

Pre-Process

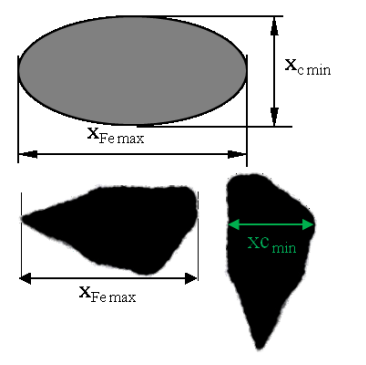
An image based system for powder particle quantification as well as a scenario for representative sampling of fine powders was introduced. In comparing a range of materials (see Table 5) that all differ significantly in terms of their shape, a precise and reliable shape factor, the sphericity, was determined. Three different PSDs for the experimental TPU SLS 4 have been established applying an air classification process leading to a sharp separation of particle sizes. With the Hausner Ratio it was possible to get an indication on the effects of changing PSD on powder packing and flow. With this information, further studies as described in section 4.1 will investigate the magnitude of the effects of different PSD on powder, process and part scale for TPU SLS 4 and the commercial reference DuraForm[®] Flex in order to systematically interconnect the effects of varying powder properties to part quality.

In Process

In section A.1.2 a parameter study was presented with the aim to assess the mechanical capabilities of an experimental LS powder and the generated parameter setup builds the starting point for all subsequent investigations. The upper limit for the energy densities applied was constituted by the phenomenon of fuming at relatively high energy densities. This was probably a first indication on potential degradation of the polymer melt during exposure. This effect was further investigated throughout the preliminary investigations.

It was shown that Desmosint TPU was processable even at temperatures lower than the onset of the crystallization of the material. This would not be possible with typical semi-crystalline polymers such as PA12 as described by the quasi-isothermal model. However, in order to support this hypothesis throughout the principle investigation in section 4.3, the degree of crystallinity in TPE parts is going to be determined in dependence of different processing conditions such as laser energy input and build temperature. Other than on the crystallization kinetics, temperature was suggested to have a major influence on the tensile properties as shown throughout this section.

A.2 Shape Indices image-based Particle Analysis (Camsizer XT)

Shape Characteristic	Graphical Representation	Description
<u>Breadth to length ratio</u> (b/l): $\frac{b}{l} = \frac{x_{c \min}}{x_{Fe \max}}$ $x_{c \min}$ and $x_{Fe \max}$ over all measured directions		The two values $x_{Fe \max}$ and $x_{c \min}$ are based on/correlated to the minimum respectively maximum mesh size needed to get the particle through the meshes of a corresponding sieve. Therefore this value is most common in sieve analysis. $\frac{b}{l} = 1$ = compact shape Also referred to as “sphericity” in literature [340]
<u>Sphericity</u> (SPHT): $\frac{4 \pi A}{U^2}$ U: measured circumference of a particle projection A: measured area of a particle projection		For a sphere or a circle, SPHT = 1. In all other cases SPHT < 1 that equals a rather oblong or rough particle.

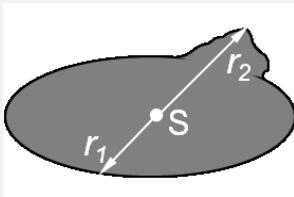
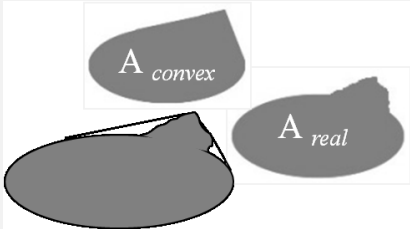
<u>Symmetry (Symm):</u> Symm $= \frac{1}{2} \left[1 + \min \frac{r_1}{r_2} \right]$ r1 and r2 are the distances from the centre of area S to the borders in the set measuring direction.		"Symm" is the minimum value of symmetry values in all measured directions. For asymmetrical particles, $\text{Symm} < 1$. If the centre of the area is outside the particle, i.e. $\frac{r_1}{r_2} < 0$ then $\text{Symm} < 0.5$.
<u>Convexity (Conv):</u> $\text{Conv} = \sqrt{\frac{A_{\text{real}}}{A_{\text{convex}}}}$		Ratio of the real area of the particle projection and its convex area. A convex area arises if a rubber band is placed around the particle and the area is measured within the rubber band. A convex particle has a convexity = 1.

Table 26: Shape characteristics of the Camsizer XT [232]

A.3 Thermography – Input Variables for Calibration of Thermal Imaging System

A.3.1 Results of Laser power adjustments DTM 2500 plus and DTM 2500 HS

	Laser Power (Set Point) [W]	Laser Power (actual value) [W]	Difference [W]
Measurement (on-site, old)	15.00	16.29	+ 1.29
	8.00	8.06	+ 0.06
Calculated Values (new)	18.75	20.04	+ 1.29
	5.00	5.06	+ 0.06

Table 27: Results of Laser Power Measurement of DTM 2500plus (BMW)

	Laser Power (Set Point) [W]	Laser Power (actual value) [W]	Difference [W]
Default Value (old)	15.00	13.27	- 1.28
	8.00	7.40	- 0.06
Default Value (new)	18.75	16.96	- 1.79
Measurement 1 Fill Scan	20.00	19.86	- 0.14
Measurement 2 Fill Scan	20.00	20.00	± 0.00
Measurement 3 Fill Scan	20.00	19.84	- 0.16
Measurement 4 Fill Scan	20.00	19.92	- 0.08
Measurement 5 Fill Scan	20.00	20.02	+ 0.02
Measurement 1 Outline Scan	5.00	5.01	+ 0.01
Measurement 2 Outline Scan	5.00	4.90	- 0.10
Measurement 3 Outline Scan	5.00	4.87	- 0.13
Measurement 4 Outline Scan	5.00	5.01	+ 0.01
Measurement 5 Outline Scan	5.00	4.80	- 0.20

Table 28: Determination and validation of Laser Power for DTM 2500HS (equipped with thermography camera)

A.3.2 Results of properties for specimens built for validation on the DTM 2500HS (equipped with thermography camera)

DTM 2500HS	DTM 2500plus (BMW)
87.4 ± 0.6	86.1 ± 0.6

Table 29: Results Shore Hardness TPU SLS 4 F0

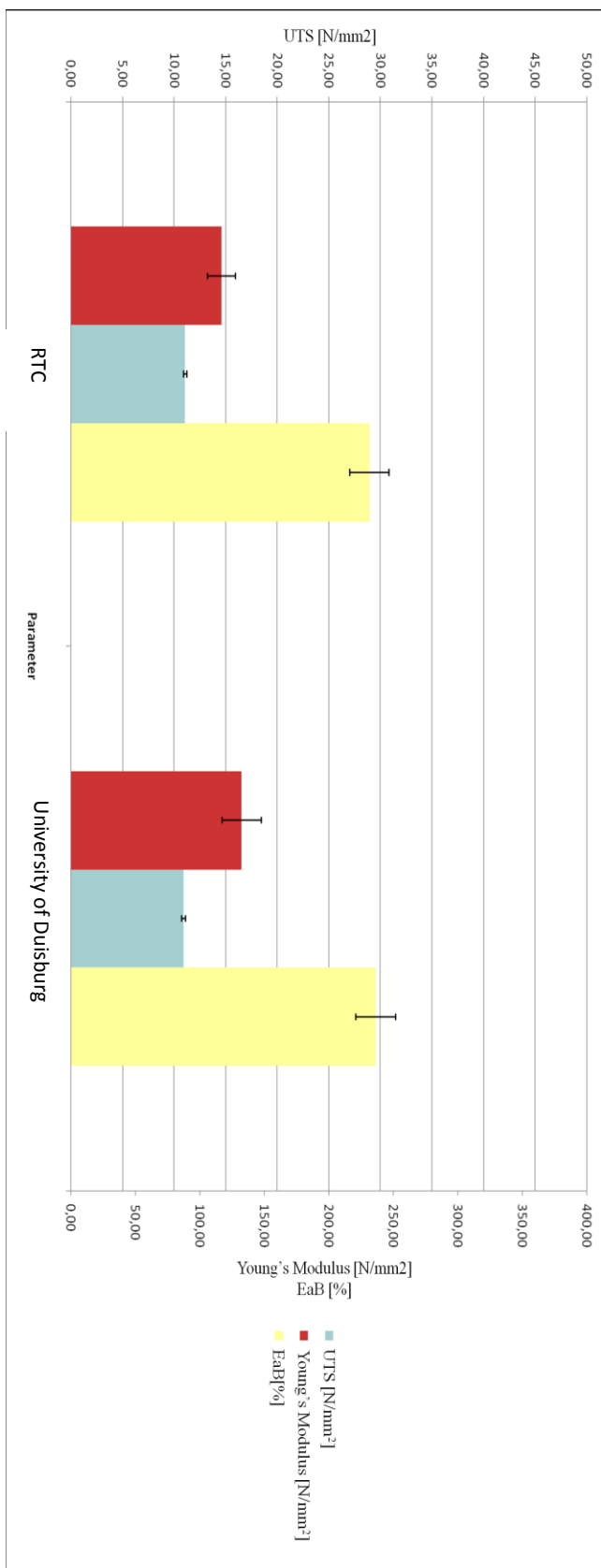


Table 30: Results for Tensile Properties TPU SLS 4 F0 DTM 2500HS

	DTM 2500HS	DTM 2500plus (BMW)
Scaling Factors	TPU SLS 4 F0	TPU SLS 4 F0
x-direction	1,002	1,024
y-direction	0,994	1,014
z-direction	0,985	0,919

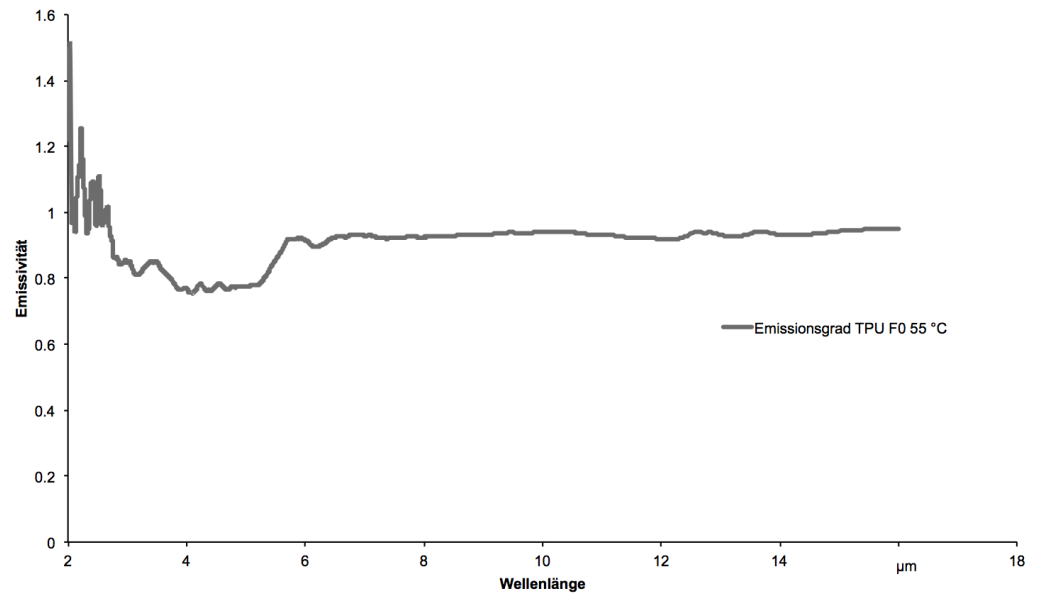
Table 31: Results for Scaling Factors

	DTM 2500HS	DTM 2500plus (BMW)
	TPU SLS 4 F0	TPU SLS 4 F0
Mean value powder bed density	0,410 g/cm ³	0,376 g/cm ³
Part denstiy	1,091g/cm ³	1,079 g/cm ³

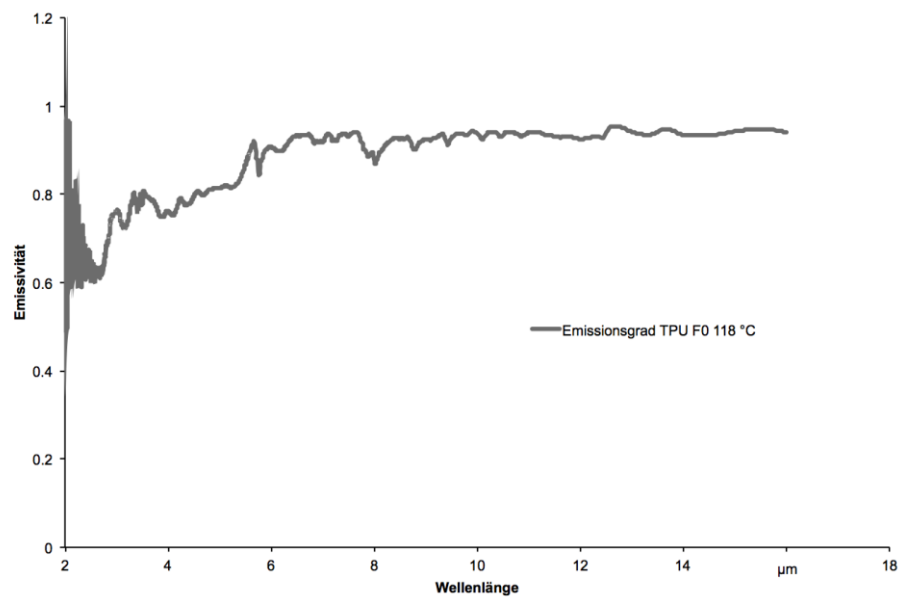
Table 32: Results for Powder Bed Density and Part Density

A.3.3 Results of Emissivity Measurements in dependence of wavelength

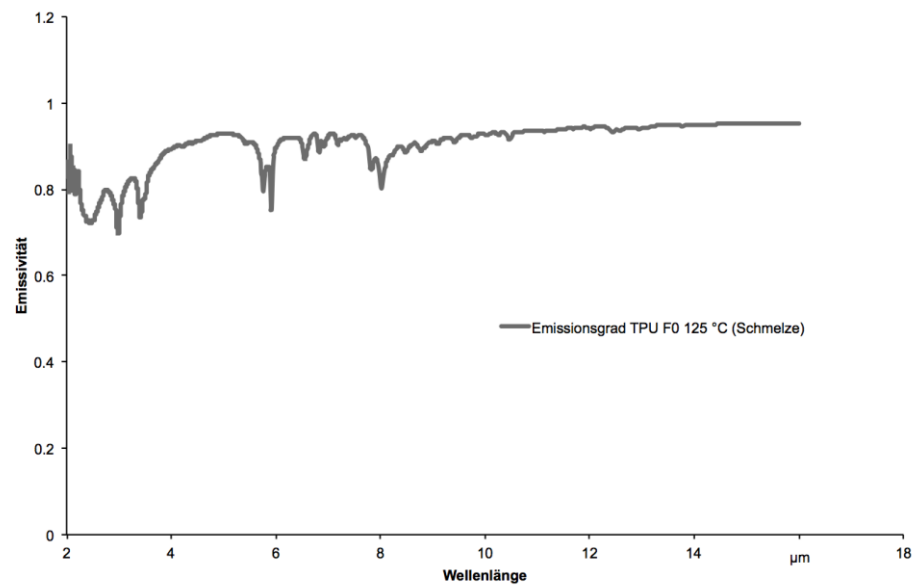
TPU SLS 4 F0 at 55°C



TPU SLS 4F0 at 118°C



TPU SLS 4F0 at 125°C



A.3.4 Report of Emissivity Measurements at the DLR

i. Report on emissivity measurements of BMW elastomer powder in the 2-16 μm spectral range in vacuum, at 120°C and 180°C

The measurements have been performed on July 3 at the Planetary Emissivity Laboratory of DLR in Berlin. The powder was poured in one of the PEL standard stainless steel cups. These cups are 20 mm high and measure 54 mm in diameter. The rim is 2 mm thick, so that the internal diameter available for the sample is 50 mm. The cup has a 5 mm thick bottom, other 5 mm of volume was filled with the powder, so that its upper layer was 10 mm under the cup rim edge, as visible in Figure 1.



Figure 1. The BMW elastomer powder placed in the stainless steel cup before measurement.

After preparation, the cup was placed in the PEL measurement chamber, on top of an aluminum disk 10 mm thick. The aluminum disk was used to decrease and slow down the effect of the induction heating system, which is designed to reach very high temperatures (above 500° C) in a short time. A temperature sensor was embedded in the upper layer of the powder, to record the effective temperature of the emitting skin, as seen in Figure 2.



Figure 2. The cup with BMW elastomer and temperature sensor in the emissivity chamber.

Then the emissivity chamber was sealed and slowly evacuated. After a pressure of less than 1 mbar was reached, the induction was switched on and the sample temperature slowly started to increase. A webcam mounted in the emissivity chamber recorded a movie of the whole experiment, while the temperature read from the temperature sensor was automatically logged every minute. After a waiting and relaxation period of 83 minutes the infrared spectrum of the sample was measured at about 118° C. It was still in powder form, as can be seen from the video. Then the inducted current was increased to reach the second step of

the measurements. In this time interval, the sample started to melt and when equilibrium was reached around 182° C, the sample was in liquid form. A second measurement was taken at this level, and then the induction was switched off. After the sample cooled down, the vacuum pump was switched off, and the emissivity chamber was slowly vented. When the pressure inside the chamber reaches ambient conditions, the emissivity chamber can be opened. Figure 3 shows the cup at the end of the experiment: the BMW elastomer powder melted with heat and then hardened when cooling, to reach a final transparent, hard, compact form.



Figure 3. BMW elastomer in the steel cup after melting and cooling.

The next day, after inspecting and cleaning the chamber and the parabolic mirror that focuses the radiation in the spectrometer entrance port; a reference body was measured at exactly the same 2 temperatures reached for the BMW powder sample. This procedure allows us to calibrate the data without simplification or a-priori assumptions, and get an absolute emissivity spectrum of the measured sample. Figure 4 shows the calibrated emissivity spectra for the measurement of the BMW elastomer powder before (at 120° C) and after melting (at 180° C). The differences between the two curves are not surprising, since the sample changed from solid to liquid state and probably released a lot of volatiles, as can be inferred from the whitish patina seen on the parabolic mirror that is positioned above the sample cup.

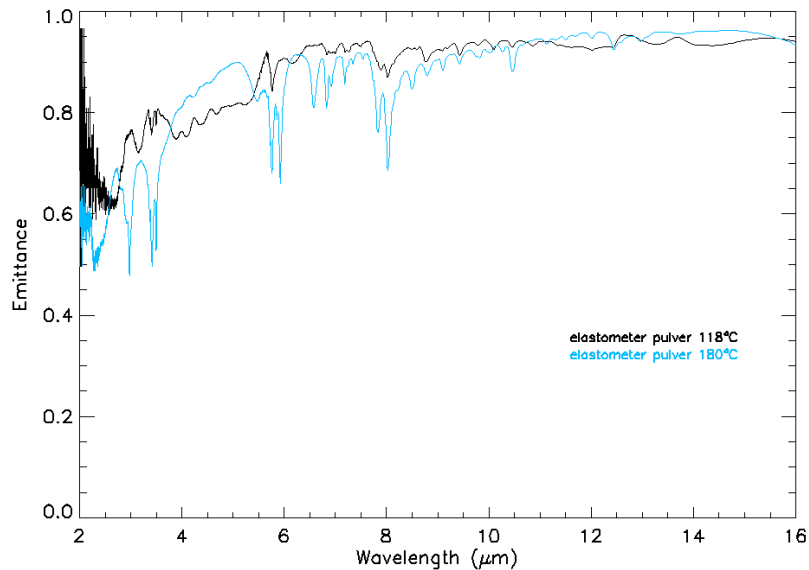


Figure 4. Emissivity (or emittance) spectra of BMW elastomer powder taken at 120° and 180° C.

All the bands between 2 and 16 microns can be attributed to C-H and probably C-O bonds. Most of them increase in depth with the temperature, but there are frequent example for a massive change in the band shape and structure when passing from one phase to the other. It should be noted that the spectra have not been smoothed or post-processed to show directly the signal-to-noise ratio (SNR) of the measurements. The SNR is decreasing in the region below 3 μm because the thermal emitted radiance becomes very weak at the temperatures used in this experiment.

ii. Report on emissivity measurements of BMW Duraflex Form and Elastomer powders in the 2-16 μm spectral range in vacuum, at various temperatures

The measurements have been performed from October 15th to 17th 2012 at the Planetary Emissivity Laboratory of DLR in Berlin. The powders were poured in the PEL standard stainless steel cups, being 20 mm high and 54 mm in diameter, while the internal diameter available for the sample is 50 mm. The cup has a 5 mm thick bottom, other 5 mm of volume was filled with the powders, so that its upper layer was 10 mm under the cup rim edge.

Duraflex Form powder received the internal PEL ID number 00001043, while the Elastomer powder already got the ID 00000772 for the previous round of measurements.

NOTE: RESULTS FOR DF FLEX ARE LEFT OUT AS NOT RELEVANT FOR THE OBSERVATIONS PRESENTED IN THIS THESIS.

A cup containing the BMW Elastomer powder (PEL ID 00000772) was placed in the PEL measurement chamber. Two temperature sensors were embedded in the upper layer of the powder, following the same rational as for the Duraflex Form sample. The measurement conditions and procedures were kept exactly coincident with the ones adopted for the first sample. In Figure 9 the measure for the Elastomer powder at 55° C is shown.

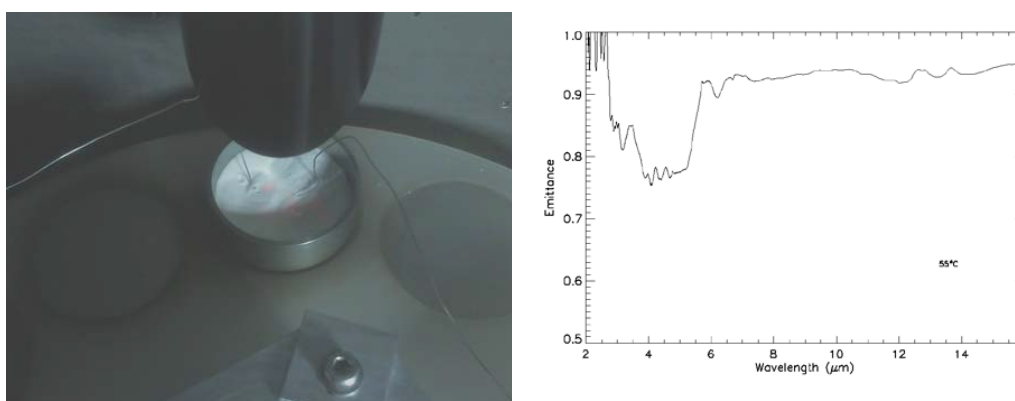


Figure 9. The Elastomer powder at 55° C (a, left), and its calibrated emissivity spectra (b, right)

The sample was then brought to melt at 200° C, as can be seen in Figure 10.



Figure 10. The Elastomer powder boiling at 200° C

Then the temperature was decreased back to 125° C. The sample solidified by cooling, reaching a semi-transparent format, as can be seen in figure 11a (left panel) and 12. The emissivity spectrum is again very different from the one taken when in powder format. This spectra confirm the results obtained with the experiment made in July 2012 and it can be noticed how good Figure 11b in this report agrees with Figure 4 in the report written after the July session.

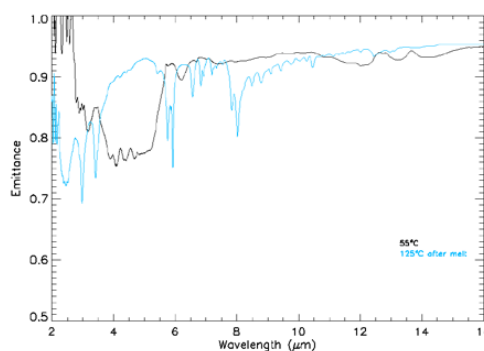


Figure 11. The Elastomer powder back at 125° C after melt (a, left), and its calibrated emissivity spectra (b, right)

Figure 12 shows the Elastomer sample at the end of the measurements session.

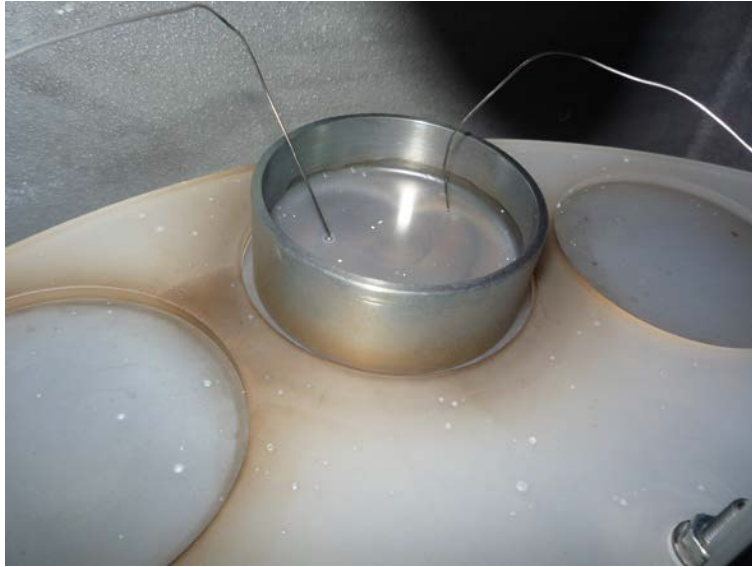


Figure 12. The Elastomer powder at the end of the measurements session.

From a spectral point of view, it can be concluded that all the bands between 2 and 16 microns can be attributed to C-H and probably C-O bonds. Most of them increase in depth with the temperature, but there are frequent example for a massive change in the band shape and structure when passing from one phase to the other. The SNR is decreasing in the region below 3 μm because the thermal emitted radiance becomes very weak at the temperatures used in this experiment. The transparent nature of the examined materials brings to often have emissivities exceeding unity, because in those cases the detector is recording the energy emitted from the very hot cup bottom, traveling through the transparent medium. This values should not be considered as real.

A.4 FSC

A.4.1 FSC endo-thermal heat flows after isothermal crystallization of TPU

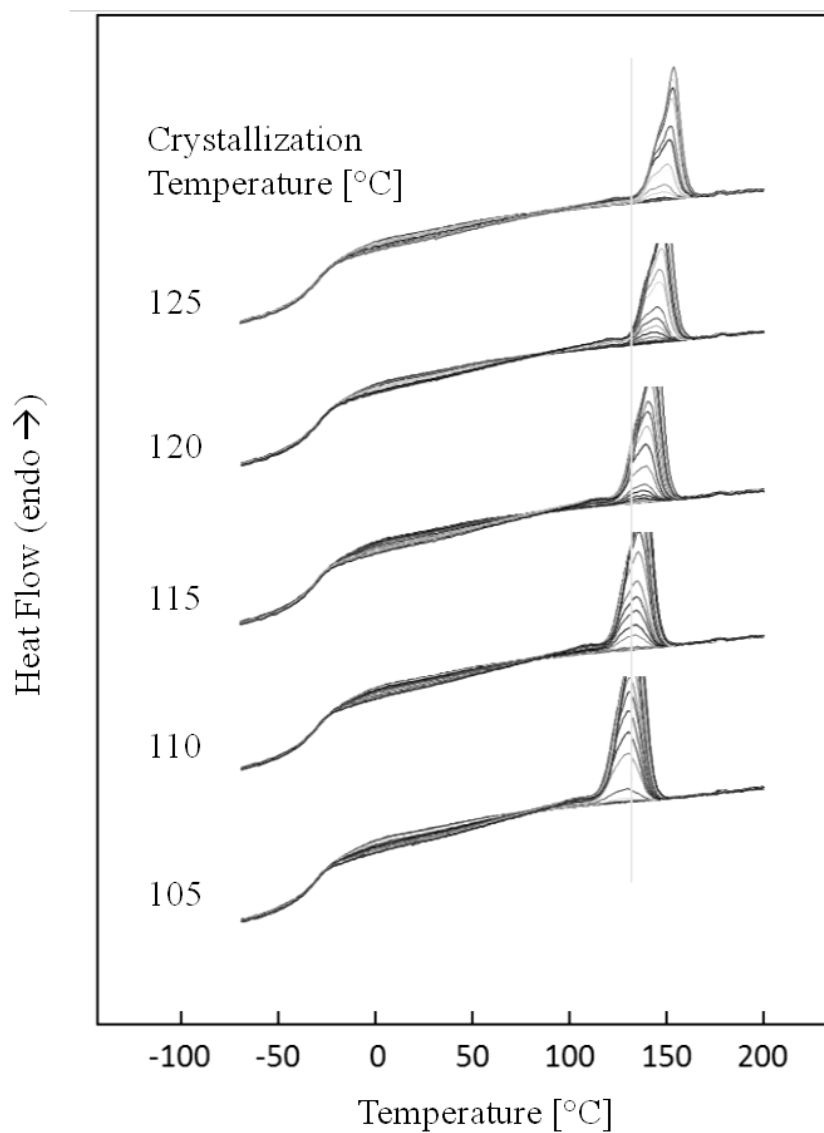


Figure 95: FSC heating runs for TPU after prior corresponding isothermal crystallization
The graphs show the glass transition at around -40°C and with increasing temperature an endo-thermal melting that is approximately 20 – 30 K higher than the crystallisation temperature of the polymer.

A.4.2 Isothermal Crystallization at 110°C and 125°C at Mettler Toledo

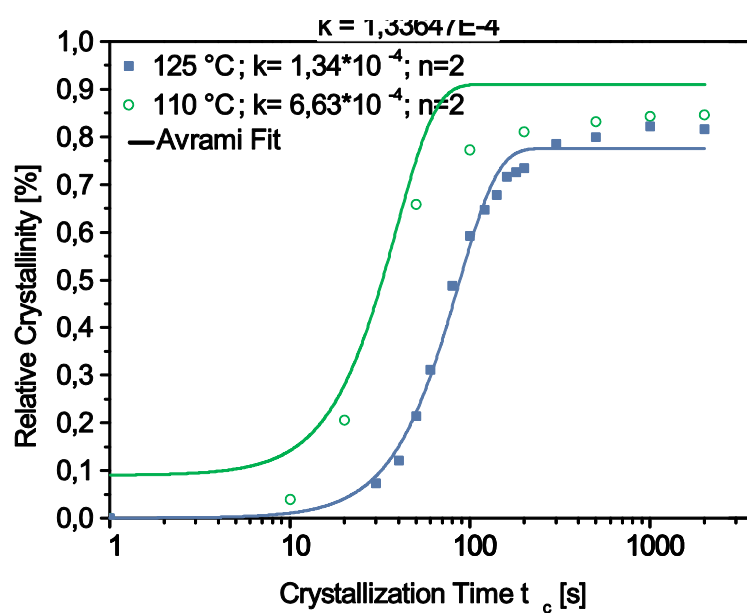


Figure 96: Relative Crystallinity as a function of crystallization time for an isothermal crystallization process at 110°C and 125°C respectively

A.4.3 FSC heating runs for PA12 at different isothermal crystallization times

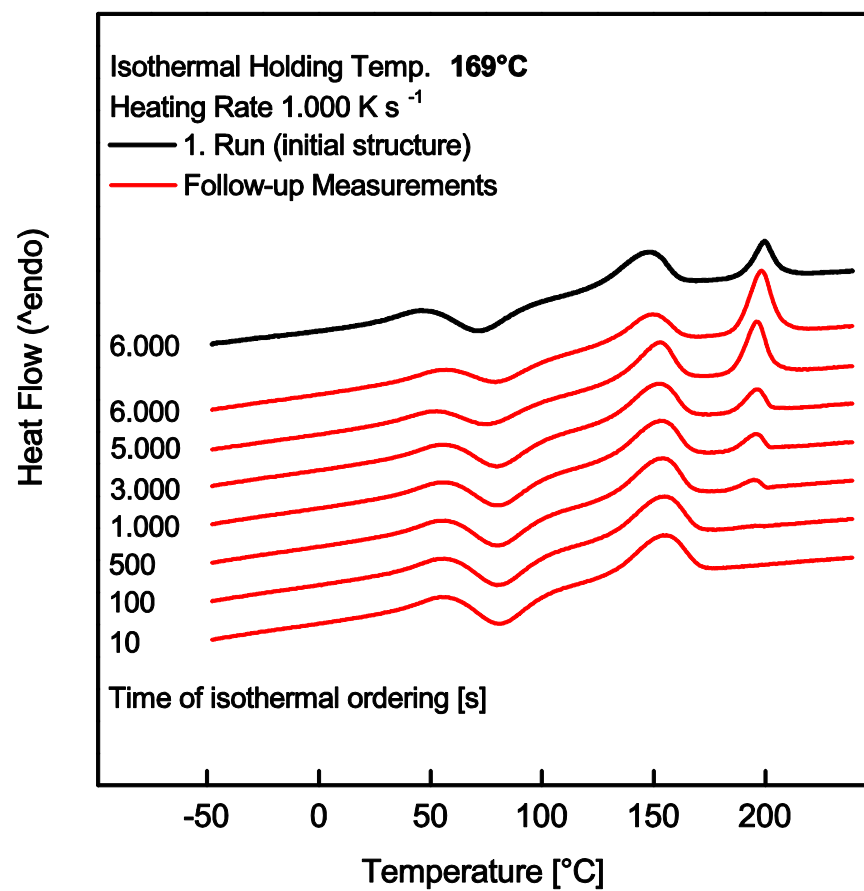


Figure 97: FSC heating runs for PA 12 after prior corresponding isothermal crystallization

A.5 Results the calculated degrees of absorption for the TPE powders in dependence of particle size distribution

Temperature [°C]	$\alpha_{\text{TPU F0}}$ [%]	$\alpha_{\text{TPU F25}}$ [%]	$\alpha_{\text{TPU F45}}$ [%]
25	95.46 $\pm$ 0.23	-	-
55	95.00 $\pm$ 0.04	95.80 $\pm$ 0.01	96.69 $\pm$ 0.08
116	95.25 $\pm$ 0.07	95.99 $\pm$ 0.04	96.84 $\pm$ 0.07
123	95.29 $\pm$ 0.05	95.97 $\pm$ 0.01	96.85 $\pm$ 0.08
160	98.83 $\pm$ 0.22	98.85 $\pm$ 0.01	99.29 $\pm$ 0.28
210	98.50 $\pm$ 1.06	-	-

Table 33: Degrees of Absorption at characteristic Temperatures for TPU Fractions (F0-F45) at a wavelength of 4 μm

Temperature [°C]	$\alpha_{\text{TPU F0}}$ [%]	$\alpha_{\text{TPU F25}}$ [%]	$\alpha_{\text{TPU F45}}$ [%]
25	99.58 $\pm$ 0.03	-	-
55	99.62 $\pm$ 0.02	99.66 $\pm$ 0.04	99.76 $\pm$ 0.05
116	99.62 $\pm$ 0.05	99.66 $\pm$ 0.06	99.77 $\pm$ 0.05
123	99.63 $\pm$ 0.06	99.71 $\pm$ 0.05	99.77 $\pm$ 0.03
160	99.59 $\pm$ 0.12	98.48 $\pm$ 0.08	99.10 $\pm$ 0.33
210	98.44 $\pm$ 0.90	-	-

Table 34: Degrees of Absorption at characteristic Temperatures for TPU Fractions (F0-F45) at a wavelength of 10,6 μm

Temperature [°C]	$A_{DF\ F0}$ [%]	$\alpha_{DF\ F25}$ [%]	$\alpha_{DF\ F45}$ [%]
25	96.12±0.17	-	-
55	95.82±0.10	96.36±0.12	96.90±0.09
158	96.17±0.19	96.50±0.11	97.05±0.09
220	98.22±0.47	98.42±0.34	97.95±0.33

Table 35: Degrees of Absorption at characteristic Temperatures for DF Fractions (F0-F45) at a wavelength of 4 µm

Temperature [°C]	$A_{DF\ F0}$ [%]	$\alpha_{DF\ F25}$ [%]	$\alpha_{DF\ F45}$ [%]
25	99.79±0.02	-	-
55	99.72±0.01	99.79±0.06	99.88±0.03
158	99.80±0.02	99.82±0.05	99.86±0.02
220	98.09±0.53	98.31±0.38	97.92±0.26

Table 36: Degrees of Absorption at characteristic Temperatures for DF Fractions (F0-F45) at a wavelength of 10,6 µm

A.6 Determination of specific heat capacity c_p

Temperature [°C]	c_p -value [$\frac{kJ}{kgK}$] 1. measurement	c_p -value [$\frac{kJ}{kgK}$] 2. measurement	c_p [$\frac{kJ}{kgK}$] mean value
20	1.533	1.614	1.574±0.041
40	1.621	1.707	1.664±0.043
60	1.696	1.763	1.730±0.034
80	1.795	1.850	1.823±0.028
100	1.953	1.984	1.969±0.026
120	2.270	2.210	2.240±0.030

Table 37: Results for specific heat capacity c_p for TPU F0

Temperature [°C]	c _p -value $[\frac{kJ}{kgK}]$ 1. measurement	c _p -value $[\frac{kJ}{kgK}]$ 2. measurement	c _p $[\frac{kJ}{kgK}]$ mean value
20	1.564	1.568	1.566±0.002
40	1.657	1.659	1.658±0.001
60	1.717	1.720	1.719±0.001
80	1.810	1.813	1.812±0.001
100	1.952	1.954	1.953±0.001
120	2.188	2.193	2.191±0.002

Table 38: Results for specific heat capacity c_p for TPU F25

Temperature [°C]	c _p -value $[\frac{kJ}{kgK}]$ 1. measurement	c _p -value $[\frac{kJ}{kgK}]$ 2. measurement	c _p $[\frac{kJ}{kgK}]$ mean value
20	1.703	1.699	1.701±0.002
40	1.794	1.792	1.793±0.001
60	1.853	1.853	1.853±0.000
80	1.948	1.951	1.950±0.002
100	2.091	2.098	2.095±0.003
120	2.327	2.337	2.332±0.005

Table 39: Results for specific heat capacity c_p for TPU F45

Temperature [°C]	c _p -value $[\frac{kJ}{kgK}]$ 1. measurement	c _p -value $[\frac{kJ}{kgK}]$ 2. measurement	c _p $[\frac{kJ}{kgK}]$ mean value
20	1.725	0.879	1.302±0.423
40	1.798	0.957	1.387±0.421
60	1.865	1.016	1.441±0.425
80	1.929	1.084	1.507±0.423
100	1.998	1.160	1.579±0.419
120	1.080	1.247	1.664±0.417
140	2.158	1.352	1.755±0.403
160	2.265	1.532	1.899±0.367

Table 40: Results for specific heat capacity c_p for DF F0

Temperature [°C]	c _p -value $[\frac{kJ}{kgK}]$ 1. measurement	c _p -value $[\frac{kJ}{kgK}]$ 2. measurement	c _p $[\frac{kJ}{kgK}]$ mean value
20	1.307	1.451	1.379±0.072
40	1.387	1.530	1.459±0.072
60	1.445	1.519	1.518±0.073
80	1.507	1.654	1.581±0.074
100	1.577	1.724	1.651±0.074
120	1.659	1.806	1.733±0.074
140	1.737	1.884	1.811±0.073
160	1.837	1.987	1.912±0.075

Table 41: Results for specific heat capacity c_p for DF F25

Temperature [°C]	c _p -value [$\frac{kJ}{kgK}$] 1. measurement	c _p -value [$\frac{kJ}{kgK}$] 2. measurement	c _p [$\frac{kJ}{kgK}$] mean value
20	1.412	1.457	1.435±0.023
40	1.486	1.529	1.508±0.022
60	1.539	1.581	1.560±0.021
80	1.597	1.639	1.618±0.021
100	1.665	1.707	1.686±0.021
120	1.740	1.783	1.762±0.022
140	1.813	1.854	1.834±0.021
160	1.910	1.949	1.930±0.020

Table 42: Results for specific heat capacity c_p for DF F45

A.7 Thermal diffusivity of TPU and DF powder bulks

Temperature [°C]	55.4	120.4
heat capacity [$\frac{kJ}{kgK}$]	1.746	2.216
thermal diffusivity [$\frac{m^2}{s}$]	0.00036	0.00024
bulk density prior to measurement [$\frac{g}{cm^3}$]	0.376	0.367
bulk density after measurement [$\frac{g}{cm^3}$]	0.489	0.489
thermal conductivity [$\frac{W}{mK}$]	0.307	0.256

Table 43: Results for thermal diffusivity of the TPU F0 powder bulk

Temperature [$^{\circ}\text{C}$]	55.4	120.4
heat capacity [$\frac{\text{kJ}}{\text{kgK}}$]	1.699	2.195
thermal diffusivity [$\frac{\text{m}^2}{\text{s}}$]	0.00034	0.00022
bulk density prior to measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.408	0.408
bulk density after measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.578	0.578
thermal conductivity [$\frac{\text{W}}{\text{mK}}$]	0.333	0.282

Table 44: Results for thermal diffusivity of the TPU F25 powder bulk

Temperature [$^{\circ}\text{C}$]	55.4	120.4
heat capacity [$\frac{\text{kJ}}{\text{kgK}}$]	1.834	2.345
thermal diffusivity [$\frac{\text{m}^2}{\text{s}}$]	0.00033	0.00022
bulk density prior to measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.435	0.435
bulk density after measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.615	0.5615
thermal conductivity [$\frac{\text{W}}{\text{mK}}$]	0.380	0.317

Table 45: Results for thermal diffusivity of the TPU F45 powder bulk

Temperature [$^{\circ}\text{C}$]	55.4	120.4
heat capacity [$\frac{\text{kJ}}{\text{kgK}}$]	1.848	2.268
thermal diffusivity [$\frac{\text{m}^2}{\text{s}}$]	0.00038	0.00021
bulk density prior to measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.365	0.365
bulk density after measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.446	0.4465
thermal conductivity [$\frac{\text{W}}{\text{mK}}$]	0.310	0.215

Table 46: Results for thermal diffusivity of the DF F0 powder bulk

Temperature [$^{\circ}\text{C}$]	55.4	120.4
heat capacity [$\frac{\text{kJ}}{\text{kgK}}$]	1.576	1.990
thermal diffusivity [$\frac{\text{m}^2}{\text{s}}$]	0.00040	0.00023
bulk density prior to measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.336	0.392
bulk density after measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.448	0.4815
thermal conductivity [$\frac{\text{W}}{\text{mK}}$]	0.286	0.202

Table 47: Results for thermal diffusivity of the DF F25 powder bulk

Temperature [$^{\circ}\text{C}$]	55.4	120.4
heat capacity [$\frac{\text{kJ}}{\text{kgK}}$]	1.568	1.951
thermal diffusivity [$\frac{\text{m}^2}{\text{s}}$]	0.00039	0.00022
bulk density prior to measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.392	0.356
bulk density after measurement [$\frac{\text{g}}{\text{cm}^3}$]	0.481	0.446
thermal conductivity [$\frac{\text{W}}{\text{mK}}$]	0.295	0.206

Table 48: Results for thermal diffusivity of the DF F45 powder bulk

A.8 In-Process

A.8.1 Build Job of DOE

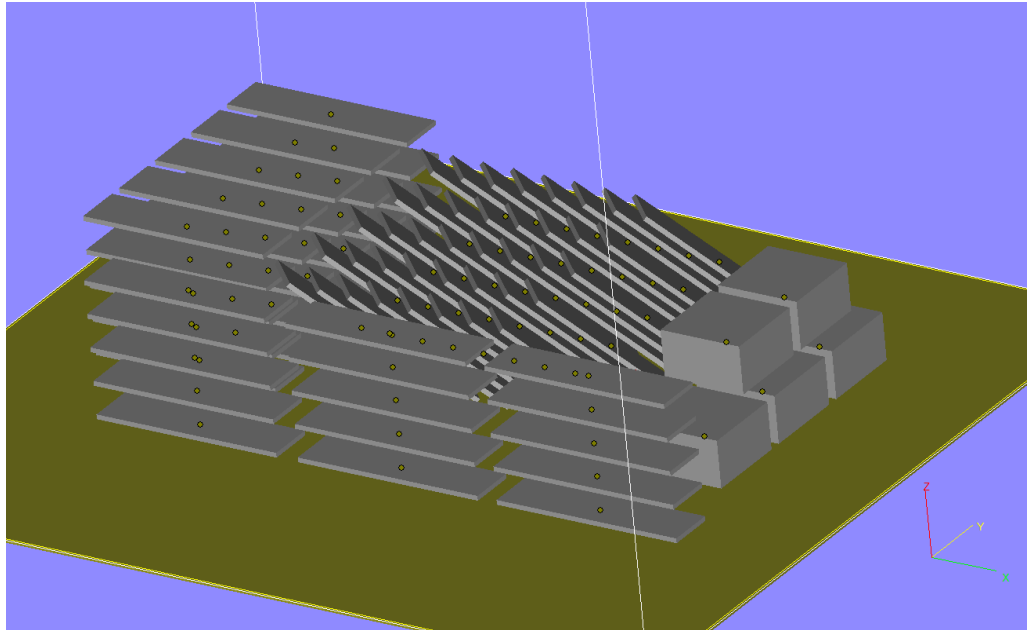


Figure 98: Build Job for DOE varying build temperature

A.8.2 Input variables for EMR calculation

Temperature [°C]	$c_p \left[\frac{J}{kgK} \right]$	$T_m [K]$	$h_f \left[\frac{J}{kg} \right]$	solid density $\rho_m \left[\frac{g}{cm^3} \right]$	packing density powder bed $\rho_p \left[\frac{g}{cm^3} \right]$
Desmosint	1850*	152***	3000*	1.2**	0.5
TPU SLS 4	2200***	155***	7500*	1.136**	0.5
DF Flex	1900***	193***	30000*	1.1**	0.5

Figure 99: Values for calculation of the Energy melt Ratio

*Netsch Database
 ** Manufacturer's data
 *** own measurements

A.8.3 Parameter Combinations for the DOE and results for UTS

Build temp. [°C]	Vol. energy density [J/mm ³]	EMR	UTS [N/mm ²]	Standard deviation [N/mm ²]
90	0.15	1.97	0.27	0.039
90	0.21	2.68	1	0.095
90	0.28	3.76	1.94	0.179
90	0.34	4.65	2.92	0.268
90	0.41	5.55	4.18	0.309
105	0.15	2.54	0.97	0.208
105	0.21	3.69	2.66	0.587
105	0.28	4.85	4.81	0.782
105	0.34	6	7.22	0.866
105	0.41	7.16	9.77	0.783
120	0.15	3.58	4.76	0.765
120	0.21	5.21	9.26	1.715
120	0.28	6.83	13.52	1.812
120	0.34	8.46	17.55	1.766
120	0.41	10.09	21.01	0.609

Table 49: UTS in dependence of given parameter combination for Desmosint in XYZ-direction

Build temp. [°C]	Vol. energy density [J/mm ³]	EMR	UTS [N/mm ²]	Standard deviation [N/mm ²]
115	0.082	1.62	0.6	0.155
115	0.14	2.72	2.5	0.383
115	0.19	3.82	4.68	0.530
115	0.25	4.92	7.32	0.500
115	0.3	6.02	9.66	0.688
120	0.082	1.85	1.2	0.344
120	0.14	3.11	4.02	0.697
120	0.19	4.36	7.04	0.795
120	0.25	5.62	9.89	0.436
120	0.3	6.88	11.97	0.600
125	0.082	2.16	2.53	0.483
125	0.14	3.62	6.04	0.917
125	0.19	5.08	9.51	1.126
125	0.25	6.54	11.31	0.661
125	0.3	8.01	12.31	0.534

Table 50: UTS in dependence of given parameter combination for TPU SLS 4 in XYZ-direction

Build temp. [°C]	Vol. energy density [J/mm ³]	EMR	UTS [N/mm ²]	Standard deviation [N/mm ²]
130	0.082	1	not testable	-
130	0.14	1.67	0.26	0.029
130	0.19	2.53	0.7	0.085
130	0.25	3.02	1.29	0.112
130	0.3	3.7	1.65	0.132
145	0.082	1.23	0.15	0.024
145	0.14	2.06	0.86	0.079
145	0.19	2.9	1.63	0.136
145	0.25	3.73	2.55	0.176
145	0.3	4.56	3.33	0.233
160	0.082	1.62	0.9	0.145
160	0.14	2.7	2.35	0.342
160	0.19	3.79	3.58	0.428
160	0.25	4.88	4.37	0.572
160	0.3	5.97	5.68	0.503

Table 51: UTS in dependence of given parameter combination for DF in XYZ-direction

A.8.4 Parameter Combinations for the validation of the influence of scan spacing on UTS at constant EMR

Desmosint		
hatch space [mm]	UTS [N/mm ²]	standard deviation [N/mm ²]
0.1	4.47	0.2
0.15	4.03	0.22
0.2	3.45	0.15
$\Delta_{\max}$ UTS [N/mm ²]		1.29
mean value Δ UTS [N/mm ²]		0.19
Δ UTS [%]		27

TPU SLS 4		
hatch space [mm]	UTS [N/mm ²]	standard deviation [N/mm ²]
0.1	9.76	0.34
0.15	8.8	0.48
0.2	7.84	0.4
$\Delta_{\max}$ UTS [N/mm ²]		1.92
mean value Δ UTS [N/mm ²]		0.41
Δ UTS [%]		20

DF		
hatch space [mm]	UTS [N/mm ²]	standard deviation [N/mm ²]
0.1	2.37	0.09
0.15	2.23	0.09
0.2	1.97	0.15
$\Delta_{\max}$ UTS [N/mm ²]		0.4
mean value Δ UTS [N/mm ²]		0.11
Δ UTS [%]		17

A.8.5 Parameter Combinations for the validation of the influence of EMR on Shore Hardness

EMR	Hardness Shore-A	Standard deviation	
1.97	41.5	1.42	
2.86	60.26	0.33	
3.76	67.3	0.89	
4.56	73.2	1.02	
5.55	77.56	1.19	
2.54	60.34	0.64	
3.69	74.2	0.73	
4.85	80.5	1.12	
6	82.98	0.68	
7.16	86.1	0.54	
3.58	75.58	0.7	
5.21	85.04	0.53	
6.83	86.28	1.11	
8.46	88.1	0.81	
10.9	87.86	1.03	
$\Delta_{\max}$ Shore-A	46.6	Mean value of standard deviation	0.848

Table 52: Hardness of Desmosint in dependence of varying EMR

EMR	Hardness Shore-A	Standard deviation	
1.62	56.26	0.69	
2.72	72.4	0.99	
3.82	76.76	1.23	
4.92	85.5	0.92	
6.02	88.84	1.23	
1.85	64.2	0.8	
3.11	78.98	1.04	
4.36	83.6	1.22	
5.62	85.58	1.43	
6.88	89.88	0.7	
2.16	72.56	0.6	
3.62	86.06	0.78	
5.08	87.92	0.89	
6.54	88.88	0.84	
8.01	87.98	1.81	
$\Delta_{\max}$ Shore-A	33.62	Mean value of standard deviation	0.252

Table 53: Hardness of TPU SLS 4 in dependence of varying EMR

EMR	Hardness Shore-A	Standard deviation	
1	6.84	0.84	
1.67	29.84	0.59	
2.53	40.12	0.58	
3.02	47.48	1.06	
3.7	53.69	1.61	
1.23	24.42	0.64	
2.06	46.42	0.28	
2.9	53.92	0.91	
3.73	62.08	1.56	
4.56	68.2	0.39	
1.61	44.96	1.16	
2.7	61.88	0.94	
3.79	75.04	1.11	
4.88	76.4	1.04	
5.97	78.52	0.98	
$\Delta_{\max}$ Shore-A	48.68 (71.68 at EMR=1 without evaluable tensile properties)	Mean value of standard deviation	0.98

Table 54: Hardness of DF in dependence of varying EMR

A.9 DSC Comparison of TPES

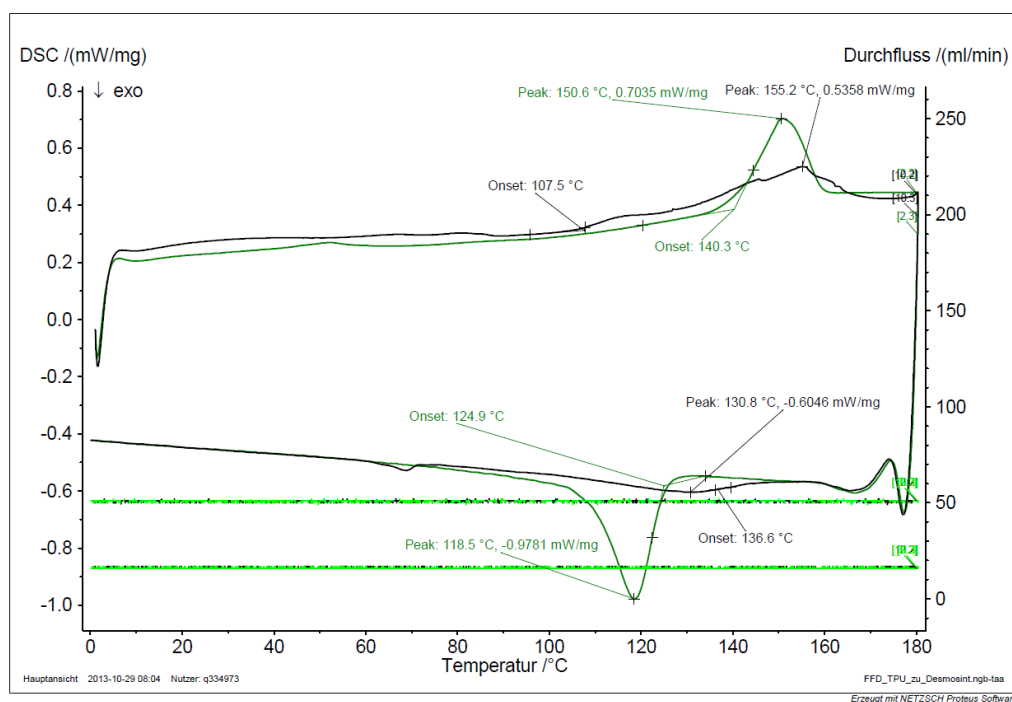


Figure 100: DSC runs for Desmosint (black curve) compared to TPU SLS 4 (green curve) at 10 K/s

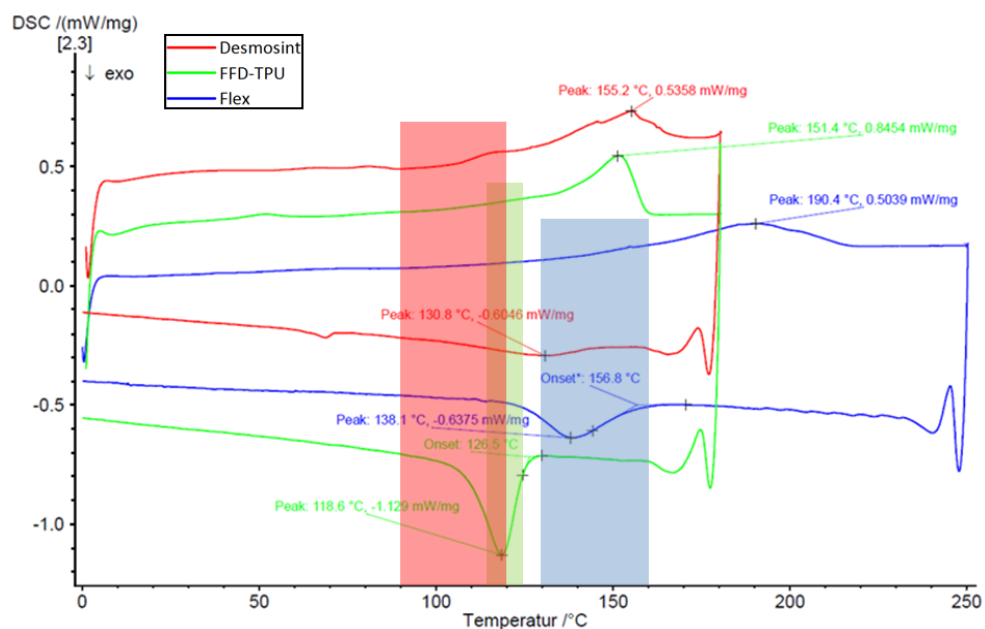


Figure 101: DSC runs for Desmosint, TPU SLS 4 and DF at 10 K/s