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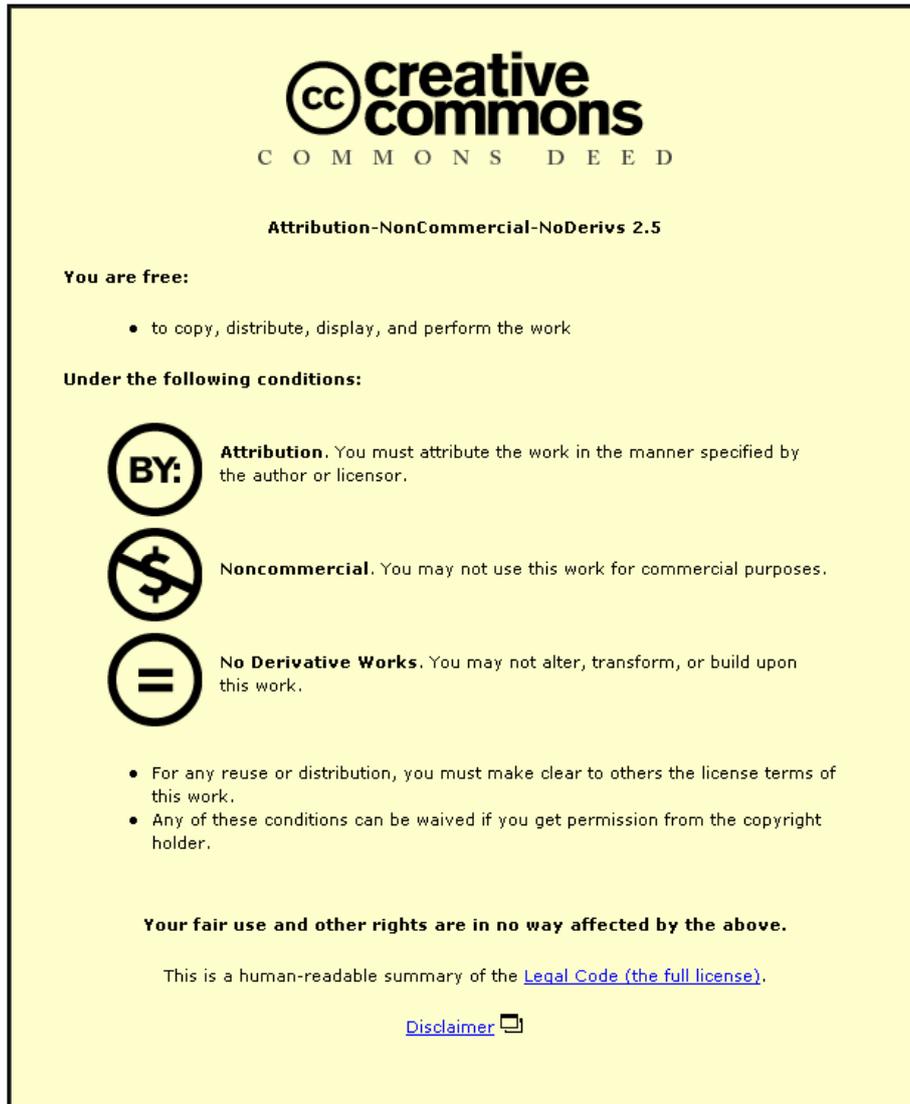
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Effects of processing on microstructure & properties of SLS Nylon 12

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Abstract

There currently exists the requirement to improve reproducibility and mechanical properties of SLS Nylon parts for ~~RR~~Rapid ~~MM~~Manufacturing (RM). In order to achieve this, further fundamental research is needed and this paper addresses this need by investigating effects of potential sources of the lack of reproducibility (i.e. build procedure/parameters and powder blend) and reports effects in relation to crystal structure, microstructure, chemical structure (molecular weight) and mechanical properties.

Different ~~and~~ γ^p crystal forms were identified and related to the un-molten particle cores and the molten/crystallised regions of the microstructure. ~~The melt point of the γ^p form varied depending on processing conditions but the γ^* remained principally constant.~~ Observable differences were also present when comparing the microstructure of the parts. ~~Molecular weight of parts was significantly higher than virgin powder but used powder (powder already held at elevated temperature) also showed an increase in molecular weight.~~ This was related to improved elongation at break of parts built from the used powder, consistent with previous studies. ~~Tensile strength showed some increase with parameters selected for improved strength but Young's modulus values were broadly similar.~~

Keywords: Rapid Manufacturing, Selective Laser Sintering, crystal structure, microstructure, molecular weight

1 Introduction

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

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

Selective Laser Sintering produces parts by using a laser to selectively sinter individual layers of a material in a powder form (polymers, metals, ceramics). ~~SLS systems are currently available commercially from two different manufacturers which are 3D Systems of the United States (previously DTM) and EOS of Germany. Prior to build a CAD model must be created and then processed which includes 'slicing' the CAD model into 0.1-0.15 mm thick 2D layers. After this the data is sent to the machine for part building which is described in Table 1. Following build the part is removed from the un-sintered powder and loose particles brushed and/or sprayed off gently using compressed air.~~

Main Part build steps	
1.	Thin layer of powder deposited across part bed.
2.	Laser 'draws' cross-section matching corresponding layer in STL file, bonding particles and adjacent layers
3.	Platform in part-build cylinder moves part downwards a layer.
4.	Steps 1-3 repeated until build completed
5.	Cooling down of powder cake

Table 1 Part Build steps

Semi-crystalline polymers (predominantly Nylon 12 and 11) can be successfully sintered with superior mechanical properties than amorphous polymers [8][9]. However, shrinkage during

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

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

Nylon 12, as with other aliphatic Nylons, has been widely shown to form stable crystal structures of either the α or γ form [14][15]. -For Nylon 12 the γ -form always melts at a higher temperature than the α form [16].- It has been demonstrated that under the majority of processing condition the liquid phase will crystallise to the stable γ form, which is therefore the most commonly found crystal form in Nylon 12. -However, certain conditions (i.e. casting from solution) do result in the α form and it has been demonstrated that the proportions of α and γ form can be altered (from 0-100% for each) by controlling the thermal history [16][17]. -Different variations of the basic α and γ crystal forms have been created depending on processing conditions and these can be transformed from one to another by numerous methods depending from which and to which crystal form the material will be transformed [18][19][20][21].

Studies reporting melting points for the γ form were reviewed by Aharoni and values ranged from 172 °C to 185 °C with most data points close to 179 °C [15]. -The melt point of the less common α form has been reported as ca. 173 °C [16]. -SLS Nylon is obtained by dissolving polyamide-12 in ethanol under pressure at elevated temperatures followed by slow crystallization thereby forming ~~a~~ crystals form with a relative high melting point of ca. 190°C and a relative high heat of melting [9][11]. The crystal structure of SLS Nylon powder or parts has not been reported on however the slow cooling rate during production would likely result in the ~~v~~ Virgin powder being comprised of relatively large crystals while the high melt temperatures measured ~~relate most likely indicate to~~ the γ -form. Published information relating to alternative methods for manufacture of SLS powder describes how standard Nylon 12 can be modified to increase the melt temperature with insignificant increase to the crystallisation temperature [22]. The process described involves heating powder or granules of the material in steam for extended time duration (up to 100 hours). It is claimed that this increases the melt temperature by allowing the molecular chains to be rearranged. It is known that 'E'even numbered' nylons such as Nylon 12 can only achieve full inter-molecular hydrogen bonding and thus crystallisation by the molecular chains aligning in an anti-parallel arrangement [14] and it is thought that this is how the chains are 'rearranged'.

Young's modulus and Tensile Strength of Selective Laser Sintered Nylon 12 is comparable with values for standard injection moulded samples [23].- However ~~Elongation at BbreakEaB~~ (which indicates ductility) is at least an order of magnitude lower. -Gornet et al [13] demonstrated how mechanical properties can vary between different machines and even for the same machine in different builds. Saleh et al [24] and Gibson & Dongping [25] showed considerable variability for different part orientation and parts built in different locations in the build volume within the same build. -Tontowi and Childs [26] investigated the effect of powder bed temperature (ambient build powder surface temperature) on density and showed that small variations in temperature have a marked effect on part density which can effect mechanical properties.

The SLS machine manufacturers supply powder and their key published mechanical (and other) properties, for their respective SLS Nylon 12 powders, are summarised in Table 2.- Since the machine parameters used to generate the data are not given by both manufacturers and because the data is generated using different standards, this cannot be compared directly. -It should therefore only be used

to roughly gauge the potential of SLS Nylon 12. Where manufactures quoted a range of values, the average has been given.

	3D Systems	EOS
Tensile Strength (MPa)	44	45
Tensile Modulus (MPa)	1600	1700
Tensile Elongation at Break (%)	9	20
Part Melting point (°C)	184	184
Particle size, average (µm)	58	58
Particle size, range 90% (µm)	25-92	(not available)
Part Moisture absorbtion, 23 °C (%)	0.41	0.52

Table 2 Manufacturers published materials properties for SLS Nylon 12 [27][28]

From the application of SLS as a production process, the requirement to improve reproducibility and mechanical properties of SLS Nylon parts for RM exists. In order to achieve this, further fundamental knowledge of the under laying mechanisms is needed. This paper addresses this need by investigating effects of build procedure, - parameters and powder blend and reports effects in relation to chemical structure (molecular weight), crystal structure, microstructure, and mechanical properties.

2 Methodology

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

Source	Specifics	Specimens	
		Powder	Parts from:
TNO	EOS PA2200 (EOS) powder, (EOS_P380 machine; (tuned for mechanical properties))	Virgin	Virgin
		Used	Used
		Refreshed	Refreshed
Lboro	3D Systems Duraform PA (3D Systems) powder, (3D Systems Vanguard machine; (tuned for accuracy))	Virgin	Virgin
		Used	Used
		Refreshed	Refreshed

Table 3. -Specimen history

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

2.1 Preparation of powder

Powder was prepared in different ways prior to building, as follows:

1. Virgin: Powder that has never been processed in a laser sintering machine
2. Used: Part cake and overflow powder that has been through a 24 hour complete SLS processrun.
3. Refreshed: A mix of 67% used and 33% virgin powder.

Powder was prepared in different ways prior to building, as follows:

1. Virgin: Powder that has never been processed in a laser sintering machine
2. Used: part cake and overflow powder that has been through a 24 hour SLS process,
3. Refreshed: A mix of 67% used and 33% virgin powder.

2.2 Part production

Standard tensile test specimens (as shown in Figure 1) were produced according to ISO 527-1. The parameters of the TNO machine were set for optimized mechanical properties while those for the Lboro machine were chosen for optimized accuracy which was anticipated to give reduced mechanical properties. The powder bed temperature of the Lboro machine was ~~adapted to~~ adjusted for each type of powder while the powder bed temperature of the TNO machine was kept constant for all powder types. Differences between the two different machines and their particular build setups are listed in Table 4. In order to ensure thermally stable conditions a base layer of two centimeters and a top layer of one centimeter were used for each run. Parts were built flat, laid parallel to the machine x-axis, at fixed places in the middle of the build area as shown in Figure 1.

	TNO	Lboro
Parameter optimisation	Mechanical properties	Accuracy
Machine	EOS P380	3D Systems Vanguard
Material	PA2200 Nylon 12	Duraform PA Nylon 12
Layer thickness	0.15 mm	0.1 mm
Powder deposition mechanism	Hopper	Roller
Feed powder	'Cold' (~50 °C)	Heated (+100 °C)
Build platform	Heated	Unheated
Laser power (fill)	45.7 W (90% 50 W)	11 W
Laser power (outline)	10.9 W (20% 50 W)	5 W
Scan speed	4000 mm/s	5000 mm/s
Scan spacing	0.3 mm	0.15 mm

Table 4. Machine differences

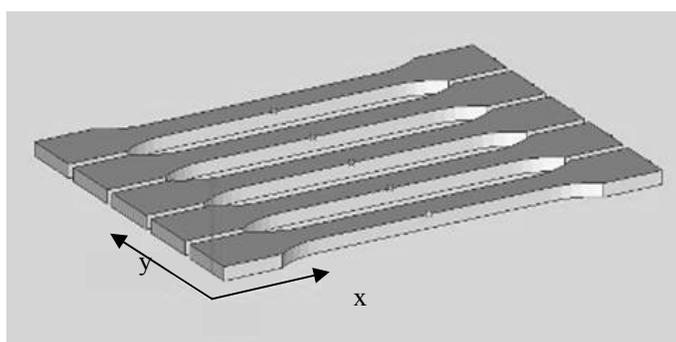


Figure 1. Build setup

2.3 Molecular weight

The molecular weight was determined by GPC by drying 25 mg samples at 120 °C for 1 hr. The samples were then dissolved at room temperature in 5 ml chloroform (stabilized with ambilene) and 0.5 ml tri fluor acetic acid anhydride (TFA). After two hours dissolving the solution was diluted with 20 ml chloroform. This solution was filtered without heating and analysed using two Waters™ Styragel® HT6E, 7.8x300 mm columns in combination with a differential refractive index detector (Waters™ 410) and a tuneable absorbance detector (Waters™ 486) at wavelength 264 nm. Polystyrene was used as the reference material.

2.4 Thermal properties

Differential Scanning Calorimetry (DSC) was used to determine thermal properties which enables in order to study melting and crystallization behaviour and to identification of crystal forms. Samples of mass ca. 10 mg were analysed in a 'Thermal Analysis' DSC machine under nitrogen flow. Samples were heated from room temperature at 10 °C/min to 2020 °C and held for [2 minutes] and then immediately cooled at 10 °C/min.

2.5 Microstructure

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

2.6 Mechanical properties

Tensile data was recorded using ~~an 80mm gauge length a~~ clip-on extensometer. Each tensile test was executed with five individual specimens and results for tensile elongation at break, ultimate tensile strength and Young's modulus were recorded.

3 Results & Discussion

3.1 Powder

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

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

The thermal conditions in the production of SLS Nylon 12 powder differ greatly from those required to form α -form crystal structure and this implies that the endotherms obtained from the virgin powder ~~either relate to a modification of the common γ form, or a new crystal structure. Published information relating to alternative methods for manufacture of SLS powder describes how standard Nylon 12 can be modified to increase the melt temperature with insignificant increase to the crystallisation temperature [29]. The process described involves heating powder or granules of the material in steam for extended time duration (up to 100 hours). It is claimed that this increases the melt temperature by allowing the molecular chains to be rearranged. Even numbered nylons such as Nylon 12 can only achieve full inter molecular hydrogen bonding and thus crystallisation by the molecular chains aligning in an anti parallel arrangement [14].~~ On the basis that prolonged molecular mobility increases the melt temperature it can therefore be inferred that the endotherms do relate to a ~~modification of the γ form with far larger and more perfect crystal structure (due to increased hydrogen bonding) than previously analysed Nylon 12 specimens. The crystal structure of the virgin SLS powder will be labelled as γ^*~~

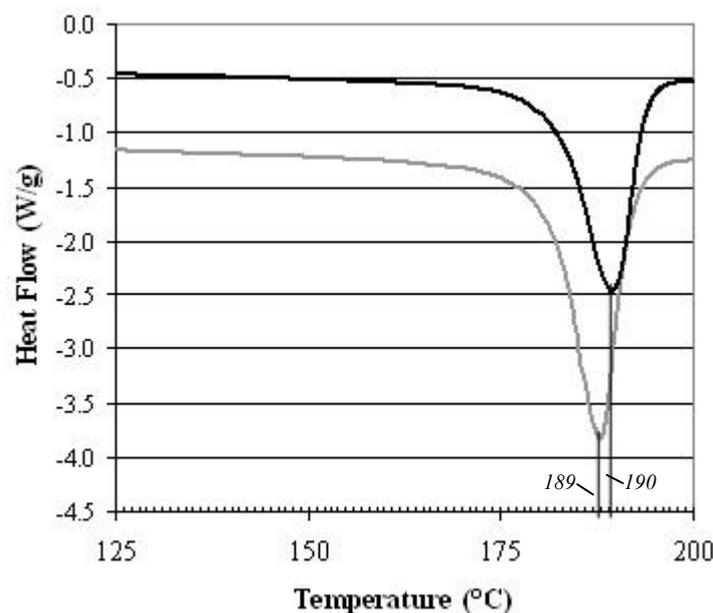


Figure 2 DSC results for Lboro and TNO virgin powder

Figure 3 shows GPC results for Lboro and TNO virgin powder. – The relative weight average molecular weight is ea. 90,000 g/m ?? for Lboro virgin powder and ea. 7090,000 g/m ?? for TNO virgin powder. The small peaks on the positive tail of each curve are possibly characteristic of anti-oxidants, which are known to be blended with the virgin nylon-12 powder from EOS [28]

[27] and therefore presumed to be the same with 3D Systems supplied powder. The higher molecular weight of the Lboro powder could indeed theoretically hinder processing and thus properties [30] however the difference is toorelatively small to be significant. (EOS powder)

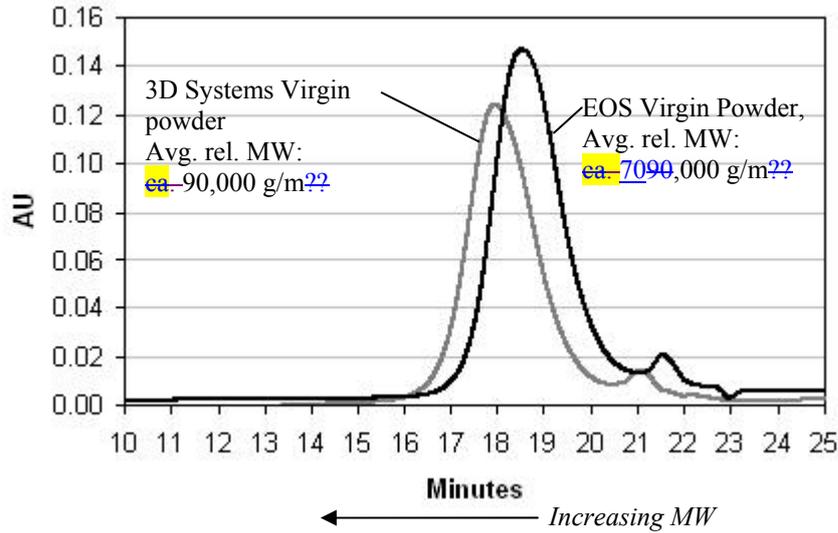


Figure 3 GPC results for Lboro and TNO Virgin powder

3.1.2 Sub-melt temperature heated powder: Comparison of Refreshed and Virgin powder by thermal analysis and molecular weight analysis

Figure 4 shows DSC results for virgin and refreshed TNO powder. –The refreshed powder shows a very slight increase in melt temperature ($< 1\text{ }^{\circ}\text{C}$) indicating only a slight change in the crystallinity structure, to which will be reverred to as γ^2 . The endotherm for the refreshed powder shows a slight ‘bulge’ to its left indicative of a polymorph likely due to the 1/3 virgin fraction of the blend.

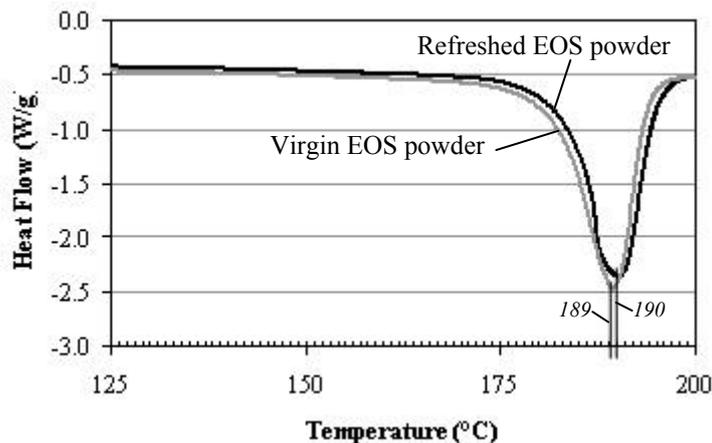


Figure 4 DSC results for virgin and refreshed TNO powder.

Figure 5 shows GPC results for virgin and used TNO powder. The relative weight average molecular weight is ea. 1720,000 g/m ?? for used TNO powder and ea. 790,000 g/m ?? for virgin TNO powder. This small increase in molecular weight indicates that polymerization occurs in the solid state powder. This may be one of the mechanisms leading to modified sintering characteristics with the reuse of SLS powder.

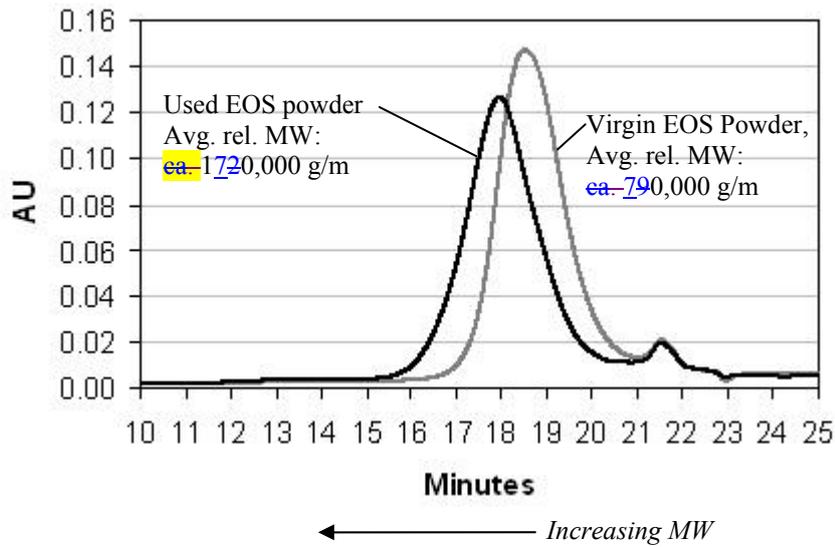


Figure 5. GPC results for virgin and used TNO powder

3.2 Parts

3.2.1 Optical analysis of part microstructure

Figure 6 shows a micrograph of the cross section of a Lboro part with annotations on the right hand side. The top of the image shows the edge of the part to which unmolten particles have fused. Moeskops et al have demonstrated how the part microstructure is composed of particle cores surrounded by spherulites [30]. These cores were described as the unmolten central regions of particles occurring when particles do not receive enough heat to fully melt. Figure 6 also shows spherulites without cores which formed from particles which were small enough to fully melt. Amorphous regions where no spherulitic structure is present are also visible. Moeskops et al [31] stated that the presence of these cores is believed to be critical to the properties and mechanical response of SLS processed materials.

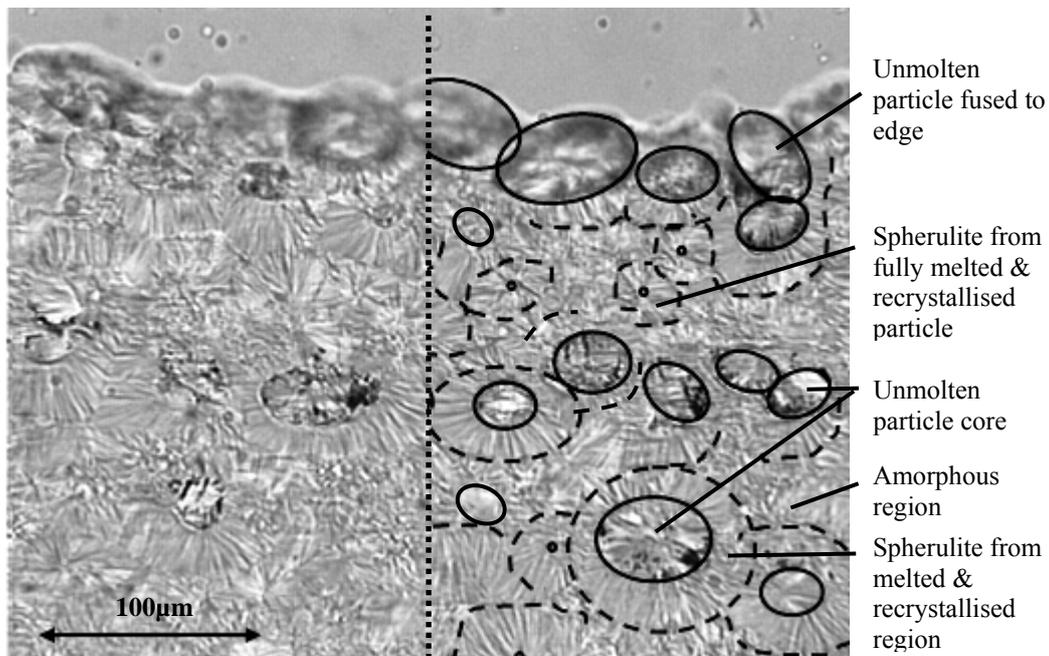


Figure 6 Microstructure of Lboro part

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

Figure 7 shows three superimposed sets of DSC results for TNO material. -The results are for virgin powder, a part built from the virgin powder and a part built from virgin powder which was exposed twice (a 2nd-second exposure of the same area prior to recoating deposition of the next layer) - (please explain recoating!!) and therefore increased energy input. -The curve for virgin powder is the same as in Figure 4 and shows one melt peak at 190.89°C. - The curve for the normal part shows two peaks, smaller than the single peak for virgin powder. The larger of these two is at 185°C and the smaller at 190°C. - The curve for the double exposed part only shows one peak which is at 185°C.

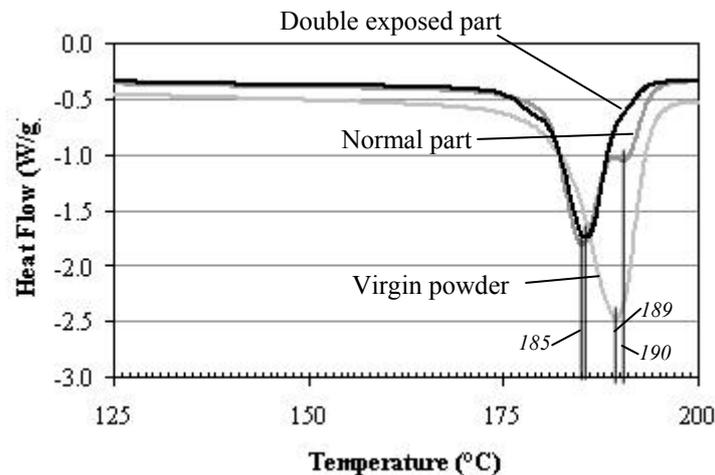


Figure 7 DSC results for TNO Virgin powder, part and double exposed part.

The interpretation of Figure 7 is that for parts the peaks at 185 °C relate to a γ new-crystal form, arising from the melting and recrystallisation of virgin meltin at 190 °C powder powder and this is a variation of the basic γ form. This crystal form, created by laser processing, is termed γ^p . -The small peak at 190 °C for the parts represents a reduced total fraction of the initial γ^i -form of the virgin material and demonstrates a similar shift as used powder of 190 to 189 °C, similar to that shown in Figure 4 (comparing virgin and used powder). Determining the area of melt peaks shows that the percentage crystallinity of both parts is much lower than that of the virgin powder meaning that the relatively high crystallinity is characteristic of the powder manufacturing process.

Figure 8 shows a DSC curve for a Lboro part built from virgin powder and an optical image of one particle core with surrounding spherulite. - This supports the idea that the DSC peak at 190 °C for the γ^i -form directly represents the unmolten particle core (which is therefore used powder material) and that the surrounding spherulitic region relates to the material which has been melted and then recrystallised. (γ^p -form).

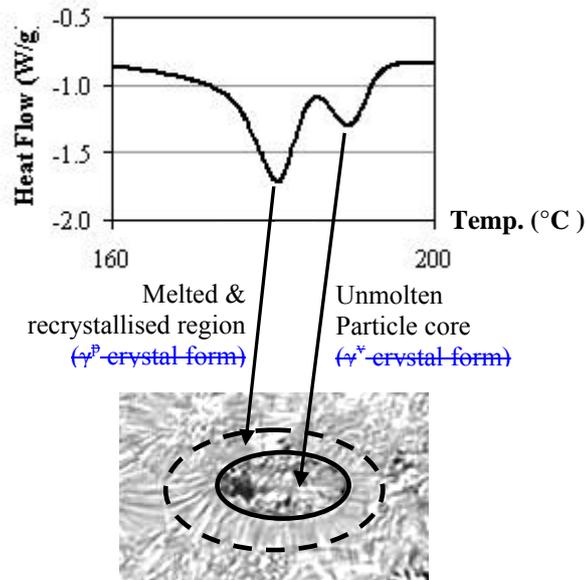


Figure 8 Identification of crystal forms

Figure 9 shows GPC results for TNO virgin powder and a part built from TNO used virgin powder. A distinct increase of relative molecular weight due to polymerization is observed as quantified by an increase from 790,000 g/m to nearly 230,000 g/m weight average molecular weight. -This increase in molecular weight with sintering might be desirable since higher molecular weight generally results in improved mechanical properties.

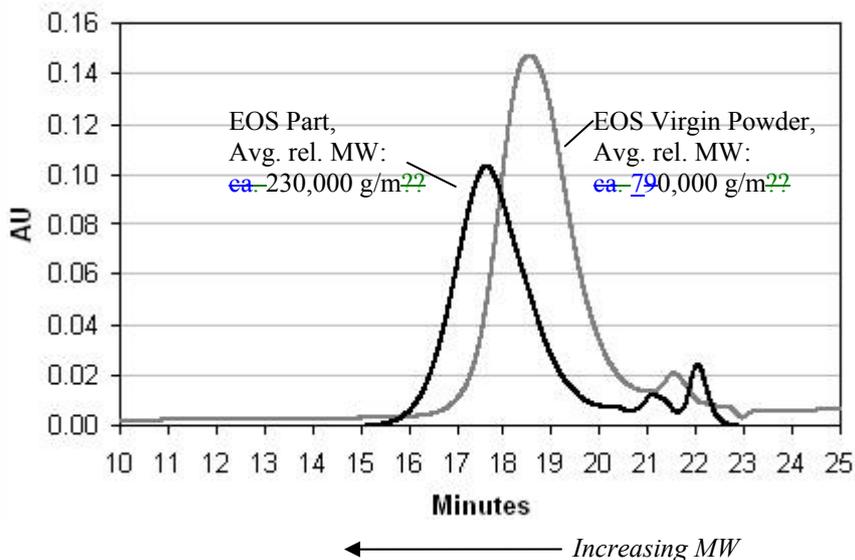


Figure 9 GPC results for TNO part and virgin powder

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

Figure 10 shows DSC results for TNO and Lboro parts built from virgin powder. -The curve for the TNO part is the same curve for the 'Normal part' in Figure 7 showing 2 peaks, one at 185 (γ^P crystal form) and a smaller peak at 190°C (γ^* crystal form). - The curve for the Lboro part also shows 2 peaks, with the γ^* crystal form peak at 189 and the γ^P crystal form peak at 180°C. Both γ^* crystal form peaks are ca. 1°C higher than their respective peaks for virgin materials as shown in Figure 2 demonstrating that the unmolten fraction in the part modifies in a similar manner to how the unmelted virgin powder

~~modifies to its 'used' state to unsintered powder.~~ The difference between the γ^p crystal form peaks indicates significant difference ~~inbetween the~~ crystal ~~size~~structure of the material melted and recrystallised for the Lboro and TNO setups. -This difference could arise from the different parameters chosen for this study (such as heated/unheated build platform) and/or inherent differences between the machine set-up.

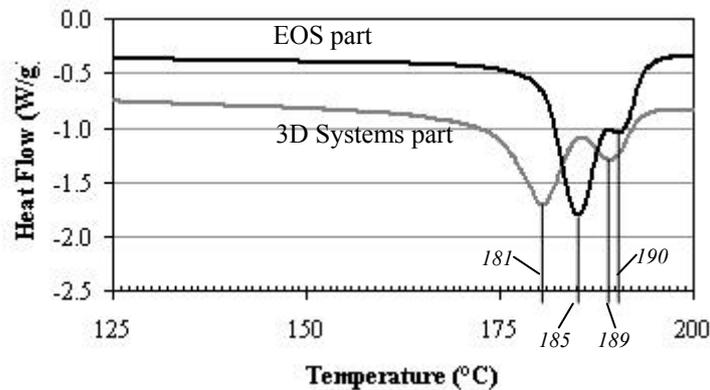


Figure 10 DSC results for TNO and Lboro parts built from Virgin powder

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

The presence of cores may be inherent to SLS processed material but higher energy input (for example TNO specimens) reduces the core size. - ~~A further explanation is a~~ higher 'degree of melting' occurring in the TNO specimen (Figure 11a) ~~and it is suspected that this could~~ indicates better fusion/sintering of particles and hence superior mechanical ~~propertiess~~. - The injection moulded specimen clearly shows no particle cores and a much more even and fine microstructure due to the feedstock being fully molten (and presumably more fluid) and followed by faster cooling.

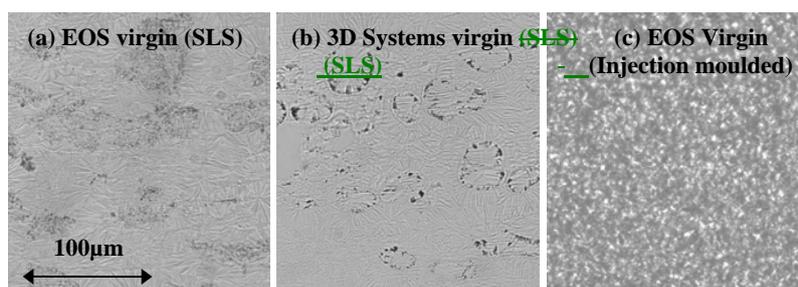


Figure 11 Microstructure of TNO and Lboro parts built from virgin powder and injection moulded specimen

3.2.4 Mechanical properties

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

The increased molecular weight of the used powder may be responsible for the improved ductility since it would ~~be reflected in~~relate to the molecular weight of the particle cores. The increase in EaB of

Lboro refreshed parts from Lboro virgin parts is 94 % of the virgin-part value. -The increase for the TNO parts is only 36%. -This may be due to the increasesd powder bed temperature for Lboro parts due to the adjustment for each powder type. However it could also relate ~~but also~~ to ~~having the~~ larger cores and hence building with more used powder (i.e. refreshed) ~~has would have~~ a more significant effect on mechanical properties. -To reiterate, the larger the core the greater the significance of the pre-melting powder history (e.g powder blend). -Likewise, the smaller the core (i.e. greater fraction of melt/crystallized region) the greater the significance of build related factors (e.g. build parameters).

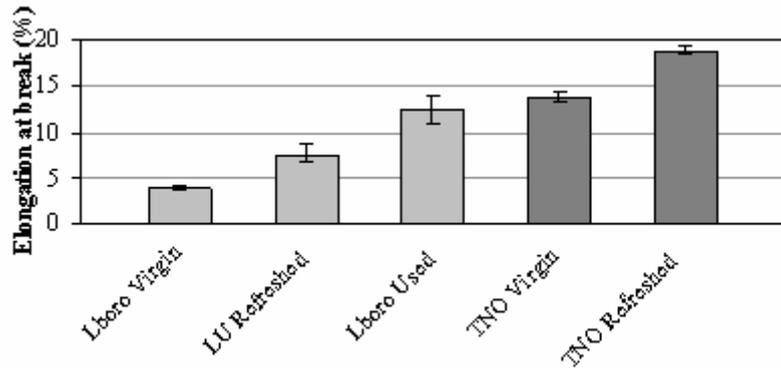


Figure 12. Tensile Elongation at break

Figure 13 shows the results for ultimate tensile strength of parts made with different powders on the different machines. Figure 13 indicates a small difference in mechanical stress response between parts built from virgin, refreshed and used powder. The variation in ultimate tensile strength between Virgin and refreshed material is small however there is a marked increase in tensile strength for used powder. - Tensile strength values are higher for the TNO parts reflecting the parameters used (see [Table 5](#)).

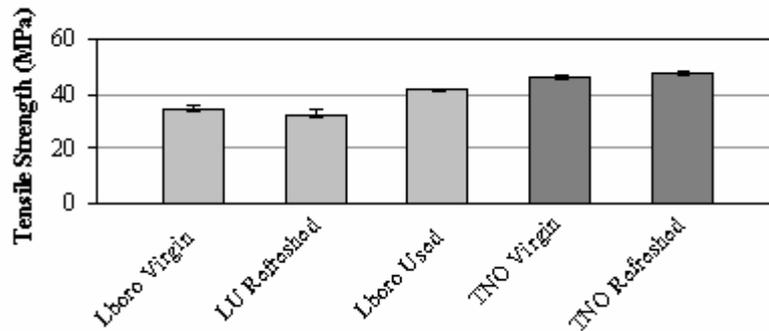


Table 5

Figure 13. Tensile Strength

Figure 14 shows the results for Young's Modulus for parts made with different powders on the different machines. -Figure 14 shows parts from refreshed powder having almost the same Young's Modulus as parts from virgin powder. As with tensile strength, Young's modulus values are higher for the TNO parts reflecting the parameters used (see Table 4).

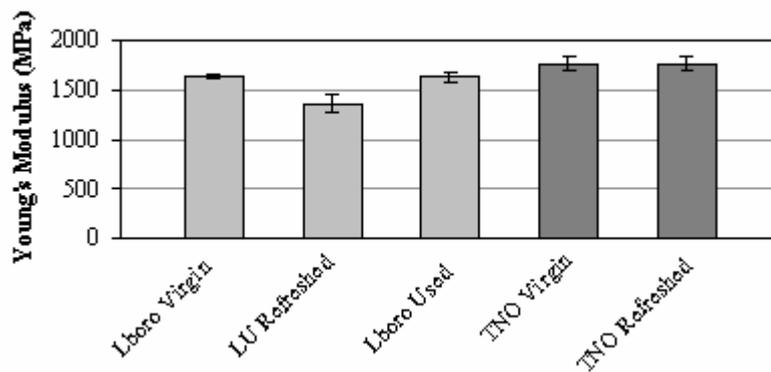


Figure 14. Young's modulus

Generally, parts built from used powder blended with virgin (refreshed) are shown to give superior mechanical properties than those built entirely from virgin powder. [This is consistent with previous studies which presented results for parts built from different grades of used powder.](#)

4 Discussion and Conclusions

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

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

The crystal structure of the material was investigated using DSC to identify different crystal forms. Unmolten particle cores were matched to used powder material and ~~termed have, most likely, the γ^v -~~ crystal form. ~~This form has here a The melting point of~~ The melting point was measured between the γ^v and γ^p form (188-190°C) which is higher than commonly reported values for non SLS processed Nylon 12 indicating particularly large crystals. ~~((The molten and recrystallised regions were observed with a lower melting points (181 and 185 °C) than virgin powder and termed γ^p crystal form which lie within the known range for the γ form. Both γ crystal forms were matched to their distinct regions within the material's observable microstructure. Processing on different machines (3D Systems and EOS) was shown to result in different γ^p forms (181°C and 185°C respectively) The difference between the melting points for the melted and recrystallised regions are presumably due to different thermal processing conditions.)) Please rephrase !!~~ Slower cooling for the TNO parts (due to parameters and/or inherent machine behaviour) likely resulted in larger crystals hence the higher melt point of the γ^p phase. - Analysis by X-ray diffraction would allow detailed characterisation of the crystal structure.

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

The most significant trends observed with mechanical properties were the changes to EaB. - TNO parts showed higher EaB than Lboro parts and, within each group, building with used powder resulted in improved EaB. -It is important to note that other important mechanical properties of SLS parts such as tensile strength and Young's modulus are similar to those obtained for traditionally processed samples such as injection moulding while EaB of SLS parts, however, lags far behind. - This highlights

the importance of investigating SLS material characteristics in relation to EaB. – In this study increased molecular weight of used powder was related potentially to improved EaB of parts. – Other factors could also be considered however.

The porous nature of SLS parts is understood to be at least partly responsible for the low EaB relative to that of conventionally produced parts [32]. – Another potential issue is that of various boundaries and interfaces within the part. – The presence of unmolten particle cores leads to a composite-like structure. – As such, intra-crystal-form and, perhaps, intra-spherulite interfaces may have varying influence ~~of~~ on mechanical properties. A strong intra-crystal-form interface (between particle core and surrounding melted and recrystallised region) (~~γ^c/γ^p~~) could lead to the highly crystalline γ^c form being locked in a γ^p form –matrix of the melted and recrystallised region with the micro-level mechanical properties of each γ^c form particle core having a strong positive effect at the macro-level i.e. the mechanical properties of the SLS part. A weak intra-crystal-form interface however could lead to rupture of the core from the ~~γ^p phase matrix~~ under relatively weak stress resulting in rapid crack formation and propagation and thus inferior mechanical properties such as low EaB i.e. brittleness. ~~((Please rephrase))~~

Further work could focus on in depth characterisation of the crystal forms present in SLS processed material and the precise effects of different processing and other parameters on these. ~~((Material interfaces particularly the γ^c/γ^p intra-crystal form interface that between the particle core and melted and recrystallised region~~ could also be investigated. Effects of molecular weight on melt viscosity and their effects on processing and mechanical properties have not been discussed in this report and would also be a useful topic to pursue. This paper considered reproducibility of mechanical properties however further work could also investigate geometry and accuracy issues since this is also important to control. Research, such as the current paper, focussed in these various avenues can lead to improvements in reproducibility using existing material and equipment and will also be useful for developing new materials and hardware.

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