Effects of Degree of Particle Melt and crystallinity in SLS Nylon-12 parts

C.E.Majewski*, H.Zarringhalam† and N.Hopkinson*
*Rapid Manufacturing Research Group, Loughborough University, Loughborough, United Kingdom. LE11 3TU,
† Materials Solutions, University of Birmingham Campus, Edgbaston, Birmingham, United Kingdom. B15 2TT

Reviewed, accepted September 10, 2008

Abstract

Differential Scanning Calorimetry (DSC) traces for SLS Nylon-12 parts display two distinct melt peaks, which have been related to the presence of both melted and crystallised regions, and un-melted particle cores within the part. The relative proportions of each region are defined by the term 'Degree of Particle Melt' (DPM), and have a large effect on the mechanical properties of a part. This paper demonstrates that the % crystallinity of SLS Nylon-12 parts is dependent on the DPM. Crucially, research has also shown that the trends for some tensile properties (notably Tensile Strength and Young's Modulus) change once full melting is complete.

1.0 Introduction

Previous research[1,2] identified that, for Selective Laser Sintering (SLS) of polymers, only partial melting occurs, whereby larger particles receive insufficient energy to completely melt. Figure 1 clearly illustrates the presence of particle cores (un-melted material), surrounded by melted areas.

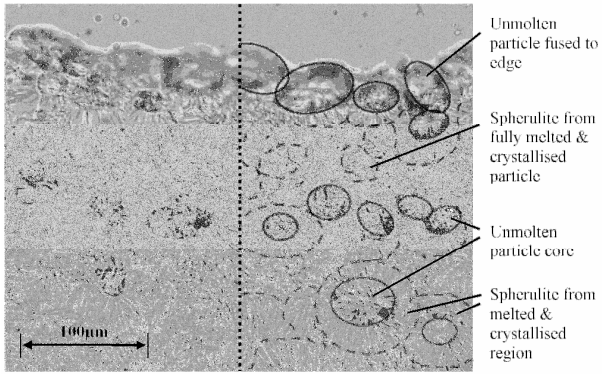

Figure 1 - Microstructure of SLS material[3]

1.1 Degree of Particle Melt

Differential Scanning Calorimetry (DSC) traces for laser sintered Nylon-12 have been shown to include two distinct melt peaks, which have been related to the melted and un-melted regions within a part (see Figure 2).

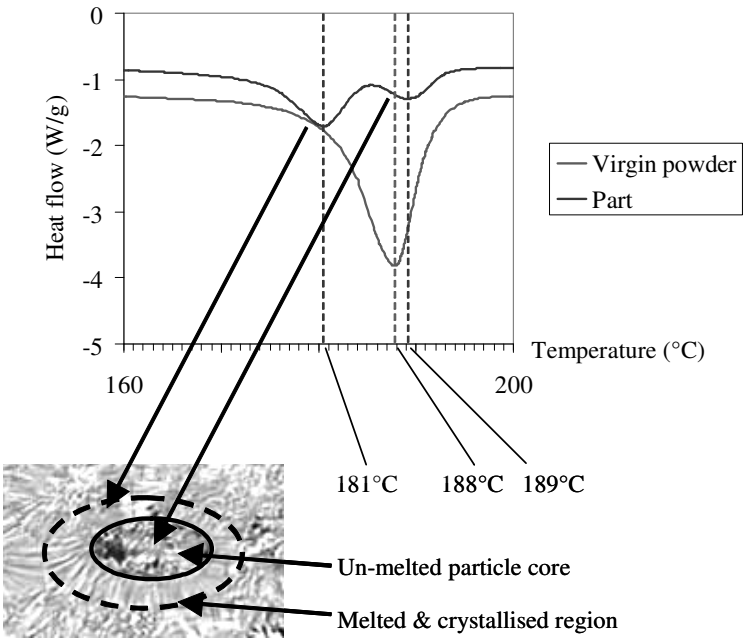

Figure 2 Relationship between DSC peaks and material microstructure (adapted from[3])

It has also been shown previously that the percentage crystallinity of an SLS part is dependent on the DPM of that part. It is known that, for traditionally processed semi-crystalline materials, an increase in the crystalline content leads to an increase in tensile strength and stiffness, but at the detriment of the ductility, as it is the amorphous regions of a polymer that provide it's ability to yield without breaking[7]. Given the correlation identified between DPM and mechanical properties, it was considered logical to expect that the DPM would have an effect on the percentage crystallinity of SLS parts.

2.0 Experimental Procedure

To establish the effect of DPM and crystallinity on mechanical properties, a series of parts was produced under different build conditions, in order to provide a range of differing DPM, as shown in previous research[6].

DSC was performed for each build, and the crystallinity calculated as described in Section 2.2.1. Tensile testing was performed from each set of build conditions, and the measured properties were compared with the crystallinity.

2.1 SLS Part Production

In order to produce parts with varying levels of DPM for this research, parts were produced on a single SLS machine (3D Systems SLS Vanguard), and parameters which would specifically alter

the energy input were varied. The material used was Duraform PA (Nylon-12). Specimens with dimensions of 180 x 10 x 4 mm were produced, from which DSC measurements were performed.

Six tensile specimens were produced in each build according to ISO-527-2:1996 type 1A, as shown in Figure 3. Parts were built in the x-axis to reduce end of vector effects, and built flat to reduce build time. The layer thickness used was the standard 0.1 mm. In addition to the tensile specimens, one 'sample' part was built to obtain specimens for DSC testing as required.

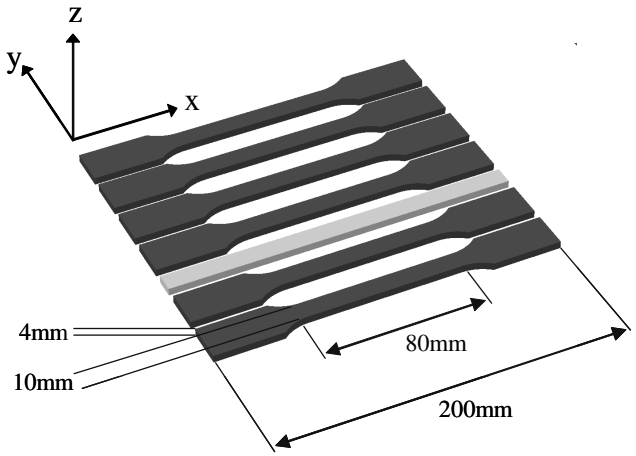

Figure 3 - ISO 527-2:1996 type 1A tensile specimen parts and 'sample' part

Standard build parameters for Duraform PA were used as default values, and for subsequent builds a single parameter was changed from the default, either to a high or a low level. Table 1 shows the main build parameters which were varied, where **Green** indicates a higher level than default, and *Red* a lower value.

Build	**Part heater set point (PHSP)**	**Slicer fill scan spacing (SFSS) (*mm*)**	**Fill laser power (FLP) (*W*)**	**Fill scan count (FSC)**
1 – Default	148	0.15	11.5	1
2 – PHSP high	**150**	0.15	11.5	1
3 – PHSP low	*146*	0.15	11.5	1
4 – SFSS high	148	**0.13**	11.5	1
5 – SFSS low	148	*0.17*	11.5	1
6 – FLP high	148	0.15	**13.5**	1
7 – FLP low	148	0.15	*9.5*	1
8 – FSC high (2)	148	0.15	11.5	**2**
9 – FSC high (3)	148	0.15	11.5	**3**

Table 1 - Machine parameters

2.2 Material Testing

2.2.1 Differential Scanning Calorimetry (DSC)

DSC measurements were taken using Shimadzu DSC 60WS equipment, and analysed using TA60 software, also from Shimadzu. Sample masses were 5 mg +/- 0.05 mg, and samples were heated from ~20 °C to 220 °C at a rate of 10 °C per minute. Samples were held at 220 °C for two minutes, and then cooled at 10 °C per minute.

Figure 4 shows an example DSC graph, with the relevant area of interest highlighted, and Figure 5 indicates the exact positions from which measurements were taken.

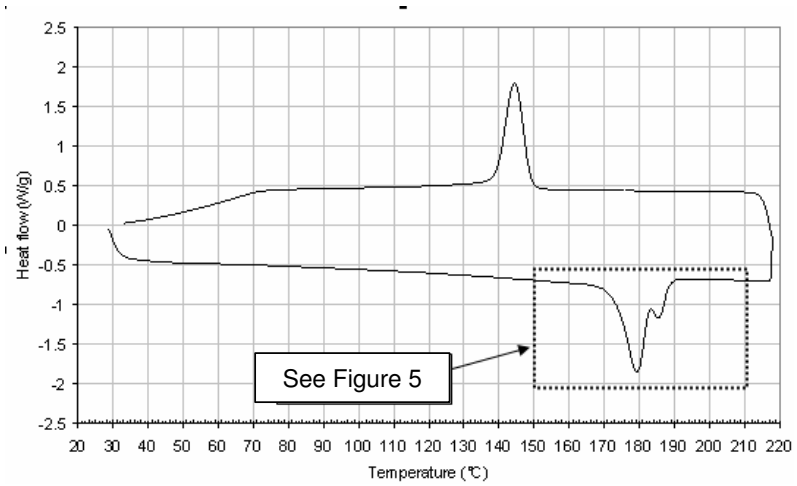

Figure 4 - Example DSC trace

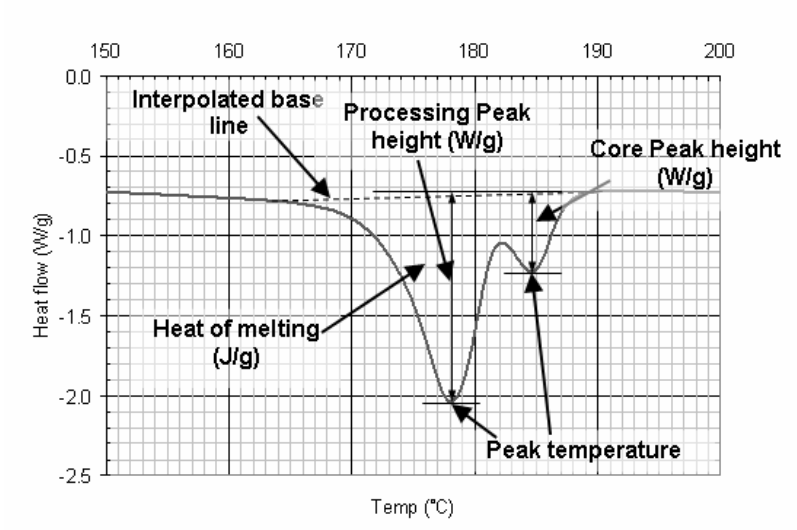

Figure 5 - Position of measurements

The percentage crystallinity was determined by dividing the heat of melting (indicated in Figure 5) by the known heat of melting for a 100% crystalline specimen. This value was taken to be 209.3J/g, as reported by Gogolewski et al[8].

2.2.2 Tensile Testing

In order to test the tensile properties, a Zwick testing machine with long travel contact extensometer was used. E-Modulus was measured using a 1 mm/min strain rate, and Tensile Strength and Elongation at Break were measured at 5 mm/min.

3.0 Results

3.1 Percentage Crystallinity

Figure 6 shows the % crystallinity calculated for each build.

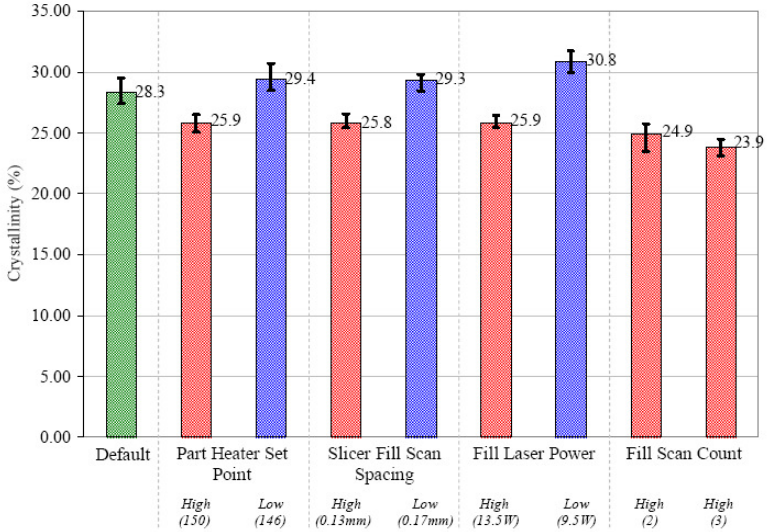

Figure 6 - % Crystallinity for each build

It can be seen that each high value of a parameter provided lower crystallinity than the default, indicating a higher DPM, and vice versa. Previously it has been shown that the point at which melting becomes complete occurs between 25.8 and 24.9 % crystallinity, falling between the lowest single scan point and the double scan[4]. From this point forward, parts containing only fully melted material will be referred to as 'single phase', and those containing both melted and un-melted material will be referred to as 'double phase'.

3.2 Tensile Properties

The following figures show the Elongation at Break (Figure 7) and the Tensile Strength (Figure 8) plotted against the % crystallinity. Young's Modulus has previously been shown[6] as being affected in no significant manner by the DPM, and therefore has not been analysed here.

It should be noted that the blue dashed line does not represent the actual boundary between the double phase and single phase regions. The actual boundary could lie anywhere between the last data point in the double phase region and the first data point in the single phase region. Therefore for each region the trend line is extrapolated into the neighbouring region. These charts show a striking difference in mechanical properties between the double phase material (cores) and single phase material (no cores).

3.2.1 Elongation at Break

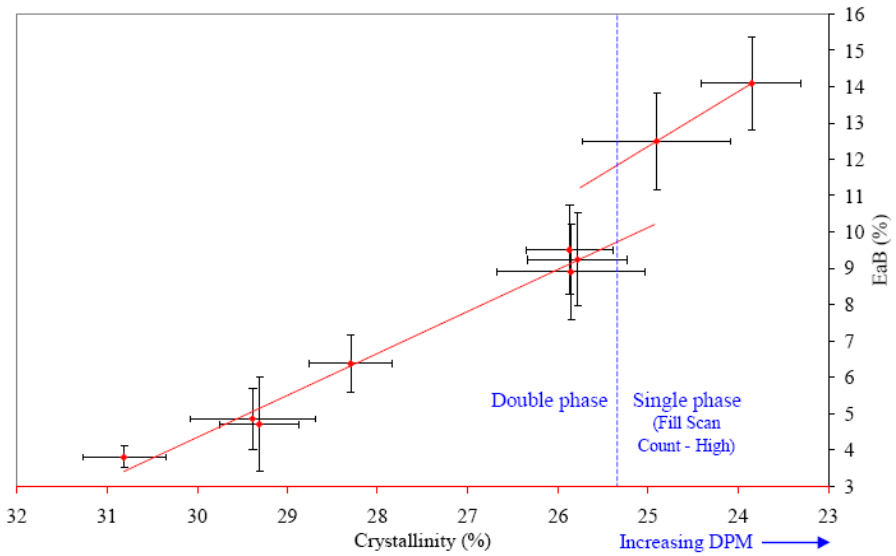

Figure 7 - Effect of % crystallinity on EaB

It can be seen from Figure 7 that, as the % crystallinity decreases, the Elongation at Break increases, as would be expected from the discussions presented in Section 1.1. However, once DPM is complete, there appears to be a definite step change in the values recorded, indicating that the effect of crystallinity changes once full melting is achieved.

3.2.2 Tensile Strength

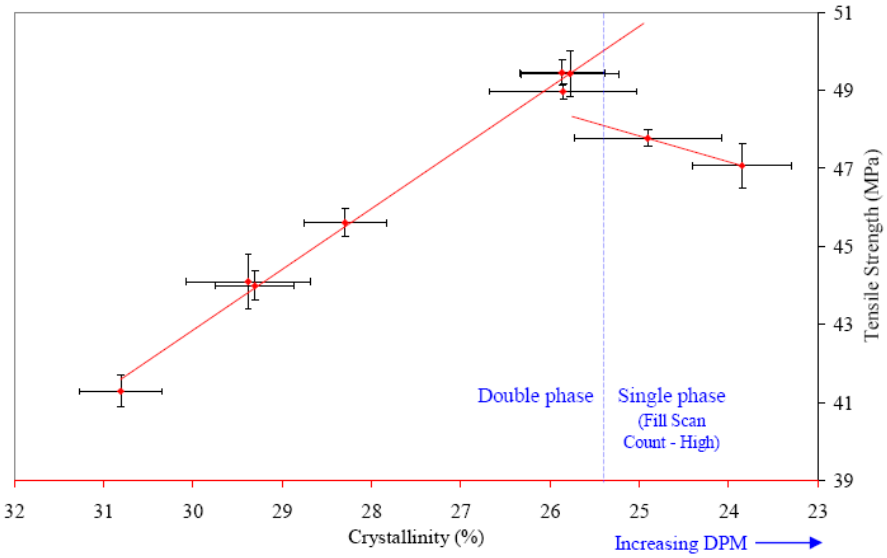

Figure 8 - Effect of crystallinity on Tensile Strength

Figure 8 shows that, as % crystallinity decreases, the Tensile Strength increases, until the point at which DPM is complete. At this point, there appears to be an instantaneous 'tipping point', at which the direction of the trend is reversed.

3.2.3 Summary

It can be concluded from these results that the % crystallinity has an effect on the tensile properties, during the period in which melting of particles is not complete. Once melting is fully complete, a new trend can be observed. In effect this leads to a distinction between fully melted and partially melted SLS parts, indicating that it may be appropriate to treat them as being two different materials – a homogenous, single phase material, and a quasi-composite material comprised of both melted and un-melted Nylon-12.

Whilst further work would be required to explain the apparent changes in the mechanical property results once melting is complete, it is possible that this is due to differences in the rate of crystallisation caused by the presence or absence of the un-melted particle cores, and therefore corresponding differences in the size of spherulites within the processed material.

4.0 Use of % crystallinity to quantify DPM

The % crystallinity of an SLS Nylon-12 part will be the sum of the % crystallinity of the un-melted cores and the melted and re-crystallised material. Figure 9 shows this in diagrammatic form. The y axes indicate the relative percentages of the part which are comprised of melted and crystallised material (MCM) and un-melted, core material. The x axes correspond to the crystallinity of each phase. The % crystallinity of the un-melted material is assumed to be that of

the powder itself, previously calculated to be 47 %. The % crystallinity of the fully melted material is taken to be 25 %, as determined in previous research[4]. Four different example compositions are demonstrated, and schematic illustrations indicating their approximate composition are included.

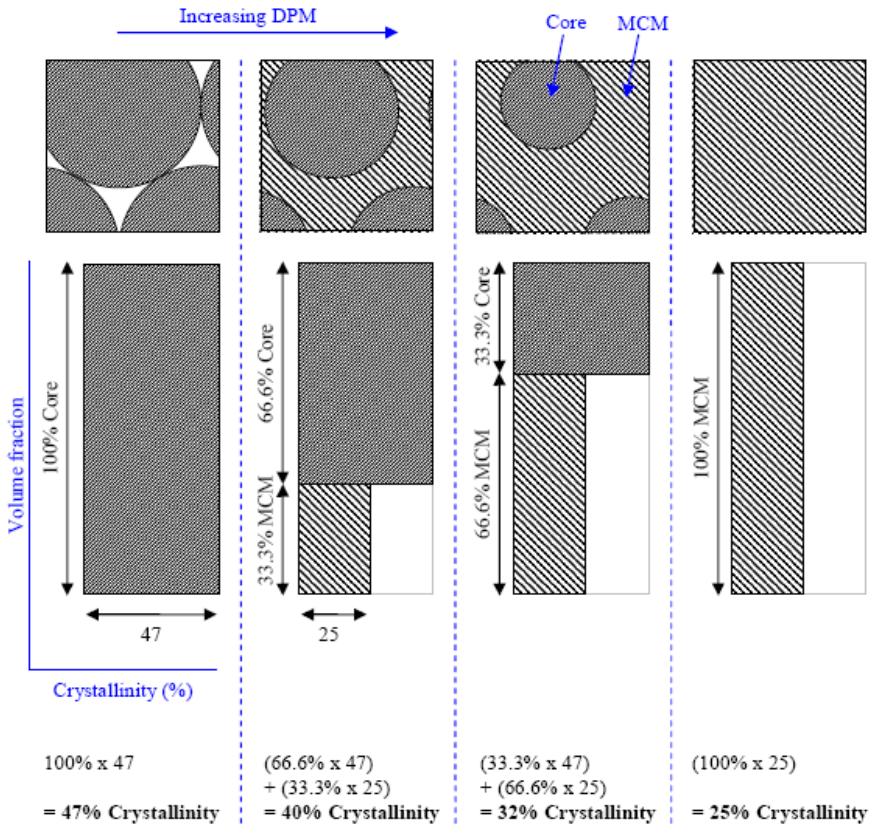

Figure 9 - Total % crystallinity as the sum of Core and MCM % crystallinity

The total % crystallinity can therefore be calculated using Equation 1 below.

Total Crystallinity = (%MCM x MCM crystallinity) + (%Core x Core crystallinity)

Equation 1

Taking % core to be 1 - % MCM gives:

Total Crystallinity = (%MCM x MCM crystallinity) + ((1-%MCM) x Core crystallinity)

Total Crystallinity = (%MCM x MCM crystallinity) + Core crystallinity - (%MCM x Core crystallinity)

Total Crystallinity – Core crystallinity = %MCM x (MCM crystallinity - Core crystallinity)

DPM (% MCM) = (Total crystallinity – Core crystallinity) / (MCM crystallinity – Core crystallinity) **Equation 2**

Assuming knowledge of the % crystallinity of the base powder, and that of fully melted material, it therefore follows that it is possible to calculate the DPM of the part using its crystallinity as measured from a DSC chart. The small size of specimen required for performing DSC would mean that it is entirely practical to include a sacrificial specimen in every build, in order to determine repeatability of melting, and therefore of mechanical properties. This is a far more practical approach than the destructive testing of parts, or the inclusion of much larger test specimens throughout builds. Further investigations, possibly involving varying only a single parameter (e.g. laser power) could be carried out in order to confirm the accuracy and repeatability of this method.

5.0 Conclusions

This work has shown that the percentage crystallinity of a two-phase SLS part, as calculated from a DSC chart, has an appreciable effect on the Tensile Strength and Elongation at Break, whereby a decrease in crystallinity leads to an increase in the mechanical property.

Crucially it has been shown that, once melting is complete, the trends become different, indicating that the material the properties and dependencies can be treated as though for an entirely new material. Further investigation in this area will be required in order to establish significance.

It has also been hypothesised that, given knowledge of the percentage crystallinity of the fully melted material, and the base powder, the relative percentages of the material within a part which are fully melted can be calculated by determining the % crystallinity of the part from a DSC trace.

Further work could focus on the use of imaging software to correlate the quantified DPM values with optical microscopy images in order to further verify this hypothesis.

6.0 Acknowledgements

This research was carried out by Hadi Zarringhalam with support from the PowderMatrix Faraday Partnership, Solid Concepts Inc. and 3D Systems UK

7.0 References

[1] Moeskops, E., Kamperman, N., van de Vorst, B. and Knopppers, R., 2004, Creep Behaviour of Polyamide in Selective Laser Sintering, Proceedings of the 15th Solid Freeform Fabrication Symposium, University of Texas in Austin, Texas, USA

[2] Shi, Y., Li, Z., Sun, H., Huang, S., and Zeng, F., 2004, Effect of the properties of the polymer materials on the quality of selective laser sintering parts, Proceedings of the I MECH E Part L Journal of Materials: Design and Applications, Vol. 218, pp 247–252, ISSN 1464-4207

[3] Zarringhalam, H., Hopkinson, N., Kamperman, N.F., de Vlieger, J.J., 2006, Effects of processing on microstructure and properties of SLS Nylon 12, Materials Science and Engineering A, Vol. 435-436, pp 172-180, ISSN 0921-5093

[4] Zarringhalam, H., Investigation into crystallinity and degree of particle melt in selective laser sintering, PhD thesis submitted to Loughborough University, UK, 2007

[5] Zarringhalam, H., Majewski, C.E.,. and Hopkinson, N, Degree of Particle Melt in Nylon-12 Selective Laser Sintered Parts, paper submitted for publication to the Rapid Prototyping Journal, June 2008

[6] Majewski, C.E., Zarringhalam, H. and Hopkinson, N., Effect of Degree of Particle Melt on mechanical properties in Selective Laser Sintered Nylon-12 parts, paper accepted for publication in Proceedings of the Institution of Mechanical Engineers, Part B, Journal of Engineering Manufacture, May 2008

[7] Kong, Y. and Hay, J.N., 2003, The enthalpy of fusion and degree of crystallinity of polymers as measured by DSC, European Polymer Journal, Vol. 39, pp1721-1727, ISSN 0014-3057

[8] Gogolewski, S., Czerniawska, K. and Gasiorek, M., 1980, Effect of annealing on thermal properties and crystalline structure of polyamides. Nylon 12 (Polylaurolactam), Colloid & Polymer Science, Vol. 258, No. 10, pp 1130–1136, ISSN 0303-402X