EFFECT OF SEGREGATED FIRST AND SECOND MELT POINT ON LASER SINTERED PART QUALITY AND PROCESSING

Ben Fulcher, David K. Leigh

Harvest Technologies
Belton, TX 76513

Abstract

Efforts to tailor laser sintering polymers to enhance part quality, performance, and processing have relied on the characterization of the polymers using Melt Flow Index (MFI) and Differential Scanning Calorimetry (DSC). Two grades of laser sintering nylon polyamide are compared and the resultant processing window, part quality, and mechanical behavior are discussed. A better understanding of characterization techniques and the processing of laser sintered polymers is leading to engineering thermoplastics for exclusive use in additive manufacturing.

1. Introduction

Thermal characteristics of a given polymer are essential in determining its suitability for use in Selective Laser Sintering (SLS). Semi-crystalline thermoplastics typically display a discrepancy between melting and recrystallization temperatures. For SLS processing, the range of temperatures that exists for a given thermoplastic between the recrystallization and melting temperatures is considered the operating temperature window of the material. Thus, the material should be kept within this temperature range during SLS processing. By keeping the sintered material in a molten state above the recrystallization temperature, part warping due to thermal variation among sintered layers is reduced. By keeping the powder material in a solid state below the melting temperature, undesired melting of surrounding powder is avoided. Once the entire SLS build is sintered, the part bed is cooled and the sintered material recrystallizes and solidifies. Differential Scan Calorimetry, or DSC, can be used to capture the melting and crystallization temperature ranges of polymers. A typical DSC curve for a semi-crystalline polymer is displayed in Figure 1**,** where heat capacity at constant pressure of the material is plotted versus the temperature of the material.

A polyamide 11 powder under the brand name Rilsan® Invent Natural (referred to as Invent in this paper) has recently been engineered for use in laser sintering by Arkema Inc. While similar to another polyamide 11 product under the brand name Rilsan® D80 Natural ES (referred to as D80 in this paper), the Invent powder has undergone development to tailor its thermal characteristics to the laser sintering process. Among various improvements over the D80 powder made by Arkema Inc., such as optimized particle size distribution, a key improvement was the introduction of a melting-point transition. First and second melting points exist in the Invent material, leading to increased ease of processing and enhanced recyclability for SLS. Preliminary results have also shown improved mechanical properties over similar polymers processed in SLS. From a thermal standpoint, a primary difference between the Invent and D80 materials is the occurrence of this melting-point transition in the Invent powder, whereas the D80 powder maintains a relatively constant melting point after a melt and recrystallization cycle.

Once the Invent material undergoes melting at a temperature of roughly 203°C, the melting temperature drops to roughly 188°C. Thus, the material is said to display a melting-point transition from a first melting point (203°C) to a second melting point (188°C).

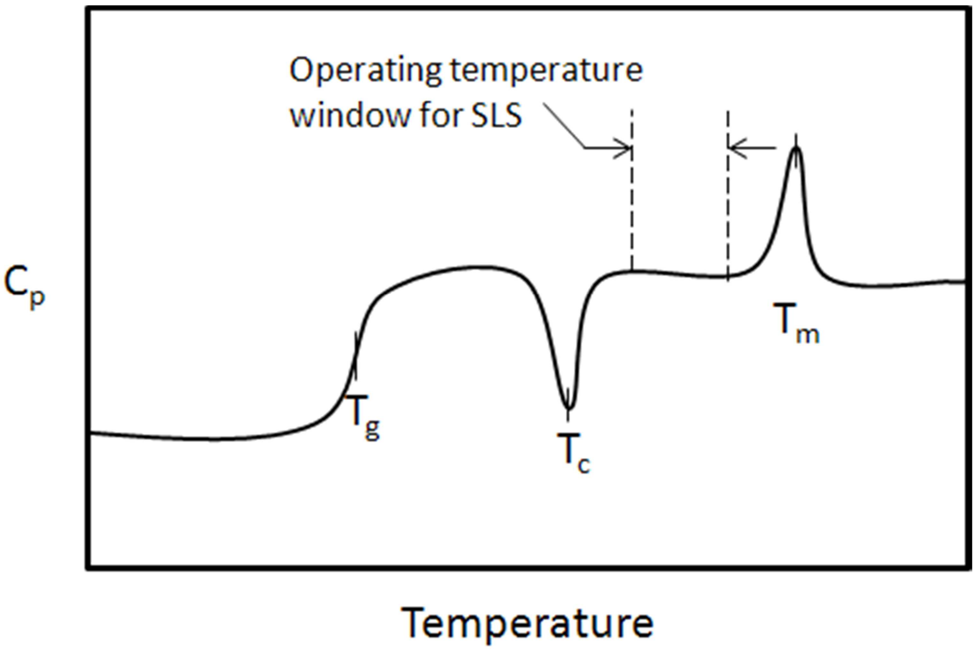

Figure 1. *Typical DSC curve for a semi-crystalline thermoplastic*

2. Single Melting-Point Materials

In SLS processing of materials with a single melting point, the powder bed is kept at a temperature level within the operating range of the material, preferably close to, but below, the melting temperature. Thus, the laser-melted powder remains molten and fluid while the surrounding powder remains solid. However, since the surrounding powder is also kept just below its melting temperature, the process often results in relatively poor feature detail due to solid state sintering of the surrounding powder to the laser-melted material [1]. If the melted material is allowed to approach its crystallization temperature, each melted layer is more likely to experience densification, leading to increased likelihood of part warping. The photograph in Figure 2 shows the effect of this solid-state sintering on the edge of a melted region. At the top of the photograph, solid particles can be seen that are fused to the edge of the part.

In addition, the surrounding powder is highly prone to thermal aging, a common issue with SLS materials as it hinders material recyclability. As the powders are cycled from room temperature to near the melting temperature, the fine particles experience solid-state sintering with each other, disrupting the desired particle size distribution of the material [1]. This effect can lead to poor powder flow characteristics as well as poor surface quality known as "orange-peel," displayed in Figure 3. Furthermore, higher temperatures can cause polymer chains to grow, thereby increasing the melting temperature of the used powder [2].

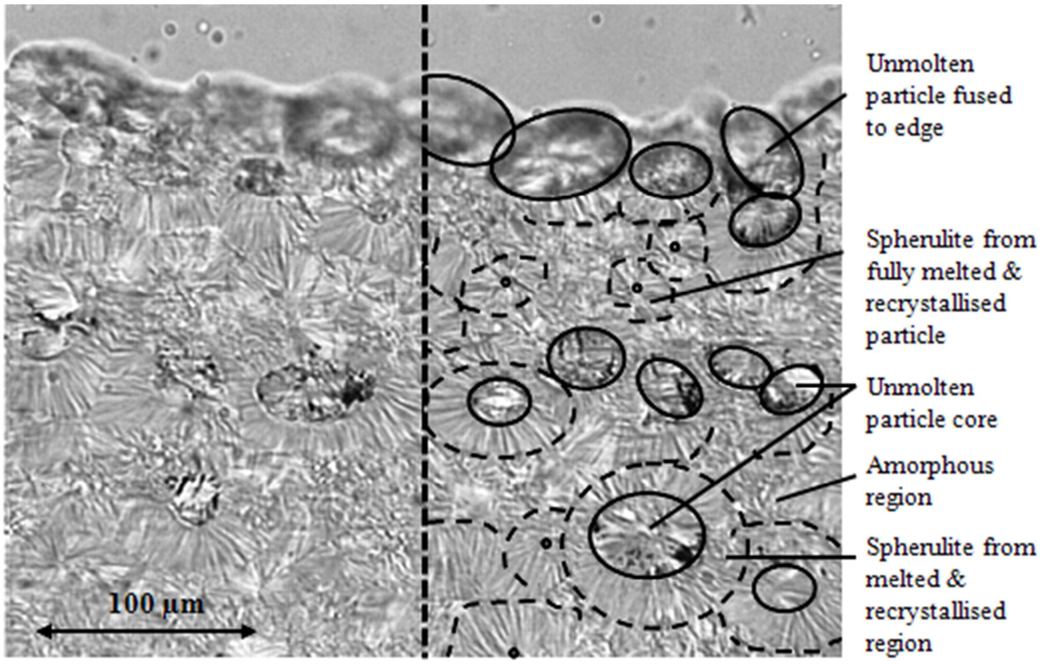

Figure 2. *Effect of solid-state sintering on edge of part [3]*

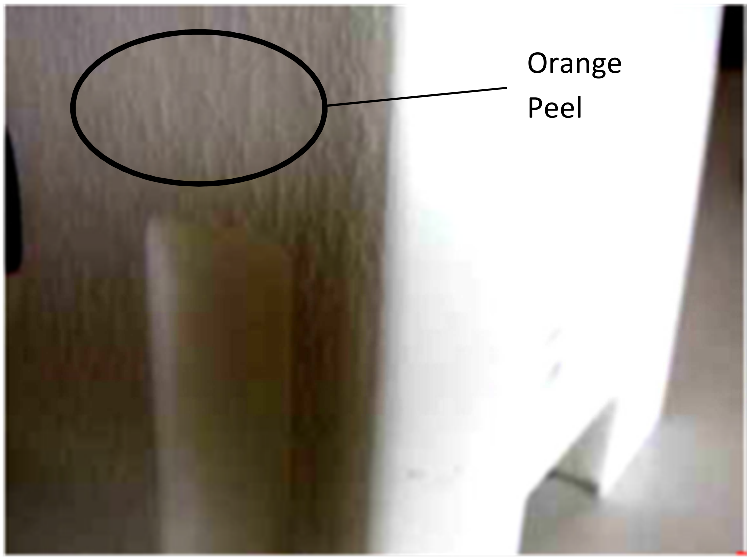

Figure 3. *Orange peel surface texture on SLS part [2]*

3. Melting-Point Transition

While some semi-crystalline thermoplastics can contain multiple melting points due to the inclusion of differing crystal structures [4], melting-point transitions, such as the one displayed by the Invent material, could be the result of thermal pre-processing. For example, one method of inducing a melting-point transition in a semi-crystalline polymer is through thermal annealing. By annealing the polymer at a constant temperature below, but near, the melting point of the polymer, crystallinity within the material can be increased. Driven by thermodynamic forces, amorphous chains are incorporated into the lamellae, thickening the lamellae. Since the melting temperature of lamellae increases with lamellae thickness, the annealing process increases the overall melting temperature of the material [5]. This increased melting temperature is referred to as the first melting point of the material for SLS processing. When the annealed powder is then melted in SLS, the melting temperature of the laser-fused material drops to its original pre-annealed value. The pre-annealed melting temperature is referred to as the second melting point of the material for SLS processing. Thus, the material is pre-processed through thermal annealing, thereby raising the melting temperature, converted into a fine powder, and then selectively melted in the SLS process, returning the melting temperature to its pre-annealed state.

The segregation of first and second melting points in the Invent powder provides various benefits for SLS. Unlike typical powders, where the part bed temperature is kept just below the melting temperature of the material, Invent powder can be successfully processed in SLS at temperatures well below its melting point. This is because once the desired material is laser-melted, the melting point of the material transitions to a lower temperature, keeping the molten material from experiencing recrystallization. To further understand this transition, examine the DSC curves displayed in Figure 4, provided by Arkema Inc. As seen in the image, the first heating curve shows a melting point of roughly 203°C. The molten material then follows curve 2 for cooling, experiencing recrystallization at roughly 157°C. When the material is heated a second time, it experiences melting at roughly 188°C. Thus, for SLS processing, the laser-melted material remains highly fluid since it can be held above the second melting temperature while still remaining well below the melting temperature of the powder. Therefore, minimal to no part warping due to layer shrinkage is expected.

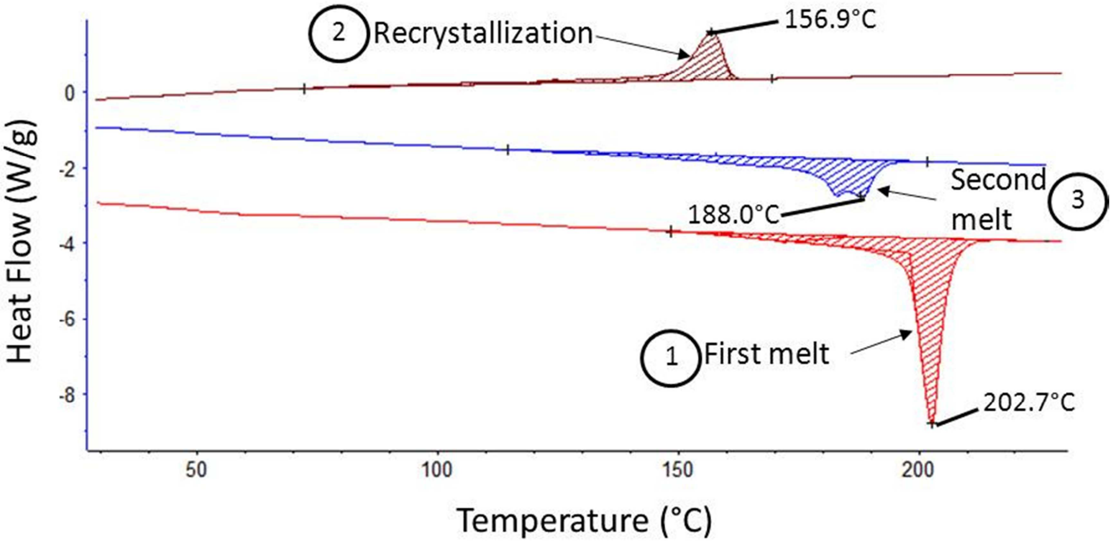

Figure 4. *DSC curves for Rilsan® Invent Natural powder*

In Figure 4, labels 1, 2 and 3 represent the order in which the processes occur. Note also that exothermic processes are considered positive in terms of heat flow, whereas endothermic processes are considered negative. In contrast to the DSC curves for the Invent powder, the DSC curves for the single melting-point D80 powder are displayed in Figure 5. Although the shape of the DSC curve changes from the first to the second heating, the melting temperature remains very similar. Thus, the D80 material is considered to be a single melting-point material.

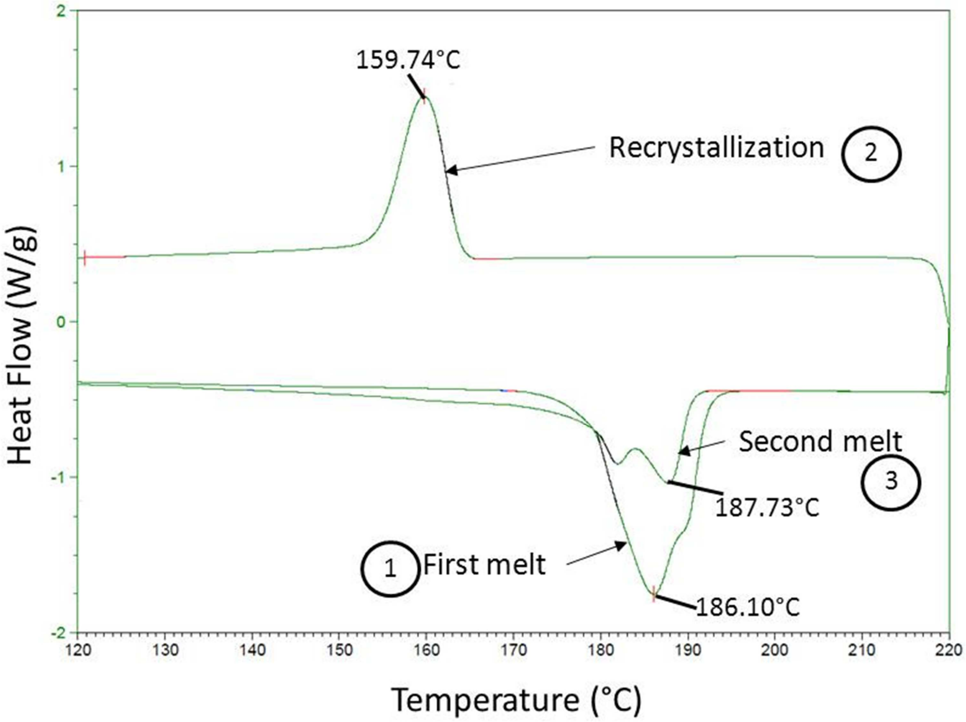

Figure 5. *DSC curves for Rilsan® D80 Natural ES powder*

4. Preliminary Trials with Rilsan® Invent

Preliminary trials with Invent powder have shown promising results. With the part bed temperature held at 192°C, well below the first melting temperature of 203°C, SLS has produced parts with good mechanical properties, very little warping, good feature detail, and good recyclability.

Tensile bars built along the z-axis of the build chamber, using D80 powder, had an average elongation at fracture of 26.7% and an average ultimate tensile strength of 7323 psi. Comparatively, z-oriented tensile bars built using Invent powder had an average elongation at fracture of 43.4% and an average ultimate tensile strength of 7855 psi. The improved mechanical properties displayed by the Invent powder are the result of a high level of layer-to-layer adhesion. This good adhesion is likely, at least in part, due to the fact that the laser-melted Invent material is held above its melting point, keeping the bars in a highly molten state for an extended period of time. Tensile data from two bars, one from each build, is plotted in Figure 6. The two bars chosen for plotting displayed the highest elongation at fracture for their respective builds.

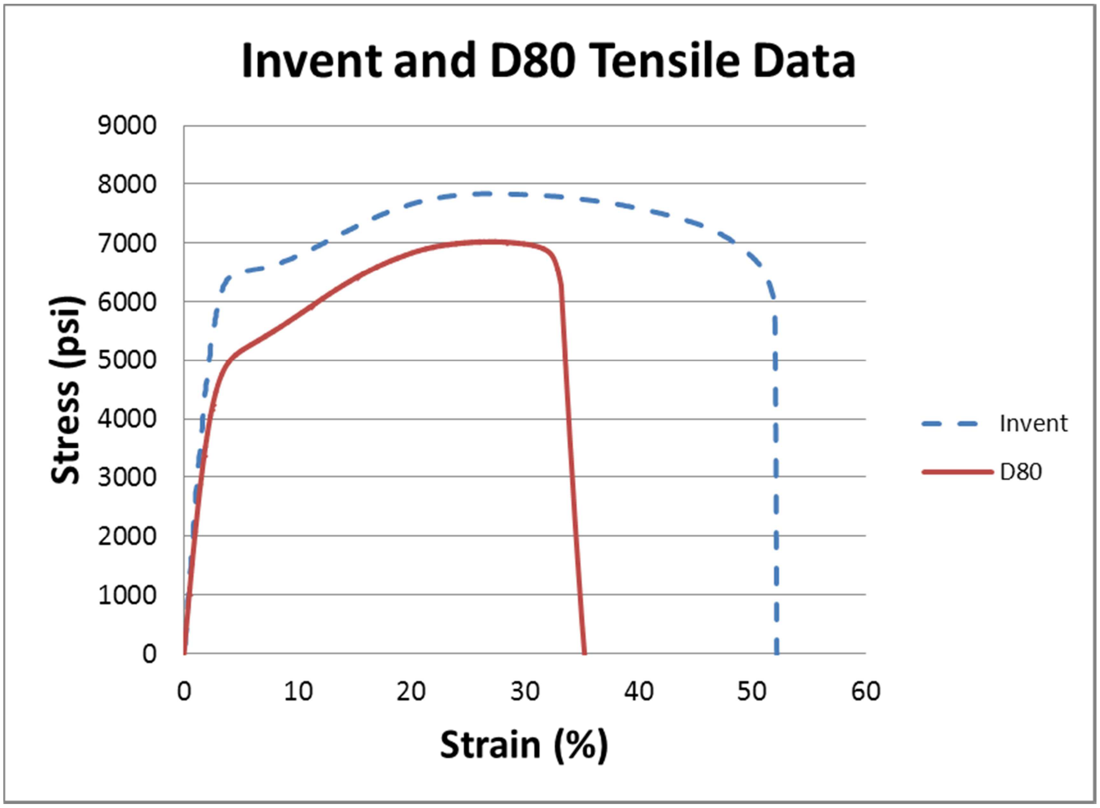

Figure 6. *Tensile testing curves for select Invent and D80 specimens*

Prototype parts built with the Invent material showed little warping. As expected, since the molten material is held far above its crystallization temperature, layer shrinkage during the build is eliminated. Thus, stresses in the parts due to layer shrinkage, which cause in-build curling of the parts, did not arise in the Invent powder trial. A prototype created with the Invent material is shown on a flat surface in Figure 7.

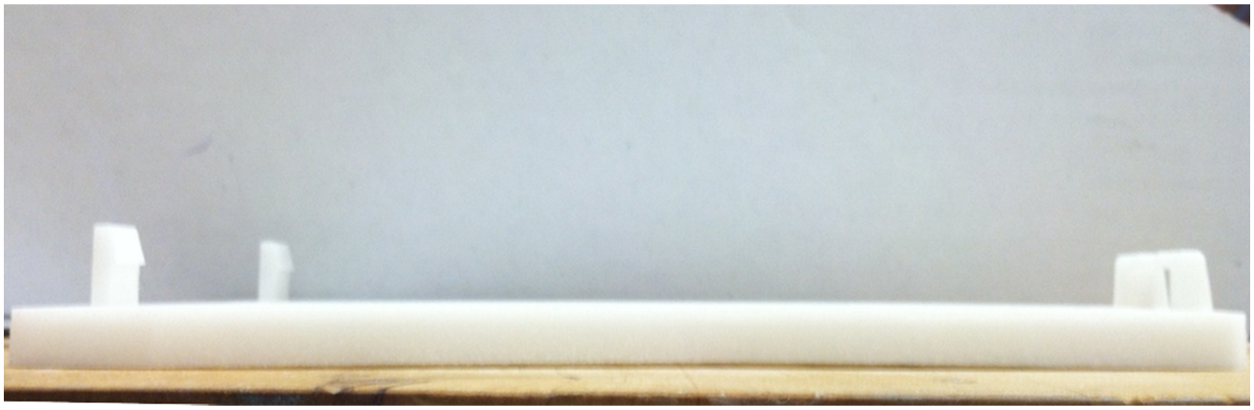

Figure 7. *Prototype built with Rilsan® Invent Natural powder displaying minimal warping*

The Invent powder was also able to produce parts with good feature detail. Small extruded lettering is often difficult to produce in SLS due to a number of reasons, including solid-state sintering of surrounding powder to the borders of the letters. However, because the

Invent powder was held well below its melting temperature throughout the build, solid-state sintering of powder to the edge of the parts did not appear to be as prevalent in the Invent powder as with other SLS materials. An image of small lettering on one of the prototype parts can be seen in Figure 8. Although somewhat difficult to read in the photograph due to the white letters and white back-drop, the phrase “Low Voltage Circuit Breakers” was clearly produced on the part.

Figure 8. *Feature detail using Rilsan® Invent Natural powder*

Although a true study on recyclability of SLS powder would involve numerous trials in which the ratio of virgin to used powder is varied, preliminary trials of the Invent powder indicate good recyclability. A qualitative indication of recyclability is the “feel” of the part cake after a build is processed in SLS. If the part cake, which includes all of the powder surrounding the parts, feels soft, it is likely that very little solid-state sintering amongst the powder particles occurred. This typically indicates good recyclability, as the particle size distribution remains relatively unaltered. However, if the part cake feels hard, the powder particles likely experienced significant solid-state sintering, resulting in an increase of average particle size. This indicates poor recyclability as larger particles reduce dimensional accuracy and alter the thermal characteristics of the powder. Trial builds with Invent powder have had a very soft part cake, indicating good recyclability. The photograph in Figure 9 shows the part cake from an Invent trial.

Figure 9. *Part cake using Rilsan® Invent Natural powder*

In preliminary trials, the Invent powder has proven relatively easy to process. Because the part cake is soft, the time required to remove parts from the cake, as well as remove excess material by bead blasting and sanding, is reduced. Furthermore, the temperature of the part bed does not need to be tightly controlled to still produce good mechanical properties. However, when the part bed temperature was held at 189°C, curling of parts was noticeable. Further studies should be conducted to fully determine the effect of part bed temperature on mechanical properties and appearance.

5. Conclusions

Melting point transitions in semi-crystalline thermoplastics have been successfully utilized in SLS to enhance part quality, mechanical properties, material recyclability, and ease of processing. By harnessing the ability of the recently developed Rilsan® Invent Natural to change melting temperatures after a first melt, preliminary trials have displayed good results in each of these areas. The melting point transition allows molten material to be held above its melting temperature, and non-molten powder to remain well below its melting temperature. These effects reduce the likelihood of in-build curling, improve layer-to-layer adhesion and therefore mechanical properties, and reduce the degree of solid-state sintering among loose powder, thereby improving feature detail and powder recyclability. Further work should be done to collect data on material recyclability and ease of processing.

References

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