LA-UR-17-28192

Title: Developing Characterization Procedures for Qualifying both Novel Selective Laser Sintering Polymer Powders and Recycled Powders

Author(s): Bajric, Sendin

Intended for: GRA paper

Issued: 2017-09-12

Developing Characterization Procedures for Qualifying both Novel Selective Laser Sintering Polymer Powders and Recycled Powders

Sendin Bajric
University of Oregon

11 September 2017

Abstract

Selective laser sintering (SLS) is an additive technique which is showing great promise over conventional manufacturing techniques. SLS requires certain key material properties for a polymer powder to be successfully processed into an end-use part, and therefore limited selection of materials are available. Furthermore, there has been evidence of a powder's quality deteriorating following each SLS processing cycle. The current investigation serves to build a path forward in identifying new SLS powder materials by developing characterization procedures for identifying key material properties as well as for detecting changes in a powder's quality. Thermogravimetric analyses, differential scanning calorimetry, and bulk density measurements were investigated.

Introduction

Selective laser sintering (SLS) is a technique of additive manufacturing, invented at the University of Texas-Austin. The technique has become commercialized by DTM Corporation and EOS GmbH.[1] SLS with polymer powders involves a laser being used to sinter powder particles according to a computer-aided design (CAD). The laser sintering is done with one layer and then repeated as subsequent layers are deposited over the previous.[1]

The technique is being investigated at the Los Alamos National Laboratory (LANL) for its potential to manufacture highly complex designed objects. Key advantages to SLS over other conventional manufacturing techniques include freedom of design, tool-less fabrication, shorter product development times, and high mechanical strength in resulting parts. The major disadvantage to SLS is a limited selection of successful materials; thus far, predominant materials include polyamide-12 (PA12), polystyrene (PS), polyetherketone (PEK), and polycarbonate (PC).[2,3]

Focus for current research at LANL is to expand the limited selection of successful materials for SLS. A PA12 material supplied by EOS GmbH, known as PA2200, is being investigated because of its desirable list of properties respective to SLS. This includes low melting temperature, low heat conductivity, large range between melting and crystallization onsets, low melt viscosity, spherical particle shape, and narrow particle size distribution.[2] PA3200, which is PA2200 with a glass bead filler, is also being investigated. The intention to investigate PA2200 and P3200 derives from the hypothesis, if we are able to fully characterize a successful SLS material such as PA2200 and PA3200 and obtain their key material properties which enable it to be a successful SLS material, then we are better suited to qualify new materials based on the characterization procedure used for PA2200 and PA3200.

Obtaining an adequate characterization procedure is imperative because the limited selection of successful materials for SLS comes from not understanding which physical properties are vital for a material to be successful in this technique.[4] Substantial research is being done on identifying the key physical properties for SLS materials and resulting, new materials are beginning to emerge.

Regarding the physical properties of the powder material, particle size and shape are important. The laser used in SLS has a spot size of 100-150 µm, so particles cannot be larger than the thickness of the laser; otherwise, two particles are unable to be sintered.[5] Therefore, size distributions between 20 µm and 80 µm are common in successful materials. Furthermore, a powder must not contain too many small particles and instead it must have a median around 50 µm.[6] Figure 1 below compares the distributions of two powders which nearly have the same median regarding a distribution based on particle volume, but not based on particle number.

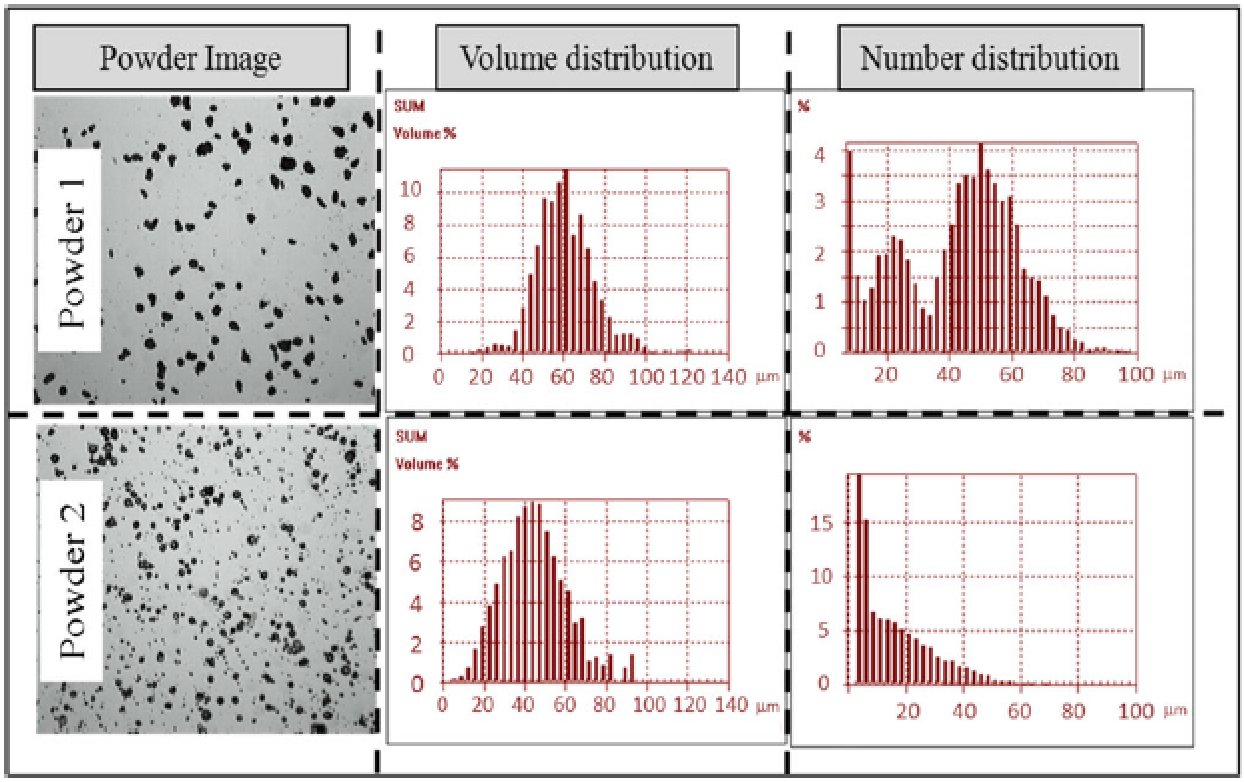
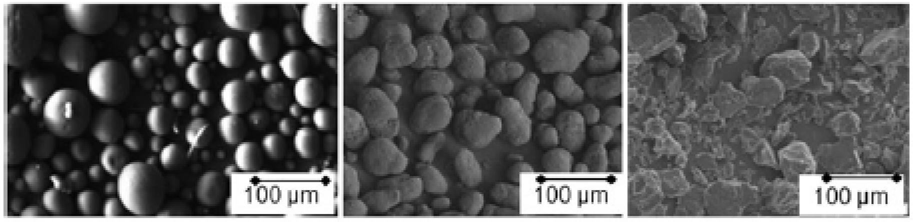


Figure 1: Volume and number particle size distributions of two SLS powder materials.[6]

Based on volume distribution, the two powders have nearly the same median. Based on number distribution, Powder 2 has noticeably more small particles than Powder 1. This poses an issue to the potential for Powder 2 to be used in SLS, because too many small particles induce a poor flow of the material. Poor flowabilty prevents SLS processing.[6]

Particle shape also affects flowability. Smooth, spherical particles minimize interparticle adhesion and friction, thereby promoting greater flowability.[5] Figure 2 shows the difference in appearance between spherical particles and other particles.



spherical particles potato shape particles cryo milled particles

Figure 2: Difference in appearance of spherical, potato-shaped, and cryo-milled particles.[6]

Powders are processed in three common ways: co-extrusion with soluble/insoluble mixtures, precipitation, and cryogenic milling. These processes develop the powder to be spherical, potato-shaped, or rough, respectively.[6] In some cases, glass beads are mixed with a powder to further enhance its flowability.[5] One such commercial material is PA3200 supplied by EOS GmbH; PA3200 is the same PA12 powder as PA2200 but filled with glass beads.

A large range between the melting and crystallization onset temperatures is vital for successful SLS processing. The range between these temperatures is known as the “sintering window."[6] Figure 3 below shows DSC curve depicting the sintering window for a PA12 material.

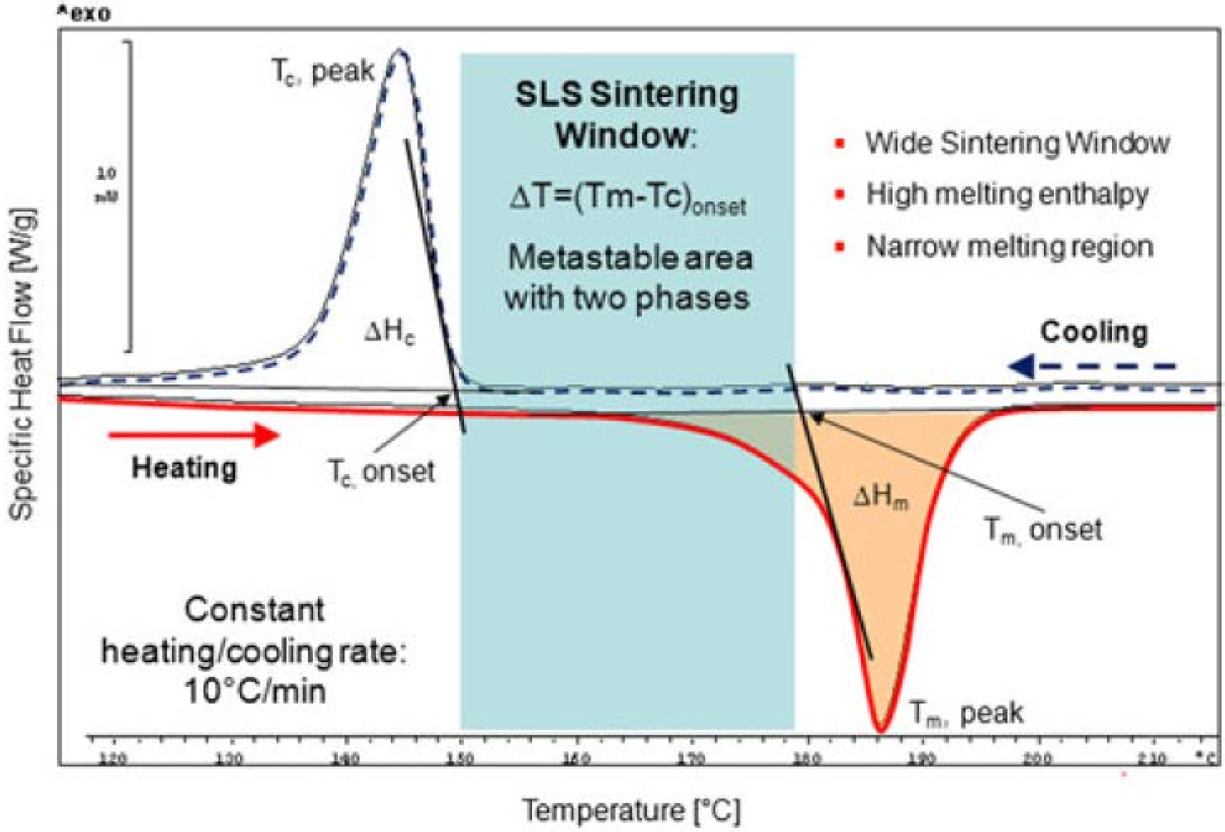


Figure 3: DSC curve performed on PA12 powder material to depict the SLS sintering window.[6]

The sintering window needs to be large because the powder is being held in between these two temperatures just before it is subjected to sintering by the laser. To promote adequate adhesion between the layer being sintered and the layer just below, the crystallization must be postponed for at least several of the layers.[6] By having a large sintering window, it becomes much easier to control the crystallization onset of these powder layers as well as prevent particles from entering a melt state prior to laser sintering.

Besides the key material properties, other investigations are being performed on a material's reusability for SLS processing. Only 10-20 percent of the powder material is used to manufacture parts in one build for SLS, while the remaining powder is utilized as support for the part but is not sintered by the laser.[7] The material not used is referred to as "recycled" material as it is replaced into the SLS machine for the next print job. The additive manufacturing community has identified differences between parts manufactured from virgin and recycled powders. Figure 4 shows these differences.

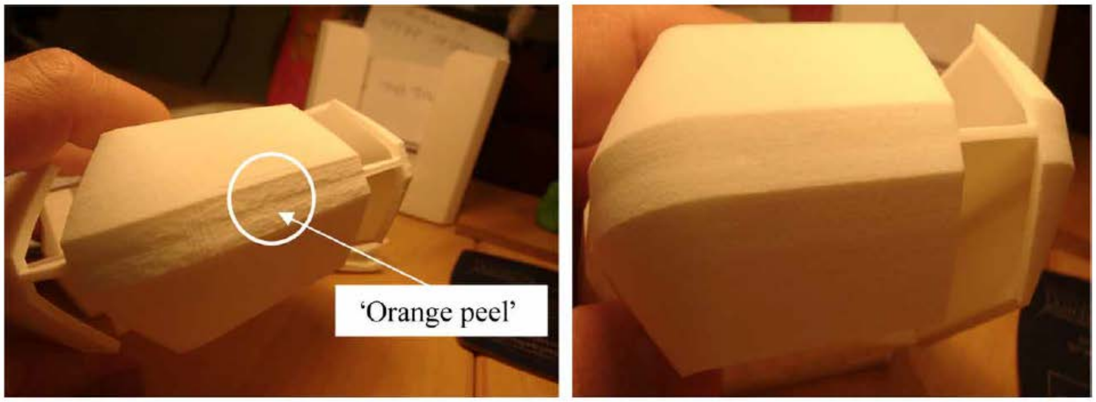


Figure 4: Surface texture differences known as "orange peel" on a part manufactured using powder material which has been recycled too many times (left). Smooth surfaces manufactured with adequate quality powder material (right).[8]

From figure 4, a surface texture known as "orange peel" is developed when a powder material exceeds the limit of time it can undergo SLS processing. Surface textures come out smooth if a powder is utilized before this limit is reached. The poor surface texture arises because the powder material is held above its glass transition temperature for the duration of SLS processing. These conditions enable the molecular chains to continue polymerizing, thereby increasing molecular weight as well as the melt viscosity.[8]

SLS powder manufacturers have thus developed guidelines regarding proper recycling techniques, but they are largely inefficient. Therefore, identifying a characterization procedure on powder quality is also of interest.

Experimental Method

PA2200 and PA3200 powders, both virgin and recycled for each, were investigated. Regarding thermal characterization, thermogravimetric analysis (TGA) measured the decomposition temperature and filler content for each powder material. A calibrated TGA Q500 from TA Instruments was used. Method used was a ramp from 25°C to 600°C at 10°C/min. Sample was held under nitrogen atmosphere throughout the measurement.

Differential Scanning Calorimetry (DSC) was employed to identify the virgin powders' sintering window and to detect any changes in melting and crystallization temperatures between virgin and recycled powders. A calibrated DSC Q2000 from TA Instruments was used. Method used was an equilibration at 25°C, followed by a ramp to 210°C at 10°C/min. The sample was then held isothermal at 210°C for 5 minutes, and then cooled to 25°C at 10°C/min. Sample measurement was performed in nitrogen atmosphere.

Bulk density (BD) measurements were used to obtain the Hausner ratio (HR) for each powder. The Hausner ratio is the ratio of the tapped BD, ρ_{tapped}, to the poured BD, ρ_{poured}. The Hausner ratio is a measure of a powder's flowability; the lower the ratio, the higher the powder's flowability.[9,10] A calibrated Mettler Toledo XS204 analytical balance was used to obtain weight measurements. A 50 mL graduated cylinder, Fischer No. 08-550E with TD ± 1.0 mL at 20°C, was used for volume measurements. Poured BD was obtained by recording the mass of a clean, empty 50 mL graduated cylinder as M_1. The powder was then poured at 60° angle into the cylinder through a funnel. The volume taken up by the powder was recorded as V_1. The cylinder was placed back onto the analytical balance and the mass was recorded as M_2. Then, the cylinder was manually tapped three times from roughly a 3-inch height onto a soft notebook. The new volume taken up by the powder was recorded as V_2. The following equations were then used for calculated poured and tapped BD.

Equation 1: $$\frac{M_2 - M_1}{V_1} = \rho_{poured} \left(\frac{g}{mL}\right)$$

Equation 2: $$\frac{M_2 - M_1}{V_2} = \rho_{tapped} \left(\frac{g}{mL}\right)$$

Three runs for each powder material were performed and an average calculated.

Results and Discussion

TGA served to measure decomposition temperatures to prepare our method for DSC, as well as to detect any changes in filler content for PA3200 between recycles. Figure 5 below displays TGA curves for all four powder materials.

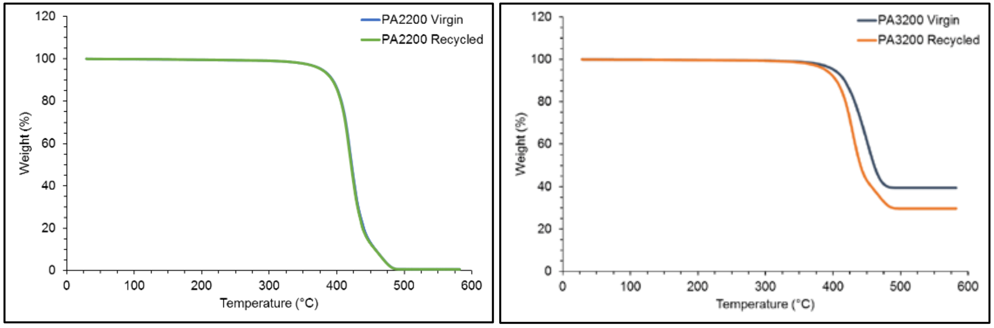


Figure 5: TGA curves of PA2200 virgin and recycled (left) and PA3200 virgin and recycled (right).

Table 1: Decomposition temperatures and residue content of PA2200 and PA3200 virgin and recycled powders.

Sample Name	Degradation Onset Temperature (°C)	Residue (%)
PA2200 Virgin	399.18	0.6017
PA2200 2x Recycled	399.38	0.5731
PA3200 GF Virgin	414.5	39.38
PA3200 GF 2x Recycled	403.1	29.68

Both the virgin and recycled materials for PA2200 produced very little residue and degraded at nearly the same temperature. There is notable difference in the onset of degradation for PA3200 powder as well as the residue content between the virgin and recycled powders. After PA3200 is recycled, the degradation occurs 11°C sooner than with virgin PA3200. The residue content is also 10% less than the virgin. Since TGA only measures the weight loss of a sample as it is heated under a nitrogen atmosphere, the change in residue content cannot be inferred to be a chemical cause. Rather, it is likely there is less glass filler content in the recycled material than in the virgin material. Throughout the recycling and SLS machine preparation processes, the glass filler is heavier than the PA12 powder, so it could have fell to the bottom and resulted in less filler content in the powder used. The change in degradation onset temperature also supports this conclusion since the recycled PA3200 degradation temperature approaches that of the PA2200 powder.

DSC successfully identified the sintering window of these powders and detected chemical changes within the recycled material. Figure 6 shows the DSC curves for each material.

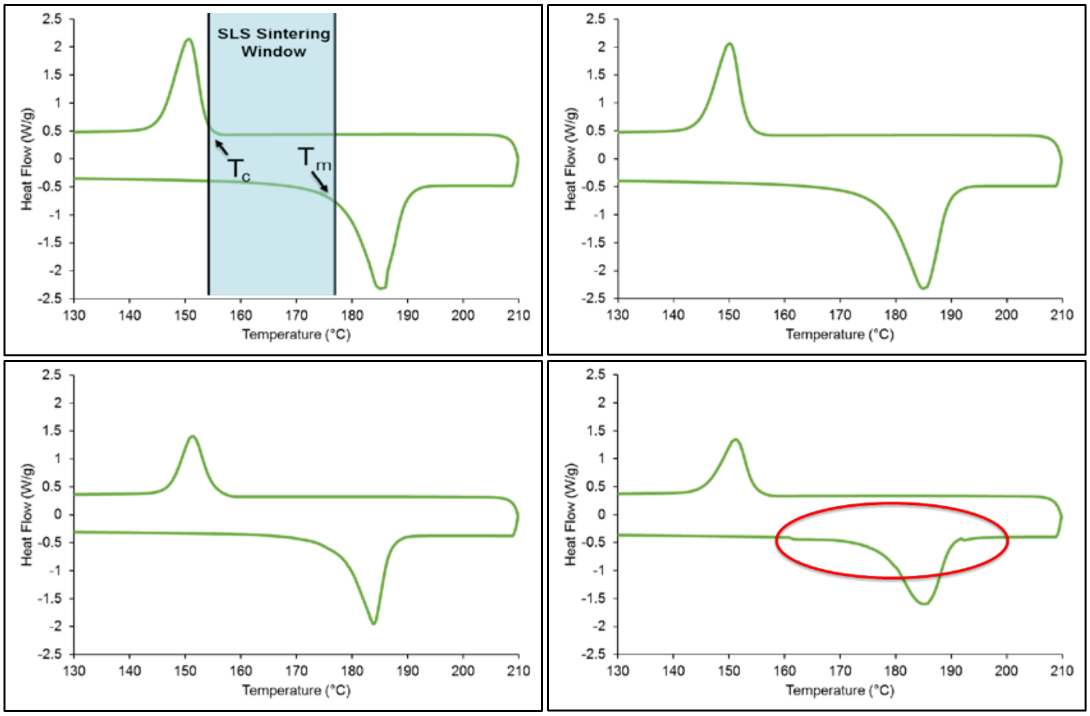


Figure 6: DSC curves for PA2200 Virgin (top-left), PA2200 Recycled (top-right), PA3200 Virgin (bottom-left), and PA3200 Recycled (bottom-right).

Table 2: Calculated sintering window values for PA2200 and PA3200 virgin and recycled powder materials using their respective melting and crystallization onsets.

Sample	Melt Onset (°C)	Crystallization Onset (°C)	Sintering Window
PA2200 Virgin	174.9	154.3	20.6
PA2200 Recycled	174.0	154.1	19.9
PA3200 Virgin	176.7	155.8	20.9
PA3200 Recycled	174.4	155.3	19.1

Regarding PA2200 virgin material, our calculated melting temperature (185.17°C) matched those found in literature.[4,5,6] The recycled PA2200 curve looks nearly the same as the virgin PA2200 curve, and there are little differences between the melt and crystallization onsets. The identification of the SLS sintering window is labeled on the PA2200 virgin DSC curve in figure 6. Regarding PA3200 powder results, recycled PA3200 shows shouldering at the melt endotherm peak, possibly indicating end of material life.

The melting endotherm is characterized by crystalline regions of the polymer material, as shown in figure 7.[6,8]

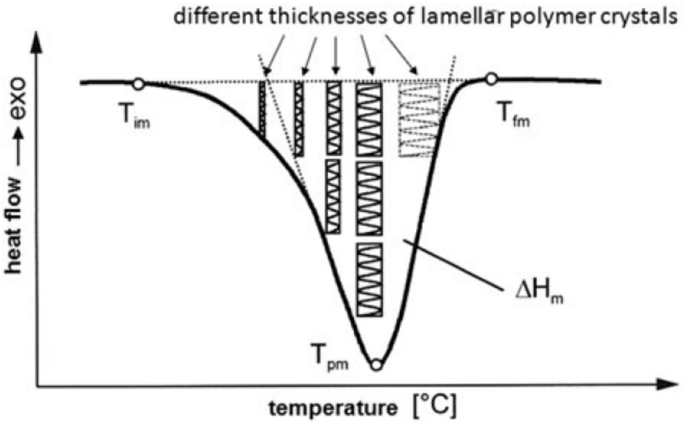


Figure 7: Depiction of how a polymer's lamellar crystal sizes can determine the shape of the melting endotherm peak.[6]

The melting peak of a polymer's DSC curve will be shaped based on the thickness of its lamellar crystals. Thus, PA3200 recycled material's crystalline regions must have changed through SLS processing since the melting peak showed shouldering. This is likely the reason since Pham et al. noted that an SLS material's deterioration occurs between the glass transition and melting temperature, where the powder begins to crystallize due to the long-range molecular motion enabled above the glass transition of the polymer.[8] Furthermore, there is a slight increase in peak melt temperature for PA3200 recycled from the virgin (183.87°C for recycled and 185.77°C). The shape for the recycled material's melting peak also seems more broad than that for the virgin material.

Hausner ratios were calculated for each powder material, but showed only slight changes between a virgin to recycled and between PA2200 and PA3200. The results are shown in table 3.

Table 3: Averaged poured and tapped bulk density measurements for PA2200 and PA3200 virgin and recycled powder materials. Hausner ratios are calculated.

Powder Material	ρ_{poured} (g/mL)	ρ_{tapped} (g/mL)	Hausner Ratio
PA2200 Virgin	0.433	0.466	1.08
PA2200 Recycled	0.403	0.433	1.07
PA3200 Virgin	0.578	0.621	1.07
PA3200 Recycled	0.494	0.537	1.09

In all powders, the tapped BD is always greater than the poured BD. This result is expected as a powder should pack more closely together when it has been put under some force. For both PA2200 and PA3200, the BD decreases as either powder is recycled. This observation infers the flowability of the powder is diminishing with recycled powders, however the calculated Hausner ratios for each recycled powder does not support this observation. If a recycled powder's flowability is less than its virgin material, then the Hausner ratio for the recycled should be higher than the virgin. However, PA2200 recycled powder produced a Hausner ratio of 1.07 while the virgin produced 1.08. The virgin is higher, inferring the virgin has a greater flowability to the recycled. The opposite occurs with PA3200, where the virgin shows a greater flowabilty with 1.07 as the Hausner ratio while the recycled has 1.09. Furthermore, PA3200 contains glass beads which serve to enhance the powder's flow properties. The Hausner ratio results in table 3 support the glass beads did enhance PA3200's flowability since its virgin ratio value was lower than the virgin ratio value for PA2200.

Conclusion

The objective of this investigation was to develop a characterization procedure which would identify key material properties for a powder material which would make it successful for SLS processing. Along with that, the second objective was to identify appropriate analysis techniques which detect changes in powder quality in recycled SLS powders; the second objective serves to build a path forward to identify when a powder is no longer useable.

TGA analysis succeeded only in detecting changes in the filler content of filled SLS powders, but was unable to detect changes between a virgin and recycled powder material. TGA can ensure a powder is mixed with appropriate filler content. On the other hand, DSC analysis identified changes in a polymer powder's crystalline structure, which is representative of the powder's quality. Shouldering around the melting endotherm peak was present in the recycled PA3200 material, which is attributed to the powder being of poor quality and spending too much time in SLS processing. DSC will be utilized in the future to detect changes in a powder's quality to ensure high quality of end-use parts.

Finally, BD measurements also identified changes in a powder's quality by detecting lower flowability between a virgin to recycled material. Both DSC and BD can be used to detect a powder's quality by chemical and physical changes, respectively. These analysis techniques serve as a start to develop both characterization procedures initially set out to identify. Future directions involve acquiring more instrumentation to support DSC and BD, and hopefully the new instrumentation will be more sensitive to changes in powder quality.

References

[1] Kumar, S. Selective Laser Sintering: A qualitative and objective approach. *Journal of Materials* **2003**, 43-47.

[2] Wendel, B.; Rietzel, D.; Kühnlein, F.; Feulner, R.; Hülder, G.; Schmachtenber, E. Additive Processing of Polymers. *Macromolecular Matierals and Engineering* **2008**, *293*, pp 799-809.

[3] Wudy, K.; Lanzl, L.; Drummer, D. Selective laser sintering of filled polymer systems: Bulk properties and laser beam material interaction. *Physics Procedia* **2016**, *83*, 991-1002.

[4] Vasquez, G.M.; Majewski, C.E.; Haworth, B.; Hopkinson, N. A targeted material selection process for polymers in laser sintering. *Additive Manufacturing* **2014**, *1*(4), 127-138.

[5] Verbelen, L.; Dadbakhsh, S.; Van den Eynde, M.; Kruth, J.; Goderis, B.; Van Puyvelde, P. Characterization of polyamide powders for determination of laser sintering processability. *European Polymer Journal* **2016**, *75*, 163-174.

[6] Schmid, M.; Amado, A. Materials perspective of polymers for additive manufacturing with selective laser sintering. *Journal of Materials Research* **2014**, *29*(17), 1824-1832.

[7] Dotchev, K.; Yusoff, W. Recycling of polyamide 12 based powders in the laser sintering process. *Rapid Prototyping Journal* **2009**, *15*(3), 192-203.

[8] Pham, D.T.; Dotchev, K.D.; Yusoff, W.A.Y. Deterioration of polyamide powder properties in the laser sintering process. *Journal of Mechanical Engineering Science* **2008**, *222*, 2163-2176.

[9] Liu, L.X.; Marziano, I.; Bentham, A.C.; Litster, J.D.; White, E.T.; Howes, T. Effect of particle properties on the flowability of ibuprofen powders. *International Journal of Pharmaceutics* **2008**, *362,* 109-117.

[10] Ziegelmeier, S.; Christou, P.; Wöllecke, F.; Tuck, C.; Goodridge, R.; Hague, R.; Krampe, E.; Wintermantel, E. An experimental study into the effects of bulk and flow behavior of laser sintering polymer powders on resulting part properties. *Journal of Materials Processing Technology* **2015**, *215*, 239-250.