

# **Investigation of the Thermophysical Properties of Recycled Polyamide Materials used for Selective Laser Sintering**

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## **Abstract**

The purpose of this research is to investigate the thermophysical properties of polymer materials used for selective laser sintering (SLS). After repeated use, the thermophysical properties of these polymer materials can be altered and by using recycled polymer material, the quality of manufactured parts from SLS could be jeopardized. The two materials being analyzed in this research are DuraForm® PA and DuraForm® GF. Differential scanning calorimetry (DSC) was used to look at the melting temperature shifts between virgin and recycled polymer material. A 4°C increase in the melting temperature of the recycled PA material was found and there was no difference in melting temperature observed for the GF material. Scanning electron microscopy (SEM) was used to analyze the particle size of the virgin and recycled polymer materials. ImageJ software was used to analyze the average particle size of the materials. The optimal average particle size is recommended to be between 75 – 150 µm. The results from the SEM images show that the recycled polymer materials fall within this optimal particle size range. The molecular compositions of the materials were also analyzed by using nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) in order to see if there was any change in either the molecular formula of the materials or shifting of functional groups. These studies confirm that the chemical composition of the recycled material is unaltered. Based on these findings, slight changes in selective laser sintering process parameters such as laser power and glaze temperature can be exploited when using recycled polymer material to manufacture parts.

**Keywords: Selective Laser Sintering, Polyamide Nylon Powder, Differential Scanning Calorimetry (DSC)**

## **1. Introduction**

Rapid prototyping (RP), also referred to as solid freeform fabrication (SFF) is a technology used for the automatic construction of three-dimensional models. Computer aided design (CAD) such as SolidWorks software is used to create cross-sections of a desired part to be manufactured and RP machines take this data and build the part layer by layer using additive polymer resins or powders<sup>5</sup>.

Selective laser sintering (SLS) is a popular form of RP and has many industrial applications. The materials used for SLS are commercially available polymers (nylon, glass filled nylon or polystyrene) or metals (titanium, steel or composite alloys). A high powered laser is used to fuse the powder material together in cross-sectional areas. Once a cross-sectional area of the part is fused, the part is lowered within the machine and another layer is fused on top of the former layer. This procedure is repeated until the part is made which is removed from the machine and cleaned<sup>4</sup>.

Parts which are created through SLS can be made from either virgin powder material or recycled powder material. However, there are many considerations to be taken into account when using recycled powder. The physical properties of these materials can be altered through repeated use within the SLS machine, which can ultimately jeopardize the mechanical strength of the parts being made<sup>2</sup>. The purpose of this paper is to explore these altered physical properties and to determine whether recycled materials are suitable or to what extent they are usable for manufacturing purposes. A few of the main physical properties of interest are average particle size, melting and crystallization temperatures and chemical structure.

## **2. Prior Studies**

In 2005, Andrew Hollett, a former Milwaukee School of Engineering Research for Undergraduates participant, performed research on the thermal analysis of the selective laser sintering process. Using an infrared thermocouple (IRt/c), the changes in DuraForm<sup>®</sup> Polyamide (nylon) powder were measured during, and after the sintering process. A temperature profile was obtained, and a linear relationship between laser power and temperature increase was found. Therefore, materials which have high melting points, require more laser power during the sintering process in order to produce higher quality parts<sup>3</sup>.

In 2004, research on the effect of the properties of the polymer materials on the quality of selective laser sintering parts was done at the Huazhong University of Science and Technology in Wuhan, China. The research looked at the effect of the properties of the polymer materials, such as molecular weight, molten viscosity, crystallization rate and the particle size of the powder, on the quality of selective laser sintering parts. The results indicated that the molecular weight affects the quality of the SLS parts through the melting viscosity. Crystallinity largely affects the precision of the SLS part and the particle size of the powder affects not only the precision but also the density of an SLS part. The optimal particle size is about 75-150  $\mu\text{m}$ <sup>1</sup>.

In 2006, research on the effects of processing on microstructure and properties of SLS Nylon 12 was done at Loughborough University, in Loughborough, United Kingdom. This research looked at how the molecular weight of parts was significantly higher than virgin powder but used powder also showed an increase in molecular weight as well. The parts had improved elongation at break parts built from the used powder and there was an increase in tensile strength with machine parameters selected for improved strength<sup>2</sup>.

## **3. Theory**

The SLS materials being analyzed are polyamide (PA) and glass filled polyamide (GF). PA is an aliphatic polyamide with a low monomer content in melt-equilibrium, low moisture absorption and low density compared with other polymers. It is not sensitive to stress cracking and has excellent impact strength at dry or low temperatures which makes this material desirable for

rapid prototyping purposes. GF is glass reinforced polyamide which gives the material an elevated temperature resistance and additional mechanical stiffness<sup>1</sup>. These materials can be commercially obtained through several manufacturing companies; the samples used during this research were acquired through 3D Systems.

### **3.1. effect of particle size on manufactured parts**

The particle size of SLS materials greatly affects the precision and density of a part. The optimal particle size should be between 75-150  $\mu\text{m}$ . If the particle size is too small, the powder can be difficult to spread on the platform bed within the SLS machine which causes self-reuniting between particles. If the particle size is too large, a step-effect can occur once the part has been made. Also, the part will have a lower density due to the large particle size which ultimately decreases its mechanical strength. In order to build high-precision SLS parts, a smaller particle size is desirable<sup>2</sup>.

### **3.2. effect of melting temperature on manufactured parts**

Materials chosen to be used for SLS have a large difference between the melting and crystallization temperature. If this temperature range is too narrow, warping can occur in the SLS part after it has been sintered. If the range is large enough, the warping will not be as serious or will not occur at all. When the material has been sintered, the melted powder will stay in the liquid phase as it is cooling down. While in the liquid phase, the material does not accumulate stress, so the cooling process should be slow and gradual. If the part cools down too quickly, then stress points can accumulate on the part which causes it to warp once it has hardened. Therefore, polymer materials which have a large difference between the melting and crystallization temperatures are desired<sup>1</sup>.

### **3.3. effect of chemical structure**

After an extended life time of use, the polymer materials used in the SLS machine may undergo molecular reformation. As the material is heated and cooled repeatedly during the part manufacturing process, cross linking can occur between adjacent particles. If the molecular composition of material is altered, then adverse effects may be seen in the parts after they are sintered<sup>4</sup>.

## **4. Methodology**

The powder specimens were analyzed for average particle size using an scanning tunneling microscope (STM) , melting and crystallization temperatures through differential scanning calorimetry (DSC), and chemical structure using infrared spectroscopy (IR) and nuclear magnetic resonance (NMR).

### **4.1. preparation of powder samples**

The powder samples were prepared from virgin stock and recycled stock. Virgin powder has never been used for part production within an SLS machine while the recycled material has been through at least one full SLS run. These materials did not come from the same stock, but are rather being used in order to find a general relationship between virgin and recycled PA and GF materials.

#### **4.2. average particle size**

Images were produced of the virgin and recycled powder samples using an Hitachi S-570 Scanning Electron Microscope. The samples were coated with 21 nm of gold using an SPI Sputter Coater. Images were taken at 30x and 100x magnification for both PA and GF virgin and recycled samples. The average size of the particles was obtained using software provided through ImageJ.org.

#### **4.3. melting temperatures**

Differential scanning calorimetry (DSC) was used to determine the melting temperatures of the samples. The samples were weighed at 12 mg and were heated from 25°C to 225°C at 10°C/min. The machine reads the amount of power used to keep the test sample at the same temperature as the reference at certain heating increments during the analysis. This allows the phase transition temperature to be found for the sample, such as the melting temperature.

#### **4.4. chemical structure**

Infrared spectroscopy (IR) was used to look at the different functional groups of the materials. In order to determine the actual molecular structure of the materials, nuclear magnetic resonance (NMR) was used. This will show if there are any changes in the functional groups of the recycled powder from that of the virgin powder.

### **5. Results and Analysis**

#### **5.1. average particle size analysis**

Using software provided through ImageJ.org, the images obtained from the SEM were analyzed in order to find the average diameter of the particles of each sample. The particles were measured along their height and width and an average diameter was found for the larger particles contained within the images for each sample. Figure 1 shows the SEM images taken at 100x magnification for virgin and recycled PA and GF material. The largest sized particles for the virgin PA sample were found to be between 110µm and 120µm which falls within the optimal particle size range, which was expected. The largest sized particles for the recycled PA sample were around 75 µm, which is still within range. The virgin GF sample showed larger particles ranging between 85µm to 115µm, which again, is within optimal size range as to be expected. The recycled GF particles ranged between 90µm and 110µm, still within optimal range. Both recycled materials still within the optimal particle size range. This indicates that even after an extended period of lifetime, these materials can still be used for further part processing without jeopardizing part quality due to material particle sizes which are either too big or too small.

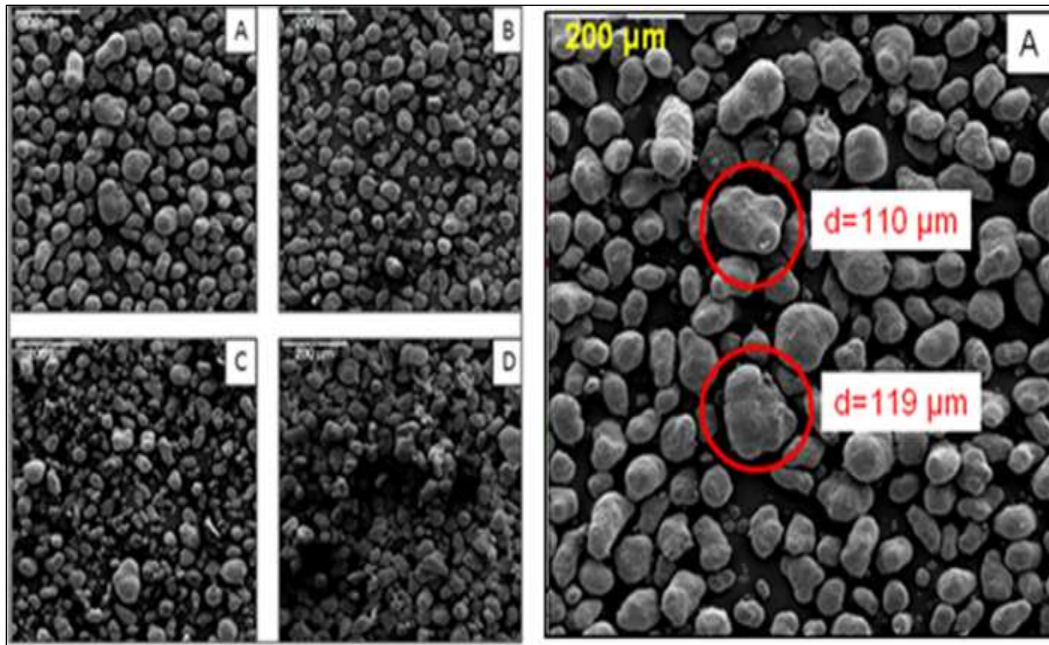


Figure 1. On the left are SEM mages taken of the samples at 100x magnification. A) Virgin PA, B) Recycled PA, C) Virgin GF, D) Recycled GF. On the right is a close up of image A) with larger sized particles circled in red.

## 5.2. melting temperature analysis

The samples were run through a differential scanning calorimeter and transition temperature curves obtained. Figure 2 shows these curves for the virgin and recycled PA and GF samples. The curves show the temperature at which each sample underwent a melting transition. The tip of the peaks in the graph, represent the exact temperature at which these transitions occurred. The virgin PA sample showed a melting point around 184°C while the recycled PA sample showed a melting point around 188°C, a 4°C melting temperature difference between the recycled and virgin PA samples. The virgin GF sample showed a melting point around 184°C and the recycled GF sample showed a melting point around 184°C as well. The melting temperature difference between the virgin and recycled PA samples suggests that SLS part processing parameters should be slightly adjusted due to the increased melting point of the recycled PA material. The laser power used to sinter the recycled PA material should be increased accordingly in order to produce higher quality parts. Since there was no change in the melting point between the virgin and recycled GF material, these SLS parameters do not need to be regarded for further part processing when using this particular material.

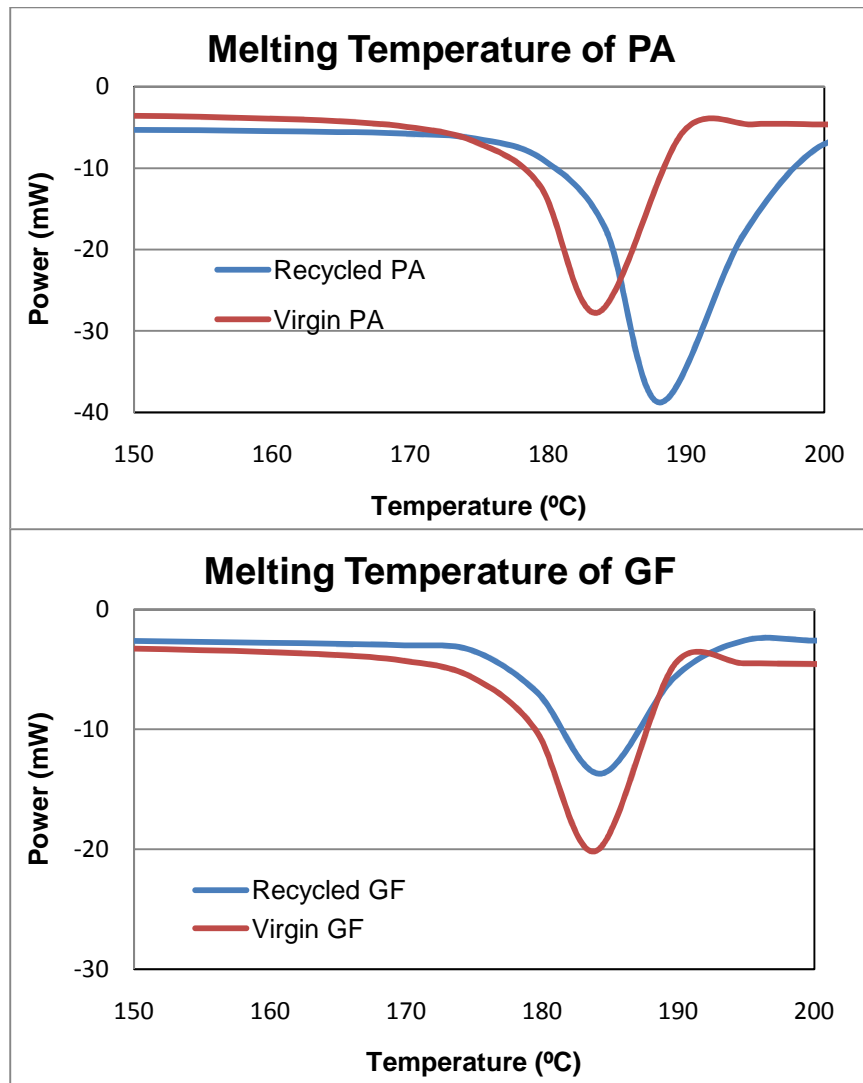


Figure 2. DSC curves for virgin and recycled PA and GF materials.

### 5.3. chemical composition analysis

The purpose of looking at the chemical composition of the recycled materials is to determine whether any chemical changes have occurred after the material has undergone part processing cycles. In order to investigate any chemical changes, infrared spectroscopy was used in order to determine the functional groups inherent in the materials. The molecular chain of the PA and GF materials are  $-\text{[NH}_2\text{-(CH}_2\text{)}_{11}\text{-CO]}_n\text{-}$  which is repeated over and over in polymer form<sup>6</sup>. These functional groups: amide, alkane and carbon double bond oxygen should all be accounted for after analyzing the IR data. The amide will show absorbance peaks at frequencies of  $3050\text{-}3325\text{ cm}^{-1}$ ,  $1510\text{-}1570\text{ cm}^{-1}$  and  $670\text{-}800\text{ cm}^{-1}$ . The alkane should show peaks around  $2800\text{-}3000\text{ cm}^{-1}$  and  $1370\text{-}1470\text{ cm}^{-1}$ . The amide carboxylic group will show a peak right around  $1645\text{-}1690\text{ cm}^{-1}$ . Figure 2 shows the absorbance spectra for the virgin and recycled PA materials. The amide, alkane and C=O functional group fingerprints are all represented in the spectra. The recycled powder spectra is nearly identical to the virgin spectra, which suggests that no chemical changes

have occurred within the recycled material. Figure 3 shows the absorbance spectra for the virgin and recycled GF materials. Again, the functional groups are accounted for, and there are some slight changes due to the glass pellets imbedded in the GF powder. Again, there is no change between the virgin and recycled GF absorbance spectra which suggests no chemical changes have occurred.

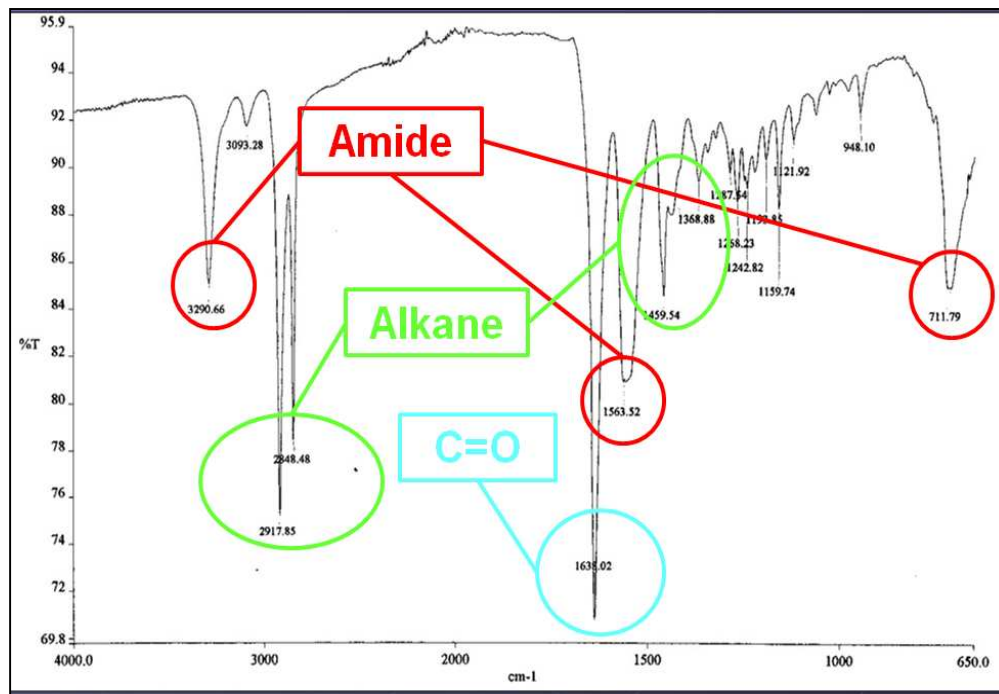


Figure 3. IR absorbance spectra for recycled PA material.

The NMR data, once analyzed, showed the same results as the IR data. When comparing the recycled material chemical shifts with the virgin material chemical shifts, there was no change in chemical composition between the recycled and virgin materials. Again, this suggests that while the material undergoes some processing time, the chemical properties of the material are not changed or altered in such a way that the part quality during processing will be jeopardized. Figures 4 and 5 show the NMR data for the virgin and recycled PA and GF data. These chemical shifts represent the types of function groups present in the material as well as how many hydrogen molecules there are. Since this material is a polymer, there is an unlimited number of hydrogen molecules present on the alkane chain. However, the NMR data shows that there are no chemical changes occurring in the recycled materials, since the readouts are identical to the virgin readouts.

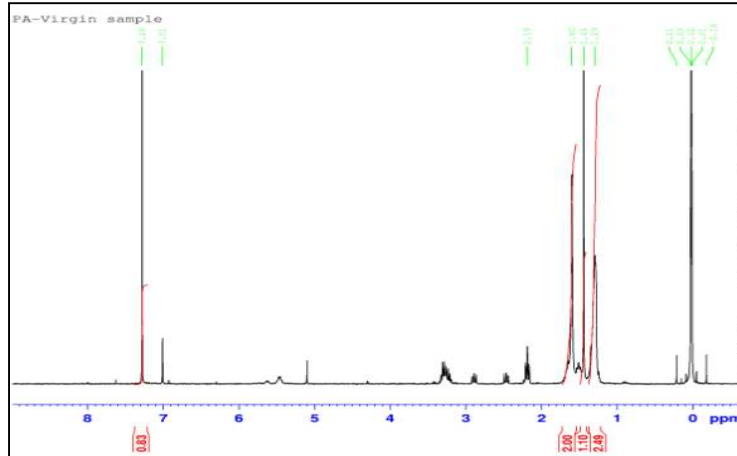


Figure 4. NMR results for virgin PA material.

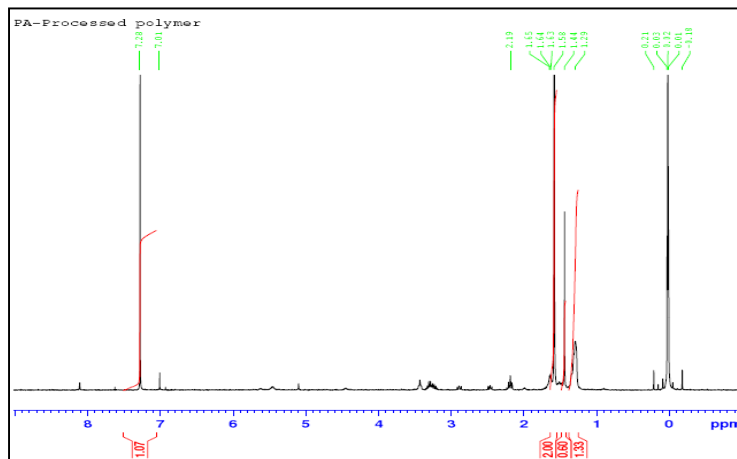


Figure 5. NMR results for recycled PA material.

## 6. Conclusions

After analyzing the average particle size, melting temperature and chemical structure of the PA and GF recycled materials, it was found that the recycled material can still be used for further part processing. The average particle size of the recycled materials still fell within the optimal particle size range in order to build high quality parts during the SLS process. The melting temperature of the recycled PA materials increases slightly from the virgin material. This suggests that SLS parameters such as laser power and holding temperature should be adjusted accordingly in order to use the recycled material to continue building high quality parts. After analyzing the IR and NMR data, there was found to be no chemical structure changes occurring within the recycled materials.

These materials can be considered to be green materials since they are capable of being recycled in order to build high quality SLS parts. SLS parameters such as laser power and holding temperature should be taken into account when using the recycled materials, though the quality of the parts can be controlled and adjusted for. Future research on these materials would

include a study of the molecular weight between processed parts from both virgin and recycled materials. As well, the samples could be prepared from stock which has a known processing lifetime and both virgin and recycled materials originate from the same base stock for the materials.

An interesting study might be done on how all of these characteristics, such as melting temperature, average particle size, chemical structure and molecular weight change with processing life time of the powders and to see what kind of relationship these parameters have with time. Another characteristic that would need to be found for these materials is the crystallization temperatures. In order to accurately describe these materials, the difference between the melting and crystallization temperature would need to be assessed in order to find out how long these materials stay in the liquid phase during the cooling process inside of the SLS once a layer has been fused together.

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## 8. References

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