SLS Processing Studies of Nylon 11 Nanocomposites

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Abstract

Selective Laser Sintering (SLS) is widely used for rapid prototyping/manufacturing of nylon 11 and nylon 12 parts. This processing technique has not been explored for nylon nanocomposites. This study investigates the technicalities of processing nylon 11-clay and nylon-carbon nanofiber nanocomposites with SLS. Microstructural analyses of the SLS powders and parts were conducted under SEM. Results suggest that SLS processing is possible with the new nylon 11 nanocomposites. Yet the SLS parts built have inferior properties relative to those of injection molding, suggesting that more fine tuning for the processing is required.

Introduction

Selective Laser Sintering (SLS), which is widely used for rapid prototyping (RP) and Solid Freeform Fabrication (SFF), is a layered manufacturing method that creates solid three-dimensional objects [1]. The powdered material is sintered together, layer by layer (0.003” to 0.006”); by a computer-directed CO_2 laser [2]. Additional powder is deposited on top of each solidified layer and again sintered, until the parts complete. Selective Laser Sintering can be used in every stage of the product development cycle, from the production of one-shot models to functional test parts, to series of components [3]. Very little laser power is required to sinter the material in SLS because the parts are built in an atmosphere that controls the thermal distribution. Furthermore, no support structure is required because the part is supported by the powder in the build chamber during the fabrication [4]. The SLS process has arguably the widest range of engineering-grade rapid prototyping materials available in the rapid prototyping industry.

It is believed that any material that can be densified by traditional sintering techniques can be processed by SLS, for example Al_2O_3, SiC, and Zr composites [5]. Yet, the polyamide material, such as nylon 11 and nylon 12, is more widely used in the industry because it allows the production of fully functional prototypes with high mechanical and thermal resistance comparing with other materials currently used in SLS. In addition, polyamide SLS parts have excellent long-term stability and resistance against most chemicals [3]. However, the flammability, thermal, and mechanical properties of such kind of materials are inferior to those of the polymer nanocomposites required in high-end use. Polymer nanocomposites were formed by the introduction of selective nanoparticles into the polymer by melt blending. These nanocomposites are new materials to SLS, and the goal of our project is to develop some basis for characterizing and setting new materials up for SLS manufacturing. This project is aimed to develop a systematic characterization of new materials for SLS manufacturing, using selected new polyamide nanocomposites as examples.

Experimental

Selective Laser Sintering Principle

SLS operates on the principle that fine powders (50-80 microns) would be warmed, and laser would bombard on selected locales and sinter the material. Thus, the material in the middle must be maintained at slightly below melting point, and the laser would sinter at a temperature above the melting point. The difference between the melting temperature of the part bed and the recrystalization temperature of the sintering powder is, then, the window of operation. Nylon 12 has a wider window than nylon 11; but due to its higher cost, the development of nylon 11 is deemed necessary.

Manufacturing Parameters

Hitherto, several operating parameters are critical for SLS manufacturing process. Careful controls and extensive empirical testing are usually required for a new material. The laser power controls the sintering temperature, and the part bed temperature controls the recrystalizing temperature. The scan speed, scan spacing, and other technical parameters are also important for the manufacturing process. For the PA 11 nanocomposite new materials, we mainly adopted conventional PA 11 operational standards for our first empirical attempts.

Sample Preparation

Polymer powders have to be considerably dry, and ground down to an approximately equal size (50 to 80 microns). For the selected PA 11 nanocomposite, selected nanoparticles are first melt-blended with PA 11 by twin-screw extrusion, then chopped into pellets, and cryogenically ground down to 50 microns.

Material Characterization

Although SLS is very useful and convenient for prototyping, the number of kinds of materials currently used in it is still very limited. Nylon 11 and 12 (polyamide 11 and 12) are the most popular thermoplastic polymer powders used in SLS. They have the attractive features of being self-supporting, and comparatively high mechanical and thermal resistance. Polyamide SLS parts have an excellent long-term stability and are resistant against most chemicals. Some SLS machines are even fine tuned for these materials. Although polyamide already has many attractive features, there is still room for improvement. We would like materials with higher mechanical, thermal, and reduced flammability properties, and polymer nanocomposite was found to serve well. Since SLS is such a useful tool, we would like to enhance and expand it with such kind of material.

For every new material, all parameters of the SLS machine need to be tuned. Therefore, the material needs to be characterized before the building of the SLS parts. Certain common characters of the material/powder are also needed for the successful and good SLS processing.

Melting Temperature CO_2 laser is used in SLS to sinter the powder together. Therefore, the power of the laser needs to be tuned to the level that the material will be melted for sintering, but will not be degraded. Glass temperature can be obtained by Differential Scanning Calorimetry (DSC). Part bed temperature also needs to be adjusted during the process. Since the part bed will lower a little bit after a layer of powder is sintered, heat will be trapped in the part bed. If the temperature is too high, the part will be melted after the build is finished. On the contrary, if the temperature is too low, the part will be tilted.

Particle Shape and Size The ideal shape of the powder/particle is spherical. The conventional size of particle used is about 80µm. Scanning Electron Microscopy (SEM) can be used to check these properties. It was thought that smaller particles may yield better build. It may not necessary be the case. Smaller particles may be harder to be picked up and affect the build. The size of our powder is 50µm and the shape is irregular due to the processing method.

Particle Flow Dynamics and Melt Flow Index Moisture will affect the flow of powder and the powder pick-up by the roller of the SLS machine, which may result in the uneven powder covering on the part bed. Therefore, dry powder is required. Although the index may not directly tell us the dryness of powder, it may give us the idea if extra drying procedure or additive is needed when comparing with the index of dry nylon 11.

These material criteria are critical information for optimizing the operational parameters. The information is extremely helpful in presetting parameters; however, further empirical studies are required to quantify an exact correlation.

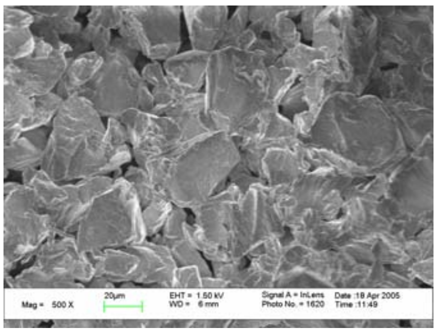
Discussion of Results

Our new materials are PA 11 melt-blended with the following nanoparticles at different weight percent as shown in Table 1.

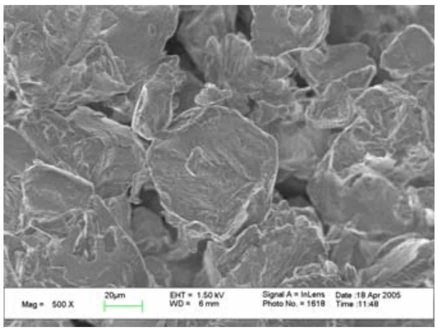
Table 1 Material Matrix for Resin/Nanoparticles

RESIN (WT PERCENT)	NANOPARTICLES (WT PERCENT)	NANOPARTICLES TYPE
PA11 100%	0%	None
PA11 95%	5%	Cloisite® 30B
PA11 95%	5%	Cloisite® 93A
PA11 95%	5%	PR-24-PS Carbon Nanofiber
PA11 93%	7%	PR-24-PS Carbon Nanofiber

The composite polymer was grinded to 50 microns after the blending, with a narrow size distribution. The powder is then observed under SEM for shape analysis. Figure 1 and 2 shows selected SEM images.



(a)



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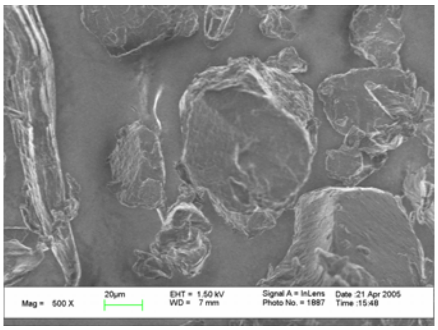
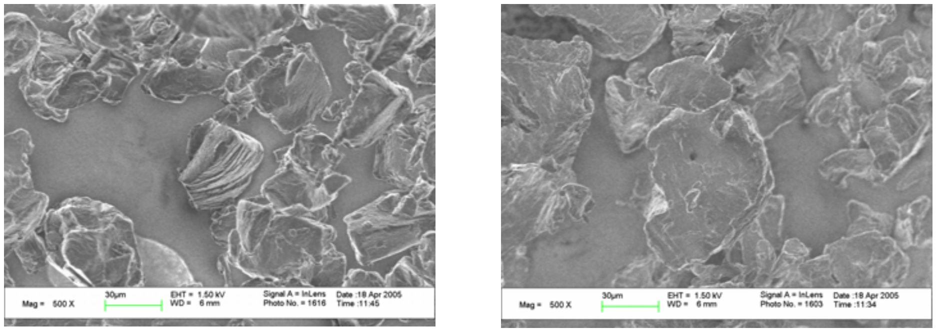


(c)

Figure 1 SEM micrographs of SLS powders: (a) Baseline, (b) 5% Cloisite® 30B, (c) 5% Cloisite® 93A



(a) (b)

Figure 2 SEM micrographs of SLS powders: (a) 5% PR-19-PS CNF, and (b) 7% PR-19-PS CNF.

As previously noted, we conducted the SLS manufacturing operation under conventional PA 11 settings. Figures 3 through 5 show some of our finished products.

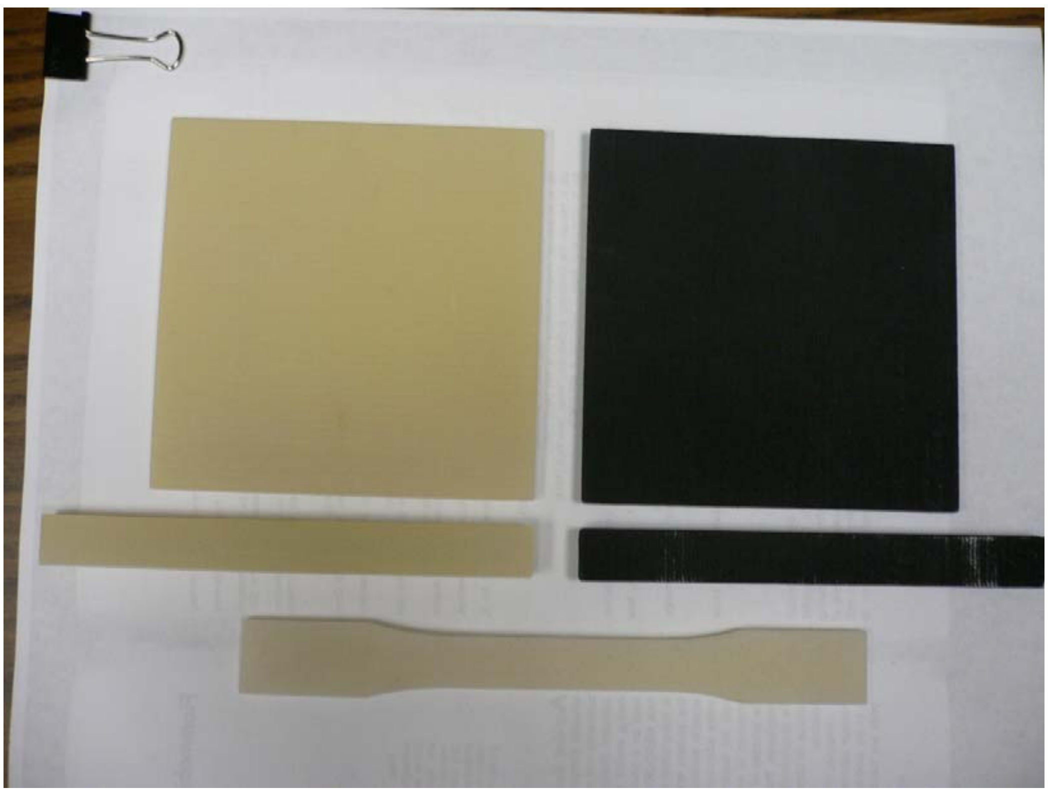


Figure 3 Finished products from SLS process: Cloisite® 30B (light) and PR-19-PS CNF (black).

Figure 4 SLS processed part, a plate for cone calorimetry, made of Nylon 11/5% PR-19-PS carbon nanofiber.

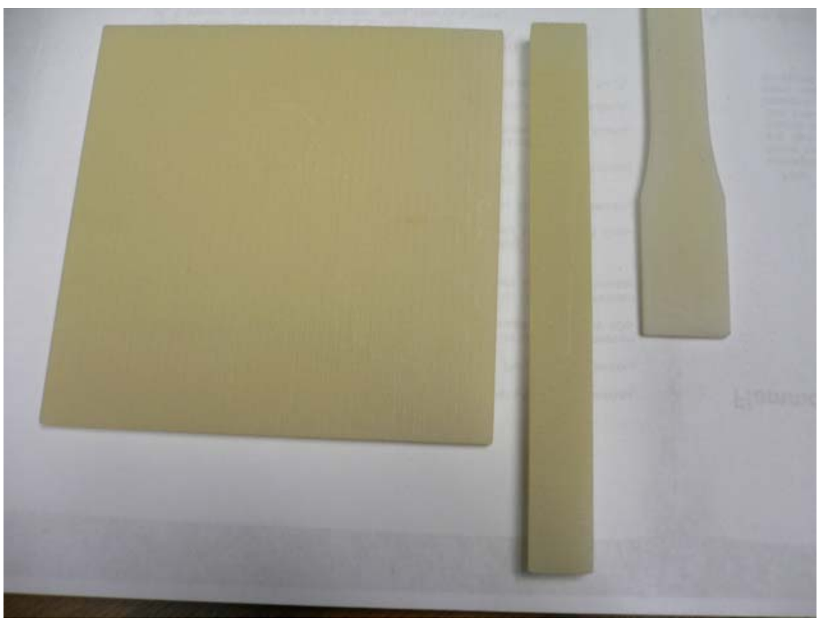


Figure 5 SLS processed parts, a plate for cone calorimetry (left), a HDT specimen (middle), and tensile specimen (cropped, right), made of Nylon 11/5% Cloisite® 30B nanoclay.

Figure 6 shows the SEM images of the fracture surface of a tensile specimen of 5% CNF PR-19-PS. Pores are observed at this magnification in SLS parts.

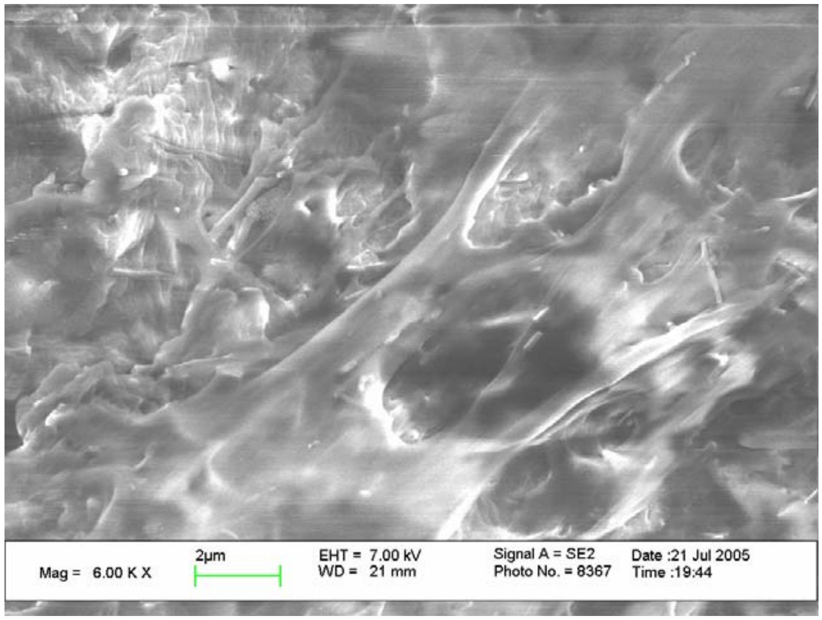


Figure 6 SEM image of the fracture surface of a tensile specimen (Nylon 11/5% PR-19-PS CNF). Pores are noted.

Particle flow is studied by melt flow index and a qualitative study of powder dynamics. Next, DSC is obtained from each of the selected materials, such that the operating window can be determined. Lastly, the melting point of the material is obtained, such that the part bed temperature is ensured to stay below the melting point.

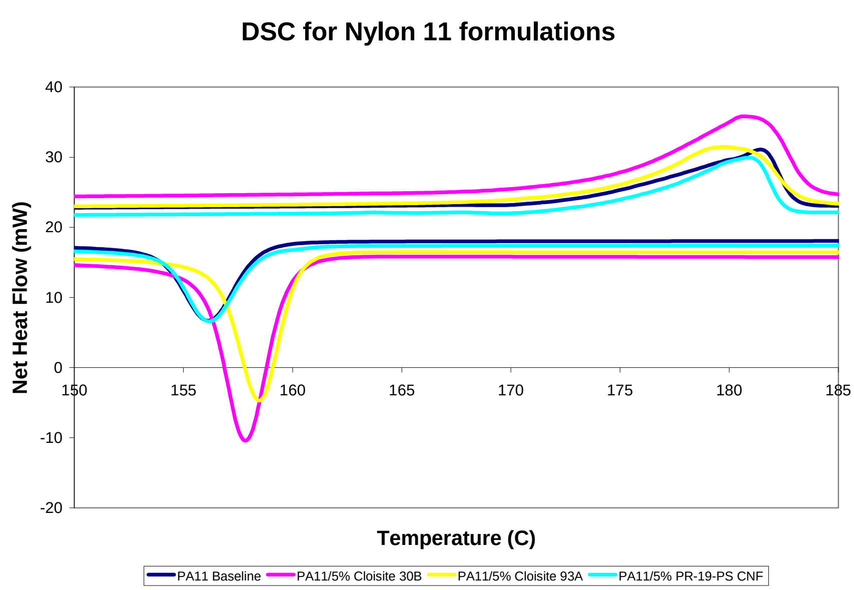


Figure 7 DSC plots of selected Nylon 11 formulations.

Two problems are noted. First, the products appeared overheated. From Figure 7, it is apparent that the new materials have different thermal properties and require different operating parameters, namely, lower laser power and lower part bed temperature. Further trial-and-error testing will be required to fine-tune the process. Secondly, from the SEM images shown, it is noted that there is a substantial fraction of pores in the SLS part, which yields a lower specific gravity and thus impede upon mechanical and thermal properties. It is believed that a better powder geometry and powder flow dynamics could improve the specific gravity of the products.

Summary and Conclusion

Nylon 11 polymer nanocomposites, which were compounded via twin-screw extrusion, were introduced as new SLS materials. Material powders were characterized using SEM, melt flow index, DSC, etc. Operating parameters such as laser power, part-bed temperature, roller speed, etc. should then be set based on the material characters. Our SLS manufacturing operation, however, was conducted under the conventional PA 11 settings since no information was available for comparison because no SLS operations using similar materials were conducted. SEM images of the finished parts were analyzed.

The following conclusions were drawn from this study:

1. SEM images showed that the particles shape and size of our powder were irregular and around 50μm, whereas the ideal shape of the SLS powder was spherical and the conventional powder size is 80μm.
2. Different materials have different thermal properties, and therefore, different operating parameters are needed for the SLS operation.
3. Changes in any parameters may affect the thermal, mechanical, and flammability properties of the finished SLS parts.
4. Materials characterization helped presetting the operating parameters.
5. Further systematic testing is required to fine-tune the process/parameters.

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