

THE DEVELOPMENT OF A SLS® COMPOSITE MATERIAL

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ABSTRACT

The development of a commercial SLS nylon-based composite material (LNC 7000) is described. Nylon composite candidate systems with different volume fractions of a number of glass fiber and glass bead reinforcements were screened. It was found that fully dense SLS parts with excellent mechanical properties could be made from a number of reinforced nylon materials. An optimized material containing 29 volume percent 35 μm diameter glass beads was selected based on the processing behavior and mechanical properties of the candidate systems. The performance of this optimized material is described. In addition, complementary aspects of the composite nylon and unreinforced nylon materials (LN 4010 and LNF 5000) are discussed.

1. INTRODUCTION

Composite materials are widely used in the polymer industry, particularly where increased stiffness and strength are required. There are many types of polymer composites. The reinforcement phase can be in the form of continuous roving, a woven fabric, short fibers, irregular particles, or regular spheres. Expensive, high performance reinforcements such as carbon/graphite are available, as are inexpensive, lower performance reinforcements such as glass. The polymer binder phase can be thermoset or thermoplastic, depending on the type of process used to make the part and the desired properties. Injection molded composites, which typically consist of a ductile, thermoplastic binder reinforced with short fibers or a particulate, are a particularly important type of polymer composite.

Selective Laser Sintering (SLS) is now widely used to produce fully-dense functional prototypes from nylon (LN 4010 and LNF 5000). Nylon parts produced with the DTM™ SLS process have properties representative of some common injection molded engineering thermoplastic parts (1). These parts are produced directly from CAD data without support structures or post-curing (2).

Composite material parts have been produced with SLS technology at the University Texas at Austin and at DTM Corporation. These composite parts have typically been made from polymer coated metal and ceramic materials in which the polymer binder is less

than 20 volume percent of the part. These porous SLS parts are typically post-processed at high temperatures to obtain the final desired properties (3 - 6).

In this paper, the development of a SLS composite material (LNC 7000) based on nylon is described. The goal was to produce full density parts with properties more representative of injection molded thermoplastic composites. In contrast to previous SLS composite work, the polymer binder in this material is greater than 70 volume percent of the part. The experimental screening and optimization, and work performed to develop the commercial system are described, as are the performance and processing advantages of this material.

2. EXPERIMENTAL

2.1 Screening Nylon composite candidate systems with different volume fractions of various glass fiber and glass bead reinforcements were screened. The screening experiments were limited to composites containing fibers or beads, since only discontinuous reinforcements are compatible with current SLS powder feeding. In addition, only glass reinforcements were examined because of their availability and cost-effectiveness. Parts from the screening experiments were evaluated based on mechanical properties, ease of processing, breakout, and post-finishing. The screening experiments were followed by an optimization of the SLS nylon composite system based on the above criteria.

2.2 Fiber Reinforcements Fibers are a relatively efficient reinforcement geometry, typically increasing the stiffness, strength, and heat deflection temperature of parts relative to the unreinforced polymer. Two different types of glass fibers were screened for use as a SLS nylon reinforcement. The first fiber had a mean length of 85 μm , and a mean diameter of 10 μm , while the second had a mean length of 70 μm , and a mean diameter of 16 μm . The composite material based on the smaller diameter fiber exhibited poor bulk flow properties. One of the material requirements for SLS processing is that the powder flows freely, even at elevated temperatures, since powder flow is required to form each new layer. It is speculated that the poor flow of this system was due to the aspect ratio (8.5) of the fiber which results in significant fiber-fiber contacts and considerable fiber entanglement. The powder flow properties of the composite prepared with the larger diameter fibers were not adversely affected. The aspect ratio of this fiber material is 4.4. Composite parts with this fiber were fabricated with reinforcement levels of 9.6, 15, and 22 volume percent.

The fiber reinforced parts all showed greater modulus and strength compared to unreinforced nylon. SLS composite parts reinforced with 15 volume percent fiber showed an increase in tensile modulus of approximately 50%, and an increase in tensile strength of about 25%. The fiber composite parts were also found to exhibit complex anisotropy. Since the mean fiber length was 70 μm and the typical layer thickness approximately 100 μm , some degree of in-plane anisotropy would be expected. However, it was also found that stiffness and strength in the x direction (the direction of roller travel) were

significantly higher than in the y direction (transverse to the direction of roller travel) as shown in Figure 1. This effect is consistent with fiber alignment in the direction of the roller travel during leveling. The data in Figure 1 were generated by testing the tensile properties of specimens reinforced with 15 volume percent glass fibers built both in the x and y directions.

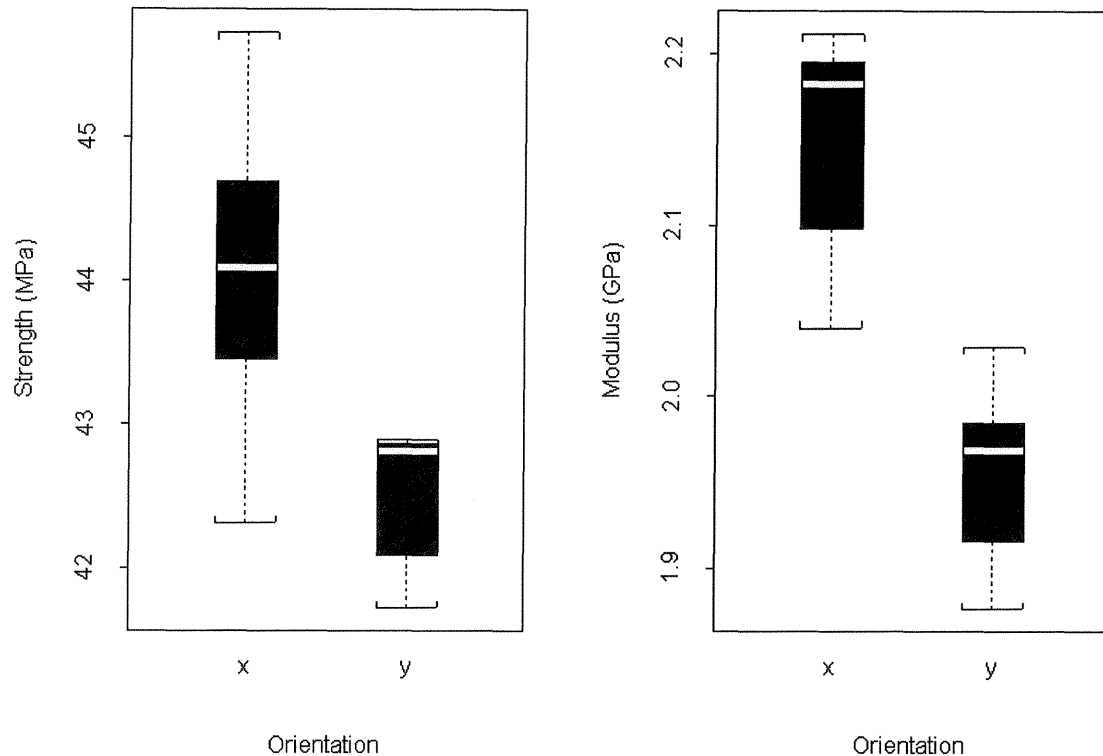


Figure 1: Anisotropy in Short Fiber Nylon Composite

This work clearly demonstrated that it is possible to produce SLS polymer composite parts with a short fiber reinforcement, with certain restrictions on the fiber geometry. Since the scale/offset compensation software allows different scale values to be applied in the x, y, and z directions, it should also be possible to build accurate parts with such a material. It was decided, however, to pursue isotropic systems which would offer many of the advantages of a fiber reinforced material without the complications of anisotropic shrinkage and mechanical properties.

2.3 Glass Bead Reinforcements Glass beads are a less efficient reinforcement than glass fibers, but parts made with spheres exhibit isotropic properties. Polymer parts reinforced with glass beads typically have a much higher modulus than unreinforced parts, but show only a small improvement in strength. In initial screening work, it was found that fully dense, isotropic parts with improved modulus could be produced with a number of glass bead materials. Further optimization work focused on materials made with a range of reinforcement levels and glass bead diameters.

2.3.1 Effect of Glass Bead Reinforcement Level Glass bead reinforced composites with reinforcement levels over the range 9 to 39 volume percent were examined. The modulus of a composite material will generally increase as the volume fraction of reinforcement increases until a packing limit is reached. The relationship between the modulus of a particulate reinforced composite and the reinforcement volume fraction can be modeled by (7):

$$\frac{\bar{p}}{p_m} = \frac{(1 + \zeta \eta v_f)}{(1 - \eta v_f)} \quad (1)$$

$$\eta = \frac{\left(\frac{p_f}{p_m} - 1 \right)}{\left(\frac{p_f}{p_m} + \zeta \right)} \quad (2)$$

Where \bar{p} is the modulus of the composite, p_m is the modulus of the binder, and p_f is the modulus of the reinforcement. The factors ζ and η are parameters which depend on the boundary condition between the matrix and reinforcement as well as the moduli of the matrix and reinforcement. The assumed value of ζ for this type of reinforcement in this regime of reinforcement volume fraction is 2. The experimental and theoretical values of tensile modulus are plotted as a function of volume percent reinforcement in Figure 2. The experimental data are for composites made with a mean glass bead diameter of 35 μm , although the modulus is not a function of the bead size.

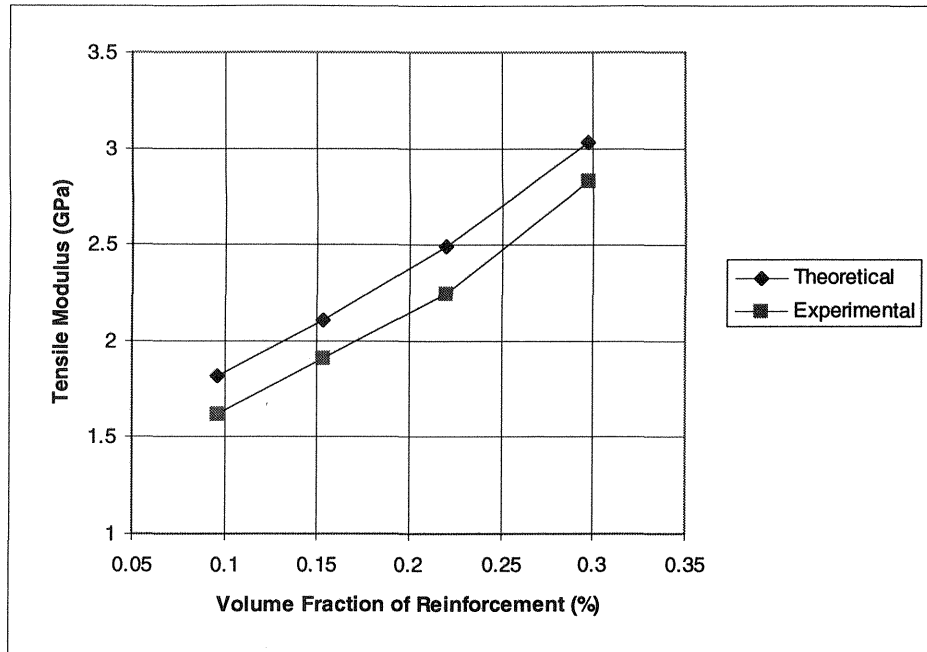


Figure 2: Theoretical and Experimental Values of Tensile Modulus

The experimental values were found to be in reasonable agreement with those predicted by the model up to a reinforcement level of approximately 29 volume percent. Up to this level of reinforcement, the composite modulus increases monotonically with increasing volume fraction reinforcement as expected. Above a reinforcement level of approximately 30 volume percent, parts were found to exhibit considerable porosity and the modulus/reinforcement level relationship predicted by Equation 1 was found to be no longer valid.

2.3.2 Effect of Glass Bead Diameter Composite materials with mean glass bead diameters ranging from 4 to 114 μm were studied. Materials made with bead diameters of 4 and 11 μm were found to exhibit poor bulk flow at high temperatures, presumably due to the higher interparticle friction found in extremely fine powders. As a result, only parts with bead diameters of 35, 49, and 114 μm were made and evaluated.

The relationships between glass bead diameter and tensile strength and glass bead diameter and ultimate elongation are shown in Figure 3. These samples all contained 29 volume percent reinforcement.

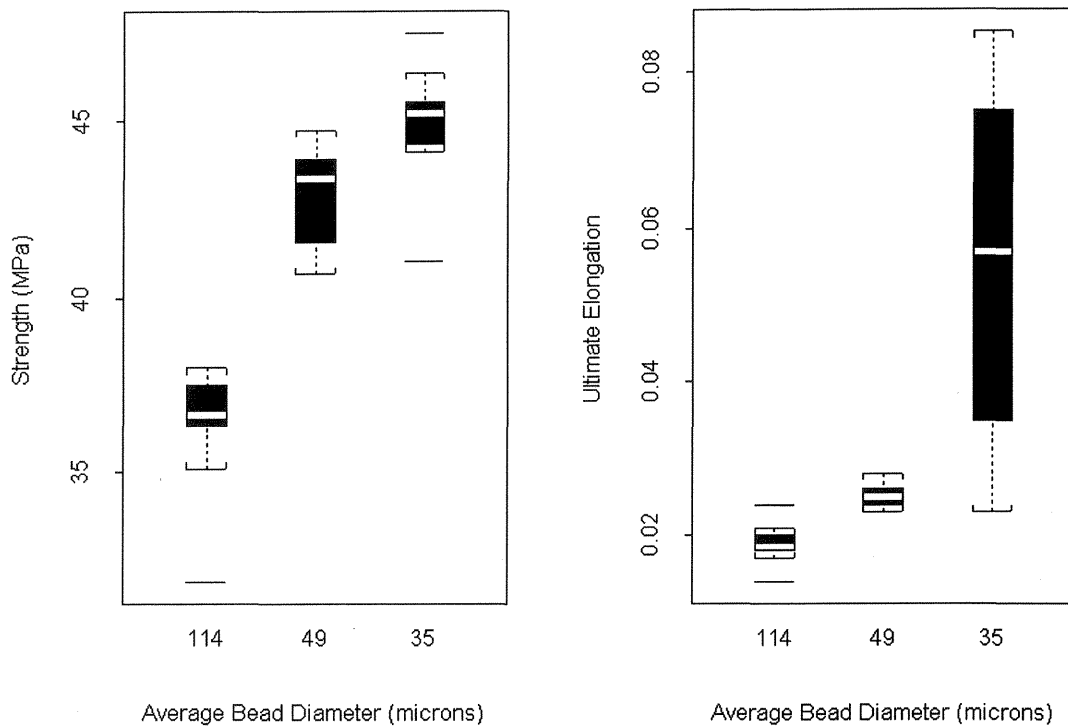


Figure 3: Comparison of Mechanical Properties by Reinforcement Bead Average Diameter

The tensile strength and ultimate elongation both increase with decreasing bead diameter. This is not surprising, since smaller size reinforcing particles generally provide a more homogeneous stress distribution and improved ultimate properties in composites (8).

A typical tensile fracture surface for a part made with 29 volume percent, 35 μm bead diameter glass beads is shown in Figure 4.

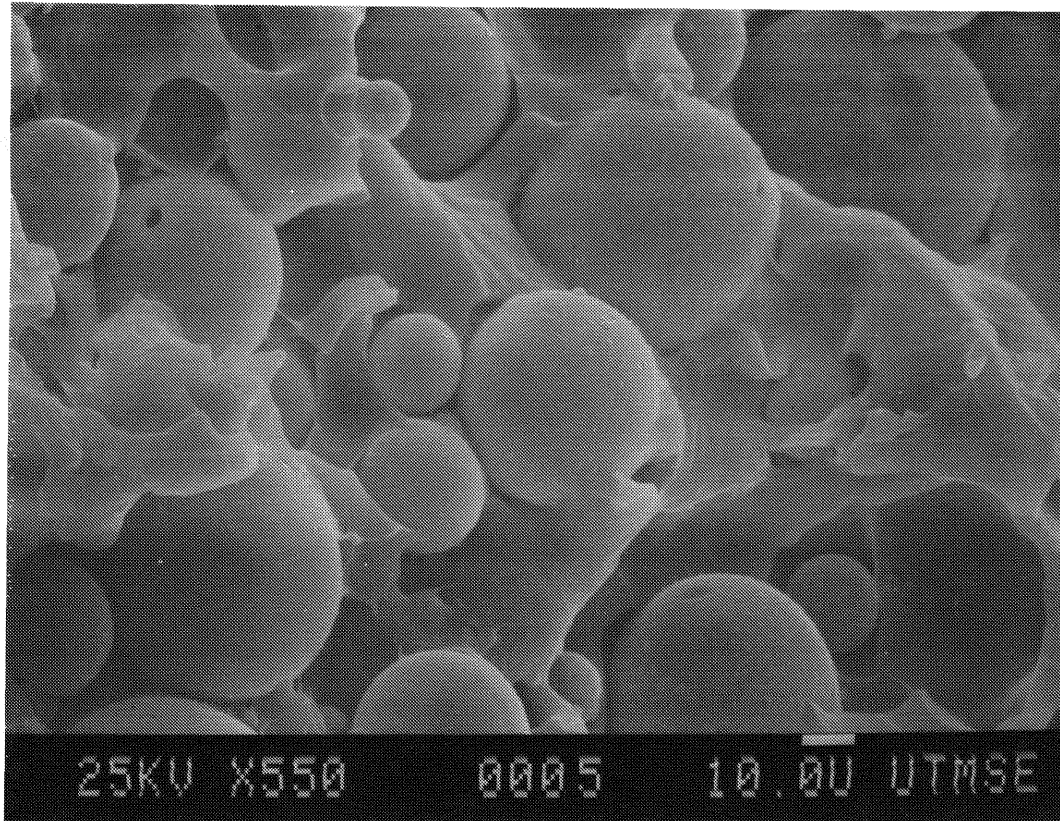


Figure 4: Fracture Surface of Nylon Composite

While there is some evidence of mixed-mode failure, the dominant failure mode appears to be debonding of the glass beads from the nylon polymer. It is speculated that the absence of consolidation pressure during the SLS process is primarily responsible for the limited adhesion. The limited adhesion probably contributes to the relatively high ultimate elongation of these composites, since failure occurs through gradual damage accumulation rather than catastrophic crack initiation and propagation.

3.1 DTM Nylon Composite: LNC 7000 Based on the data presented above, a nylon composite material reinforced with 29 volume percent 35 μm glass beads was chosen for commercialization. This material offers high modulus with good strength and ultimate elongation. Parts produced from this composite are shown in Figure 5. It was also found that the nylon composite system offers SLS processing advantages. In particular, the nylon composite material offers a broad processing window, reduced part warpage, easy part breakout, and easy finishing.

3.2 Nylon Composite Mechanical Properties The properties of the commercial nylon composite material (LNC 7000) are compared to those for unreinforced nylon (LN 4010 and LNF 5000) in Table 1.



Figure 5: LNC 7000 Nylon Composite Parts

Table 1: Comparison of SLS Nylon Composite (LNC 7000)
To Fine SLS Nylon (LNF 5000)

Property	Unit	Test Method	Fine Nylon	Composite
Tensile Strength	MPa	ASTM D638	36	49
Tensile Modulus	MPa	ASTM D638	1400	2828
Tensile Elongation	%	ASTM D638	32	6
Flexural Modulus	MPa	ASTM D790	870	4330
Notched Izod	J/m	ASTM D256	70	68
Unnotched Izod	J/m	ASTM D256	1370	443
Deflection Temp. Under Load (1.8 Mpa)	° C	ASTM D648	44	134

The tensile modulus of the composite is approximately twice that of the unreinforced nylon, while the flexural modulus of the composite is approximately five times greater than that of the unreinforced nylon. The tensile strength for the composite is approximately

30% higher than that of unreinforced nylon, while the heat deflection temperature of the composite is 90° C higher than unreinforced nylon. As expected, the tensile elongation and notched Izod values for the composite are lower than those of the unreinforced nylon due to the presence of the brittle glass phase. The two nylon systems are complimentary; the unreinforced material offers outstanding ductility with good strength and heat resistance, while the composite material offers outstanding stiffness with even higher strength and heat resistance.

3.3 Processing Window The nylon composite material has a 3 to 4° C processing "window" (defined as the part bed temperature range over which a part can be successfully built) compared to only 1° C for the equivalent unreinforced nylon. This greater process latitude is probably due to the higher feed temperature (10° C) and lower part bed temperature (2 to 4° C) setpoints available with the nylon composite. As the difference between the feed and part bed temperature is reduced, there is less chance of "in-build" part warpage which is a primary SLS build failure mode. Within this 3 - 4° C temperature window, there is a striking interaction between part bed temperature and laser power which allows the user to adjust part density and detail resolution to the desired value. At the low end of the temperature window, higher laser power can be used to attain the same density that lower laser power will produce at the higher temperature. This behavior is illustrated in Figure 6.

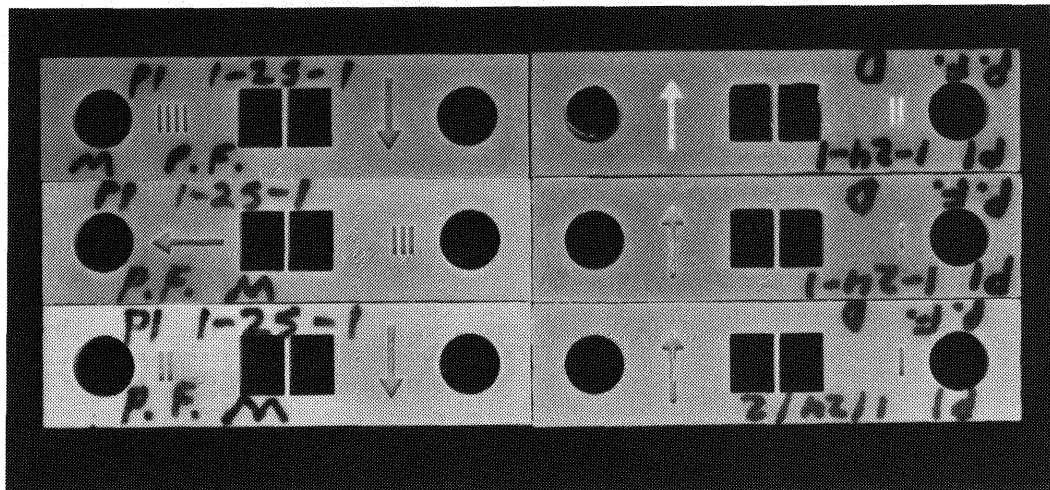


Figure 6: Laser Power Part Bed Temperature Interaction

The two columns of parts in Figure 6 correspond to two part bed temperature setpoints (194° C, and 195° C, from left to right) while the rows correspond to three laser power setpoints (0.75, 1, and 1.5 Watts, from bottom to top).

3.4 Part Breakout Nylon composite parts are generally easier to remove from the part cake (breakout) than unreinforced parts. This relatively easy breakout can probably be

attributed to reduced "growth" (unwanted powder sintering at part boundaries) which is the result of the lower part bed temperature and reduced laser power (approximately 2 watts vs. 4 watts) used with the nylon composite. In addition, the reinforced material probably has less intrinsic potential for growth due to the presence of the glass phase which cannot sinter at the nylon composite part bed temperature.

3.5 Part Warpage Parts made from nylon composite typically show less "post-build" warpage (approximately one half) than the corresponding parts made from unreinforced nylon. The composite parts shrink less than unreinforced parts (3% vs. 4%) which probably reduces their tendency to develop stresses and warpage as they are cooled from the build temperature to the breakout temperature.

3.6 Post-Finishing Nylon composite parts can typically be finished in approximately one half the time it takes to finish corresponding unreinforced nylon parts. The presence of the hard, brittle glass phase makes it easier to sand the composite parts. A typical nylon composite part can be finished to an average surface roughness of 2.5 μm RMS in 5 hours.

4. CONCLUSIONS

- Fully dense SLS parts with excellent mechanical properties can be made from nylon and a number of fiber and bead reinforcements.
- A commercial nylon composite material (LNC 7000) with 29 volume percent 35 μm glass bead reinforcement is now available. This material offers increased stiffness, strength, and heat resistance compared to unreinforced nylon as well as easy processing and post-finishing.
- The family of SLS nylon materials - unreinforced nylon (LN 4010 and LNF 5000) and composite nylon (LNC 7000) - offers a range of properties representative of many injection molded engineering plastics.

5. REFERENCES

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