**Selective Laser Sintering of Nylon 12-PEEK Blends Formed by Cryogenic Mechanical Alloying**

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## ABSTRACT

Cryogenic mechanical alloying (CMA) has been shown to be an effective means for producing composite powders with co-continuous phases throughout each particle. Consolidation of these composite particles via SLS presents the possibility of forming parts with a co-continuous microstructure. In this work the effects of milling time and PEEK volume fraction on the microstructure and mechanical properties of laser sintered Nylon 12-PEEK blends is studied. In both blends, the PEEK phase is incorporated to increase mechanical strength, stiffness and heat deflection temperature. Transmission electron microscopy and scanning electron microscopy is utilized to investigate the microstructure of the CMA powder and laser sintered parts.

## INTRODUCTION

The mechanical alloying (MA) process was originally developed in the late 1960s for solid state processing of dispersion-strengthened metal powders with fine microstructures. Pan and Shaw[1], pioneers in the field of mechanically alloyed polymers, assert that the "mechanical alloying technique promises to provide the ability to make almost infinite permutations of polymeric alloys. This means that once the process is better understood the properties of the alloy may be specifically designed resulting in a truly *Engineered Material*."

The mechanically alloyed materials are produced using a ball mill. The initial materials (in powder or pellet form) are placed in the ball mill's vial with two or more metallic or ceramic balls (Figure 1). In a vibratory ball mill, high-energy impacts between the balls and the material occur when the mill's motor vigorously shakes the vial, trapping material between the balls (and between the balls and the vial walls) with each agitation (Figure 2).

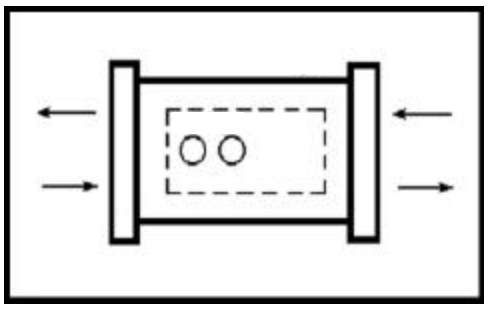

**Figure 1**. Schematic of vibratory ball mill vial and balls[2].

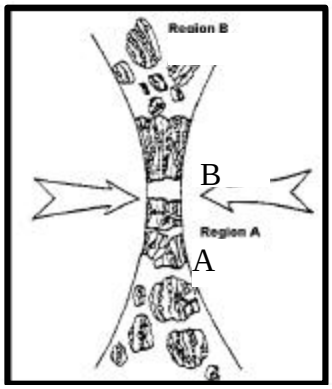


**Figure 2**. High-energy ball-powder-ball collision, resulting in welding (B), extensional flow, and fracture (A)[2].

As MA occurs, the particles are repeatedly fractured, deformed, and fused together. This process of repeated fracturing and cold-welding causes a refinement in microstructure with milling time. The result is a two-phase lamellar or plate-like microstructure with an interlamellar distance dependent on processing time[3,4] (Figure 3). Other processing parameters which affect the composite microstructure include the energy input, which can be controlled by manipulating the ratio of the total ball mass to the powder mass (charge ratio), milling temperature, ball mill design, and number and size of balls used. The milling temperature can be critical because of its affect on material ductility, recrystallization kinetics, and thermally-aided diffusion across interfaces.

Extrusion and injection molding require the polymers to flow on a macroscopic level, which would destroy the MA microstructure. Selective laser sintering (SLS), a process commercialized by DTM Corp., Austin, Texas, offers a means of consolidating polymer powders into part geometries with minimal flow of the polymers. Thus, SLS presents a means of producing functional part geometries while retaining the refined microstructure created during MA. Upon SLS of the MA powders it is postulated that co-sintering the two polymer phases present in each particle can occur (Figure 4).

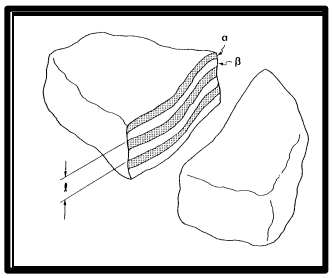


**Figure 3.** Two-phase lamellar microstructure of powder particles produced by mechanical alloying[5].

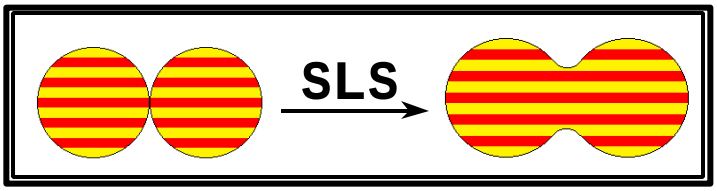


**Figure 4:** SLS of a two-phase lamellar powder.

This ongoing work investigates processing-structure-property relationships of CMA nylon-12 and poly(ether ether ketone) (PEEK). The aim of this study is to systematically control mechanically alloyed polymer-polymer composite microstructures by varying processing conditions, both in the mechanical alloying stage and the post-alloying selective laser sintering. A vibratory ball mill was used to produce blends, and electron microscopy techniques were used to investigate the effects of mechanical alloying time and temperature on the microstructure of these materials. Both powders were consolidated into tensile specimens using a lab-scale SLS unit. Mechanical testing and electron microscopy techniques were used to investigate the mechanical and morphological characteristics of the laser sintered samples.

## EXPERIMENTAL

*Mechanical Alloying Process*

A novel vibratory ball mill that is capable of operating at either ambient or cryogenic temperatures was designed and built by the authors. When operated at cryogenic temperatures, the vial is continuously exposed to a liquid nitrogen bath throughout the milling process. The ball mill can also be operated at ambient temperature by omitting the liquid nitrogen. The milling vial and balls (shown schematically in Figure 1) are stainless steel; the vial has an inside diameter of

77 mm, a length of 70 mm, and the diameter of each ball is 20 mm. A schematic of the ball mill is shown in Figure 5.

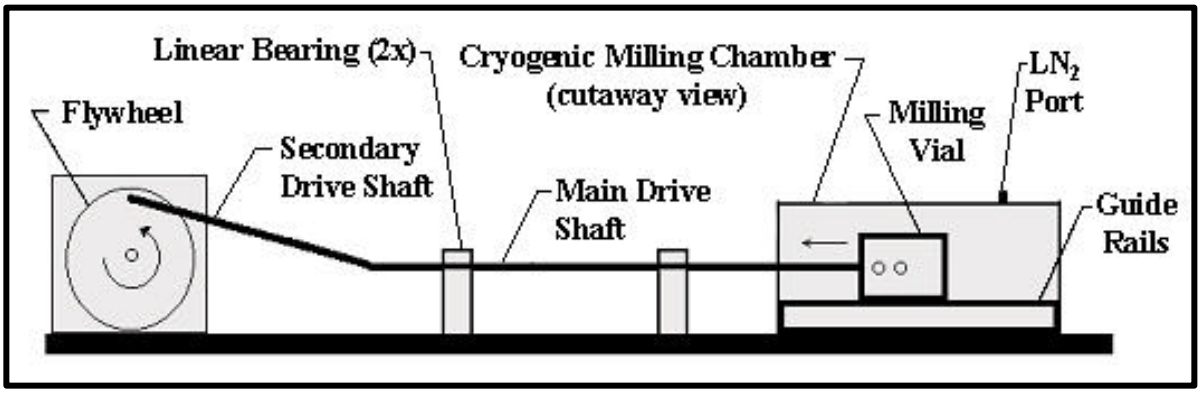


**Figure 5.** Vibratory ball mill with both ambient and cryogenic capabilities.

Mechanically alloyed micro-composites consisting of DTM DuraForm™ Polyamide (nylon 12) / Victrex® PEEK 150PF were produced from the individual components, in powder form, in 75/25 and 50/50 volume fractions. The powders were mechanically alloyed for periods of 10, 30 and 90 minutes at cryogenic temperatures. The DTM DuraForm™ Polyamide is specifically engineered for SLS applications

*Laboratory Scale Selective Laser Sintering Unit*

The selective laser sintering unit, shown in Figure 6, was designed and built by the authors to be used to test the applicability of a material to SLS processing on the laboratory-scale. Design and development of the lab-scale SLS unit was necessitated by the fact that approximately 40 ml of composite powder are produced for every run of the cryogenic vibratory ball mill. In the lab-scale SLS unit's present configuration, part geometries are limited to plaques and other flat test specimens.

The laser, mounted vertically in the SLS unit, is a $CO_2$ laser with a nominal power of 10W. The translation system, mounted in the bottom of the enclosure, has a travel of 152 mm x 152 mm. The part build area, shown in Figure 7, is a typical configuration in that the powder bed is indexed down after each layer is scanned; then additional powder is delivered by the motion of a counter-rotating roller traveling over the powder bed. Tensile specimens were fabricated from DTM DuraForm™ Polyamide in the lab-scale SLS unit to provide a benchmark for the capabilities of the unit and guide the design improvements. The average ultimate tensile strength of DuraForm™ Polyamide sintered in the lab-scale SLS unit was 38.5-3 MPa and the average strain at max stress was 9%; DTM reports a UTS of 44 MPa[6] and a strain to failure of 9%[5] for parts built using a Sinterstation® 2500plus.

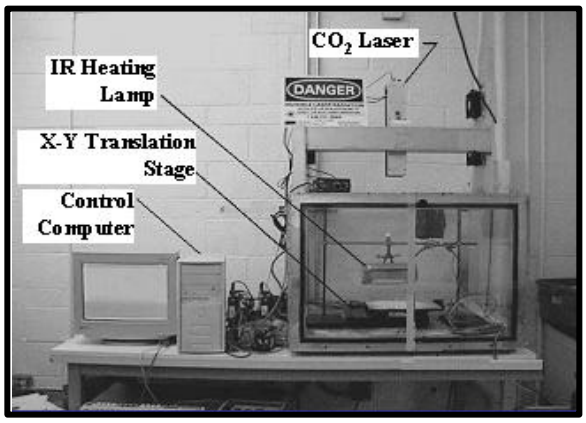


**Figure 6.** Laboratory scale selective laser sintering unit.

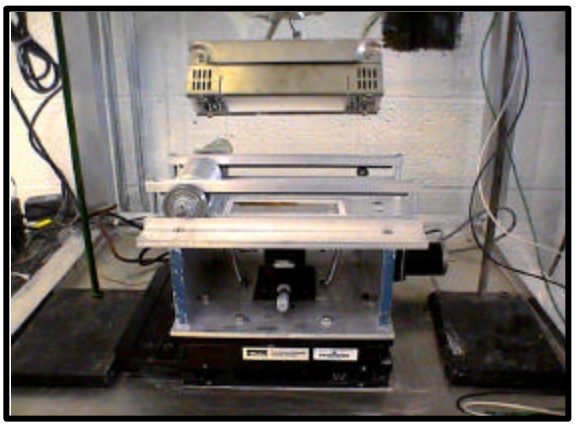

**Figure 7.** Laboratory scale selective laser sintering unit part build area.

*Electron Microscopy (SEM &TEM)*

An International Scientific Instruments SX-40 SEM was used to characterize nylon-12/PEEK powders before and after cryogenic mechanical alloying (CMA). The powders were sputtered with gold prior to imaging to avoid sample charging. Nylon-12/PEEK tensile specimens made via SLS were embedded in an epoxy mount and microtomed at room temperature. A Philips 420T Transmission Electron Microscope was used to image the microstructures at 100kV.

*Mechanical Testing*

Stress-strain curves, the ultimate tensile stress (UTS) and the strain at the UTS, were recorded for nylon-12/PEEK. Both the mean and standard deviation of the mechanical properties were calculated.

**RESULTS**

A scanning electron micrograph of a single nylon-12/PEEK powder particle MA cryogenically for 30 minutes is shown in Figure 8. While the flake-like structure of the alloyed particle is apparent from the micrograph, the individual PEEK and nylon phase domains are not discernable via scanning electron microscopy.

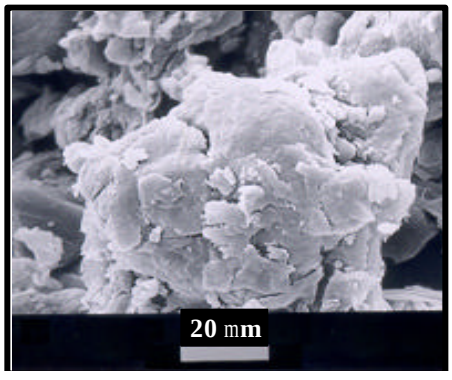


**Figure 8.** SEM micrograph of nylon-12/PEEK (75/25 vol. %) CMA for 30 min.

Difficulties in achieving a dense powder bed led to lower than desired mechanical properties in nylon-12/PEEK 75-25vol% (CMA 30min.) tensile specimens consolidated via SLS. The tensile specimens displayed visible cracks in each layer of the build due to the bed porosity. Selected mechanical property data and the SLS processing parameters are listed in Table 1. Powder bed density problems were attributed to the presence of significant fraction of powder particles with diameters of 10 microns or less, as shown in Figure 9. The small particles or fines lead to increased interparticle friction and thus decreases the flow ability of the powder.

**Table 1.** Mechanical properties and SLS processing parameters for nylon-12/PEEK 75-25vol% CMA 30 min.

| Nylon-12 / PEEK (75/25 v/v) | UTS (MPa) | % Elong. at Break |
|---|---|---|
| | 19.5 +/-2.8 | 9.8 +/-1.8 |
| Laser Power = 0.7W | Scan Speed = 17 mm/s | |
| Layer Thickness = 0.1 mm | Scan Spacing = 0.9 mm | |

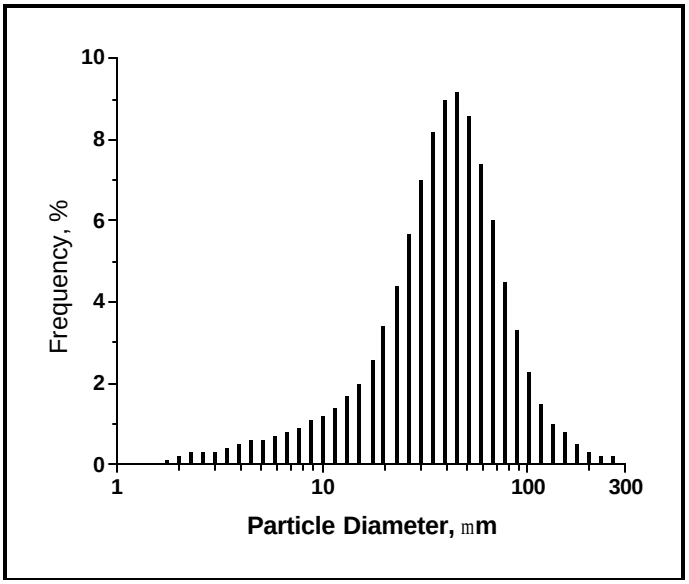


**Figure 9:** Nylon-12/PEEK 75-25vol% CMA 30 min particle size distribution.

SEM of the fracture surface of a nylon-12/PEEK 75-25vol% tensile specimen is shown in Figure 10. The fracture surface shows particles imbedded in a matrix. Figure 11 shows a TEM micrograph of a laser sintered nylon-12/PEEK 50-50vol% CMA 60 min. Again, particles dispersed in a matrix are observed. The particulate phase is PEEK and the matrix is nylon-12. The microstructure observed in Figures 10 and 11 is not the desired co-continuous phases structure. This may in part explain the low UTS of the laser-sintered composite powders.

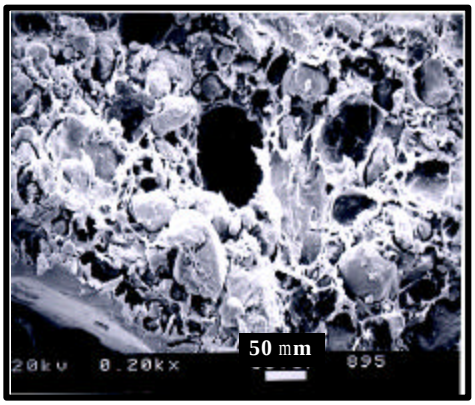


**Figure 10.** Fracture surface of nylon-12/PEEK 75-25vol% tensile specimens.

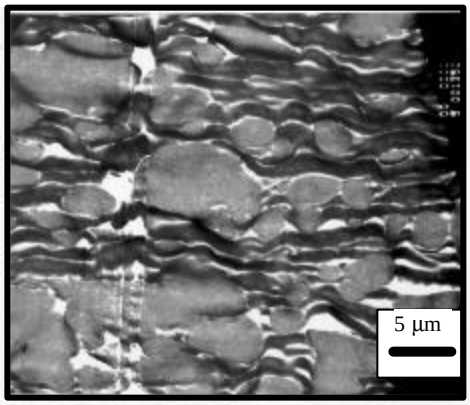


**Figure 11.** Microtomed surface of laser sintered nylon-12/PEEK 50-50vol%.

## CONCLUSIONS

This on-going research into the processing-structure-property relationship of polymer composites for SLS made by CMA has demonstrated the ability to image and quantify phase domain size in CMA polymers, consolidate CMA polymers via SLS, and image the as-laser-sintered microstructure. Powder bed density problems, which led to low mechanical strength in the nylon-12/PEEK 75-25vol%, need to be addressed in order obtain adequate strength. A Vortec C-1 Particle Classifier will be used to remove the 10 micron and smaller particles which are believed to be the cause of the powder bed density problems. Future work will include modification of MA and SLS processing parameters to determine if a co-continuous microstructure is attainable.

## ACKNOWLEDGEMENTS

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