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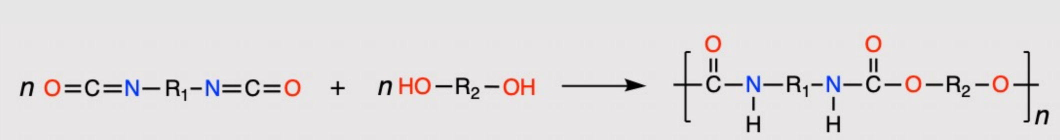
Abstract

A commercially available polycaprolactone-based thermoplastic polyurethane (TPU) elastomer product was chosen for cryogrinding and analysis. Two different product variants were chosen, referred to individually as "TPU Material 1" and "TPU Material 2," and collectively as "TPU products." The original form of both variants are in the form of colorless elliptical pellets of average 4.8 mm in length and 3.2 mm in width. The goals for processing include obtaining a particle size of 40-150 µm (longest diameter) with narrow distribution, minimal metal contamination, and acquiring data on potential thermal properties changes due to the process of grinding. With this, we are reporting the methods and results of cryogrinding, particle size analysis via scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC). Our industrial sponsor obtained results for particle size distribution via MasterSizer (light scattering) and trace metal analysis via ICP-MS.

Introduction

A thermoplastic polyurethane elastomer is a type of polyurethane-based polymer with thermoplastic and viscoelastic (viscous and elastic) properties. "Thermoplastic" meaning the material can be reshaped after heating because the physical crosslinks are thermally reversible. Polyurethane is produced from the polyaddition between a diisocyanate and a diol, but thermoplastic polyurethanes (TPUs) contain soft and hard segments in the polymer chain due to using both a short chain diol and a long chain diol. These two components give TPUs their thermoplastic and elastic properties.[1] Micron-sized TPU particles are common additives for many other materials and applications such as coatings, textiles, inks, and adhesives. Properties of increased abrasion resistance, thermal stability, flame retardancy, and tensile strength are some benefits of TPU additives.[2] Cryogrinding, rather than ball-milling or impact milling provides a low-temperature, uniform way to reduce particle size without thermal degradation of the sample.[3] Because of the low cost of liquid nitrogen that cryogrinding uses for cooling, this method is advantageous over the high-cost and high-energy consumption method of jet milling.[4]

Figure 1: General equation for synthesis of polyurethanes



Cryogrinding and Sieving

Figure 2: SPEX® SamplePrep 6875D Large Freezer/Mill, 180-L nitrogen tank, and sample vials. Liquid N_2 used to date… 6935 pounds!

SCAN ME

Table 1: Settings for cryogrinding TPU powder and pellets.

Setting	Pellets	Powder
# of cycles	10	4
# of sub-cycles	15	15
Pre-cool (1st cycle)	10 min.	5 min.
Pre-cool (subsequent cycles)	1 min.	1 min.
Grind	2 min.	2 min.
Cool	1 min.	1 min.
Rate	13 cps	13 cps

Figure 3: Fieldmaster Metal Sieves, 125 µm and 63 µm.

Particle Size Analysis via SEM Imaging

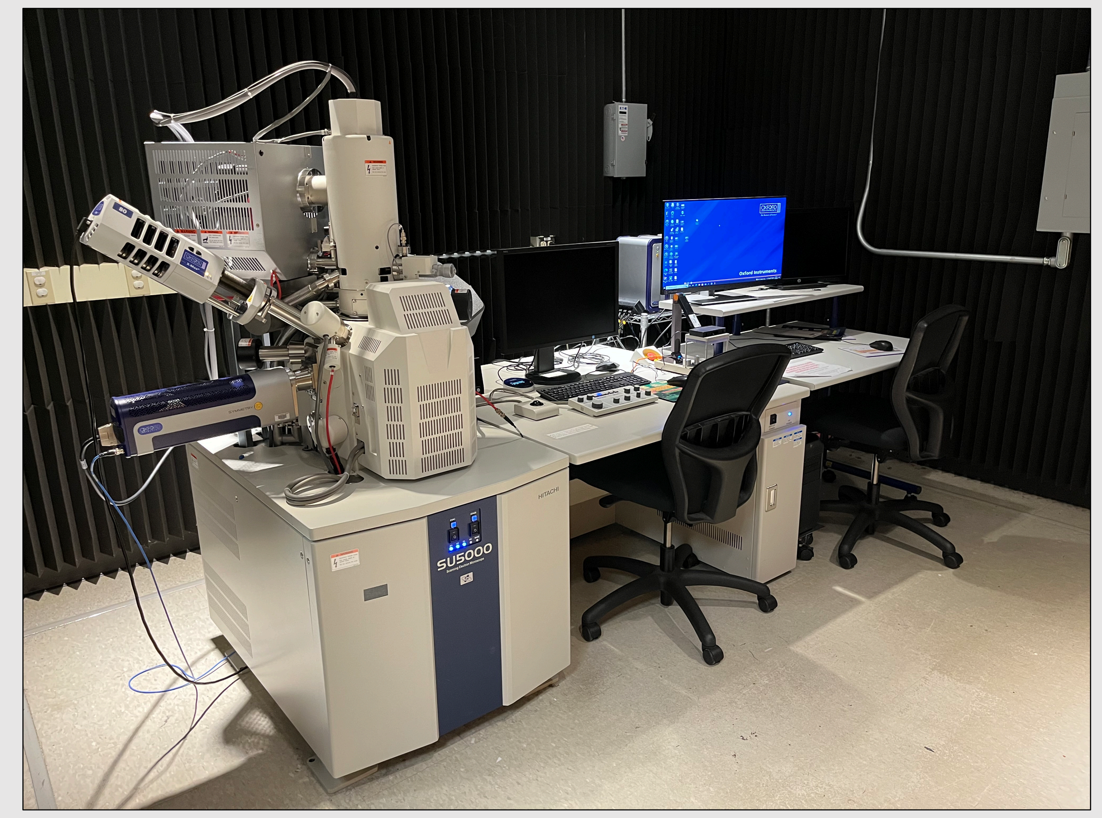
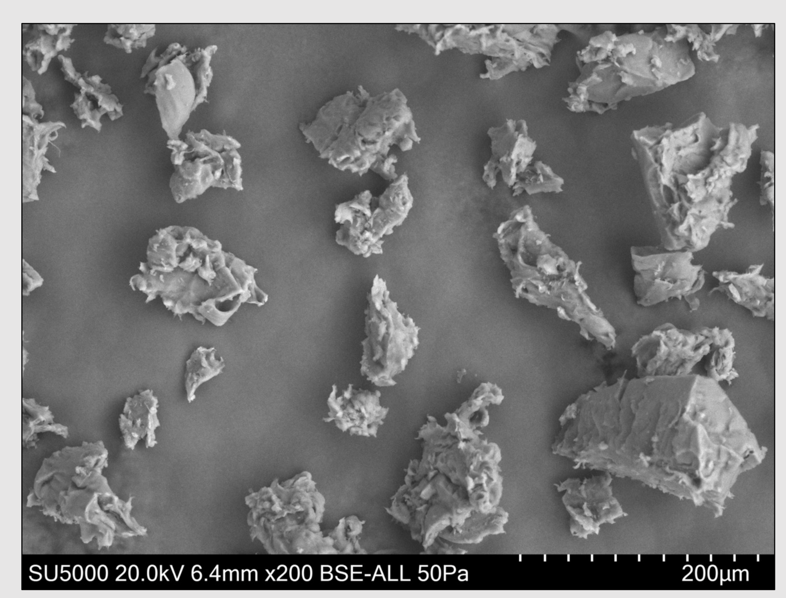
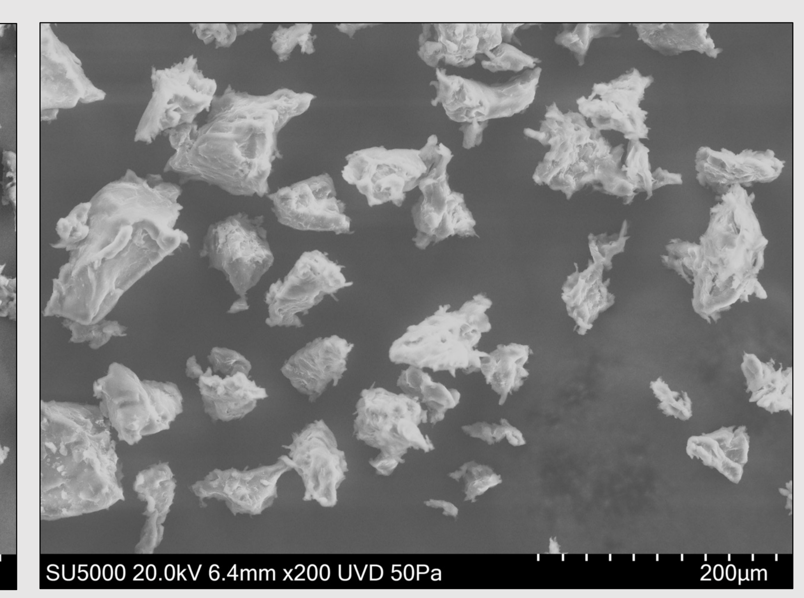


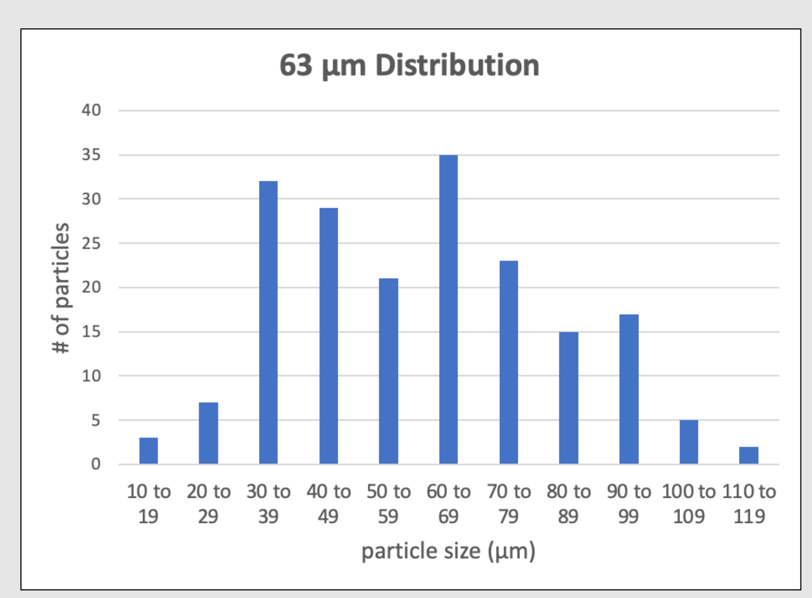
Figure 4: Hitachi SU5000 Scanning Electron Microscope (SEM)

The Hitachi SU5000 SEM was used for focused imaging of the micron sized TPU particles, in order to conduct particle size analysis. Images were taken using the Ultra-Variable Pressure Detector (UVD) and Back-Scattered Electron Detector (BSE). Magnifications of 400x for < 63 µm powder and 200x for ≥ 63 µm powder were chosen. The electron beam energy was chosen as 20 kV, and the vacuum was set to 50 Pa.

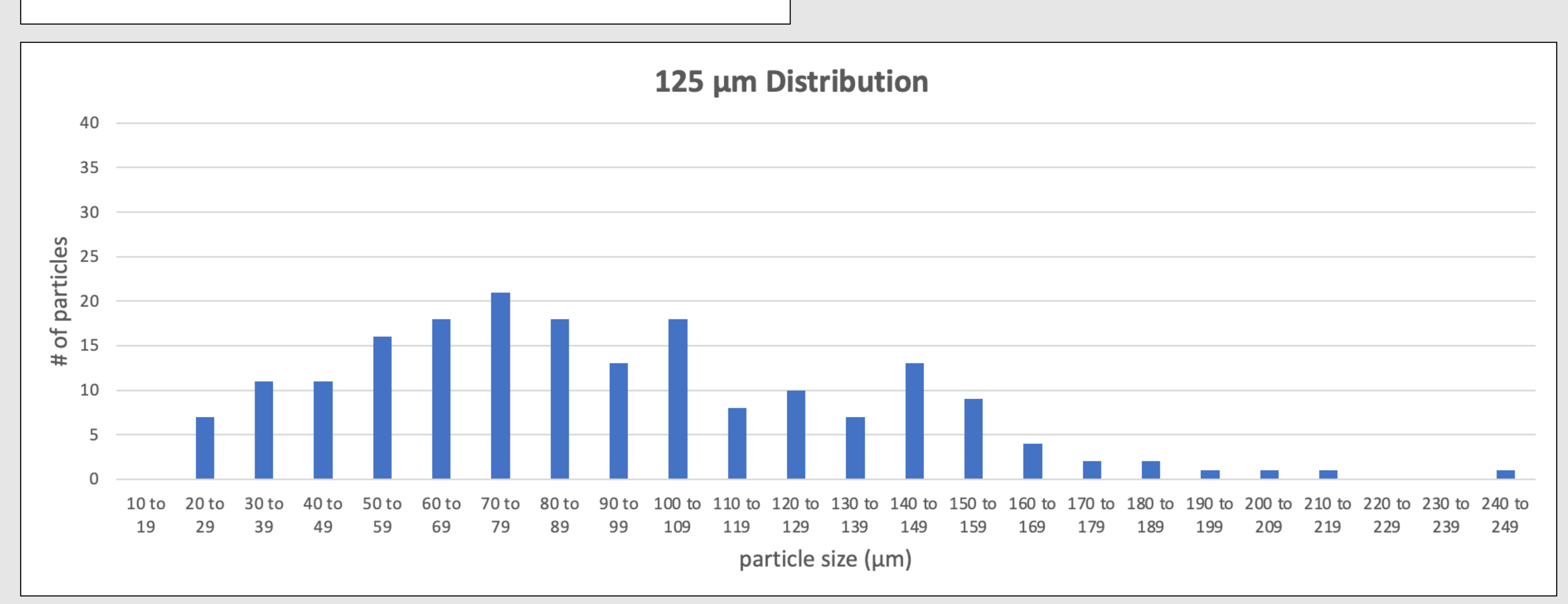




Figures 5 and 6: SEM images (BSE left, UVD right) of TPU Material 2. Particles are between 0 µm and 125 µm. Opensource image analysis software, ImageJ, was used to measure the longest diameters of distinguishable particles.



Figures 7 and 8: Particle size distributions for cryoground TPU Material 2 particles. On top, 189 particles < 63 µm sampled, average longest diameter of 60 µm, σ = 22 µm. On bottom, 192 particles < 125 µm sampled, average longest diameter of 93 µm, σ = 43 µm.



Simultaneous TGA/DSC

Figure 9: Simultaneous TGA/DSC (SDT) SDT Q600 V20.9 Build 20 Ambient to 1500 °C

Program Settings

- Select Gas 1 (N_2 100.0 mL/min.)
- Ramp 20 °C/min. to 800 °C
- Select Gas 2 (air 100.0 mL/min.)
- Isothermal for 5 min.
- End Cycle/Cool to 30 °C

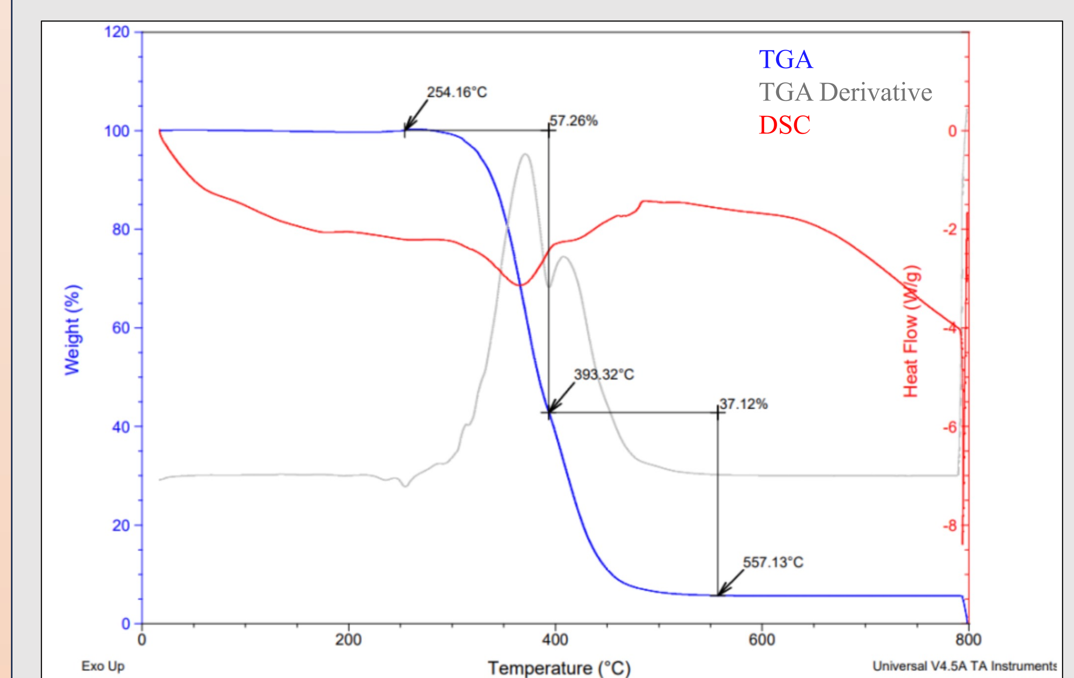


Figure 10: SDT – TPU Material 1 pellets, 10.2890 mg

1st Decomposition

- Start – 254.16 °C
- End – 393.32 °C
- Weight Loss – 57.26%

2nd Decomposition

- Start – 393.32 °C
- End – 557.13 °C
- Weight Loss – 37.12%

DSC only has one large dip.

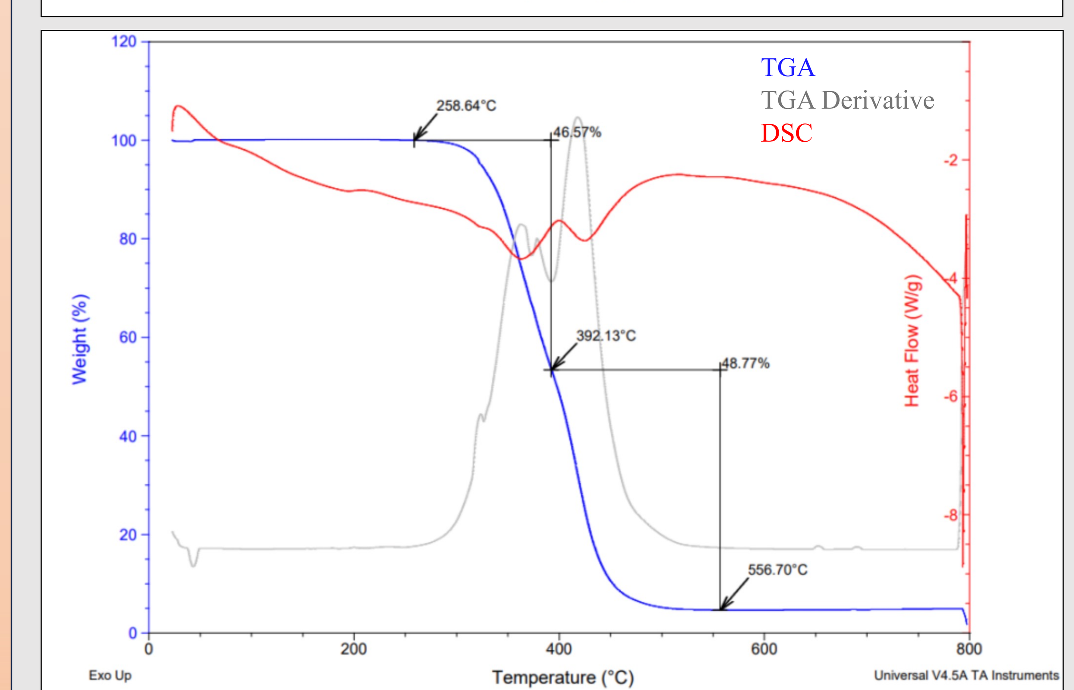


Figure 11: SDT – TPU Material 1 63 µm powder, 8.3420 mg

1st Decomposition

- Start – 258.64 °C
- End – 392.13 °C
- Weight Loss – 46.57%

2nd Decomposition

- Start – 392.13 °C
- End – 556.70 °C
- Weight Loss – 48.77%

DSC now has two large dips.

Summary and Future Work

The desired properties of the TPU products were achieved, except for significant iron contamination due to the stainless-steel end-caps and impactor of the freezer mill vials. Due to the low yields of 63 µm powder produced from cryogrinding the stock pellets of both TPU products, grinding of this material will be suspended. Future work will consist of cryogrinding and analyzing different TPUs, meanwhile investigating a method to prevent iron contamination during the cryogrinding process. One such method could be using high strength neodymium magnets instead of stainless-steel ones, and another could be using a plastic shrink-wrap coating around the impactor to prevent surface contact contamination.

References and Acknowledgments

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