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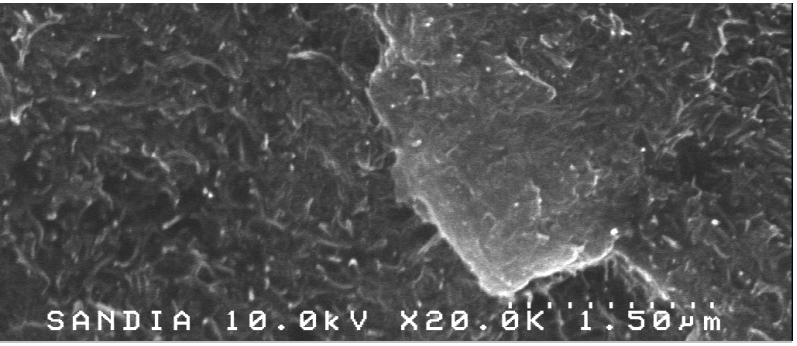

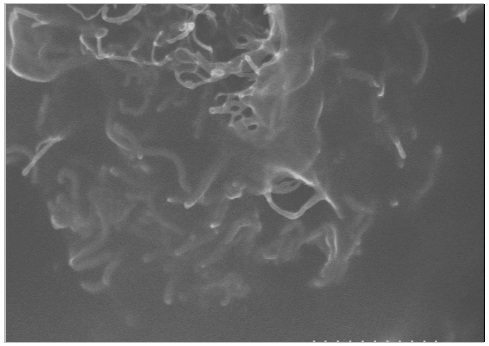

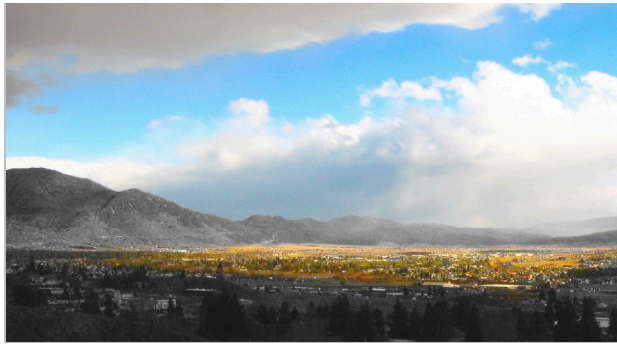

Melt-Electrospinning Polypropylene-Carbon Nanotube Microfibers

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U.S. DEPARTMENT OF ENERGY | NNSA

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About Myself

- Electrical Engineering Major at Montana Tech of the University of Montana
  - Intending to enroll in the 5 year Master's program at Tech
  - Minoring in Mathematics and Professional Technical Communications
- Working with Dr. Jack Skinner to electrospin Poly(vinyl)-alcohol with the intention on producing a conductive mat of sub-micron to nanoscale fibers.

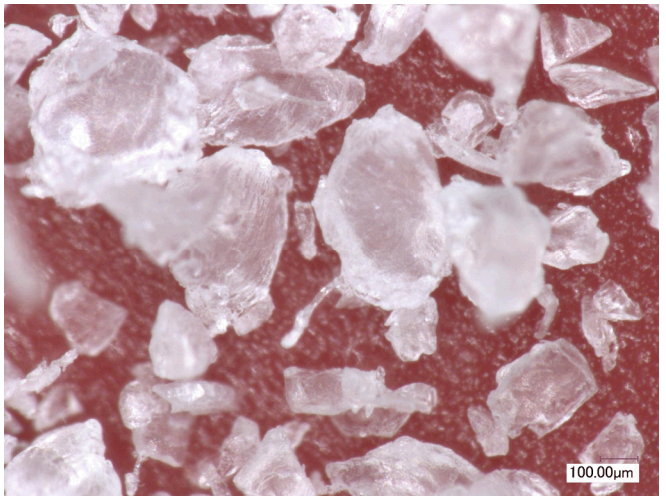
Summer Project Overview

Produce a conductive Polypropylene (PP) / Multiwall Nanotube (MWNT) composite material to be spun in the modified electrospinner.

1. Melt-mix PP and CNTs
2. Injection mold conductivity test specimens and electrospinner cartridges
   - Modify the injection molder with a heated mold and a controller capable of separately controlling the temperatures of the injection molder and the mold.
3. Electrospin PP/CNT microfibers
   - Modify the electrospinner from solvent based electro-spinning to melt electrospinning.

Melt Mixing – Initial Efforts

- Melt mixing was accomplished using the Dynisco Laboratory Mixing Extruder (LME).
- PP pellets were ground to approximately 300µm.
- Ground PP (190k M_w) was dry mixed with MWNTs in 2wt% and 5wt% concentrations.
- Dry mixture was allowed to melt in the LME and was simultaneously extruded.
  - Non conductive composite material was formed.



Ground 190k M_w Polypropylene using 500µm sieve

- Based on other work with mixing polymers and CNTs[1] high shear mixing for 10 min broke apart agglomerates and induced an even dispersion on CNTs in the polymer.
- 7.5wt% then 5wt% MWNT concentrations were dry mixed then small quantities were allowed to mix inside the LME for 10min intervals before allowing the polymer to be extruded.
  - Resulting composite material was conductive.

Melt Mixing

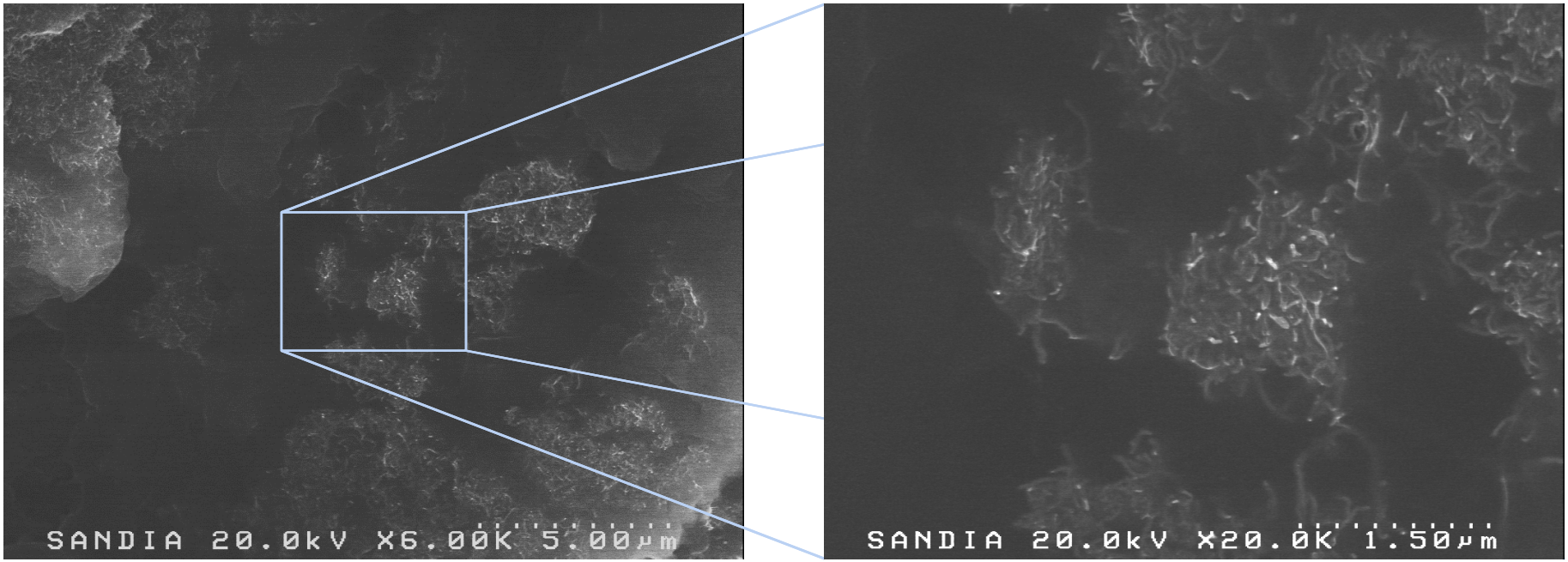
- To increase the shear rate of the mixing 14k M_w and 12k M_w polymer was used. The lower molecular weight PP has a lower viscosity which increases shear rate. [2]

- 14k M_w PP was amorphous and the 12k M_w was isotactic; the 14k M_w was tacky and would not grind however the 12k M_w was able to be ground.

- Following the same procedure 5wt% PP (12k M_w) was mixed.
  - Conductive composite was formed.

Melt Mixing

- The conductive PP/MWNT composite is highly agglomerated.
  - Studies show that using high shear mixing for periods of about 10 min significantly reduce the size of the agglomerations and allow an even spread of the CNTs. [1]



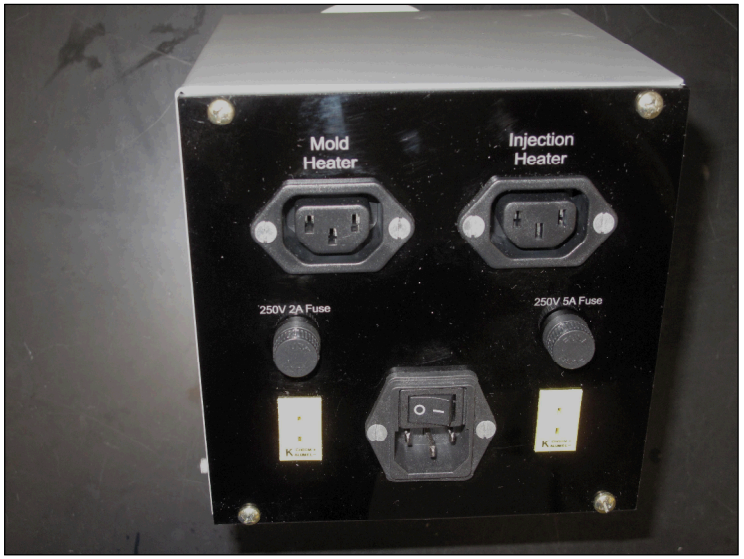
12k M_w, 4wt% PP/MWNT composite with agglomerations averaging 1.5µm ranging from .618µm to 3.066µm. Measurements were taken using ImageJ

Injection Molding

- Injection molding was used to create uniform samples for conductivity testing and uniform cartridges for electrospinning.
- To injection mold viable cartridges a heated mold was required.
- Modifications were made to the injection molder to accept heated molds.

Injection Molder Modifications

- The factory controls were removed from the injection molder and replaced with a control panel capable of separately controlling the temperature of the injection molder and the mold.
  - Unheated molds before

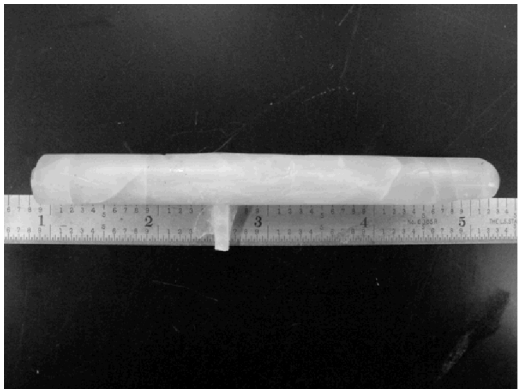


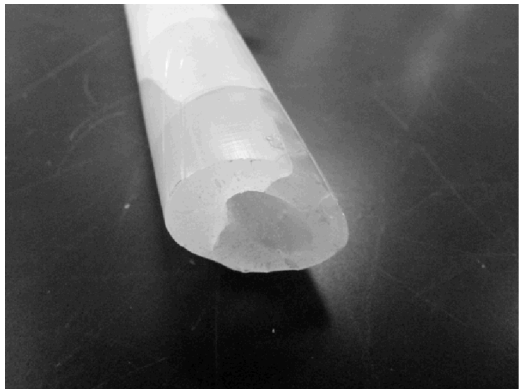
Injection Molding

- The injection molder was heated to 392°F (200°C)
- Sample Molding
  - Mold at ambient temp
  - Standardized samples for conduction calculations
- Cartridge Molding
  - Mold heated to 302°F (150°C)
  - Standardized cartridges for the electrospinner

Injection Molding

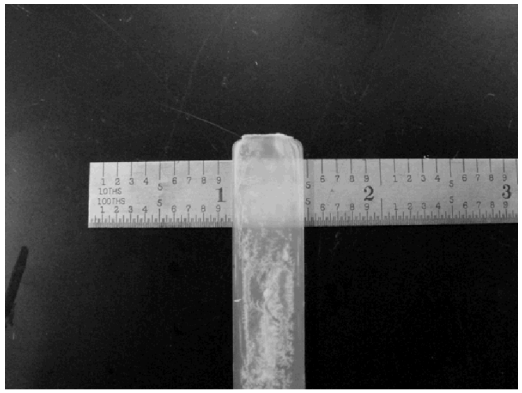
Electrospinner Cartridge

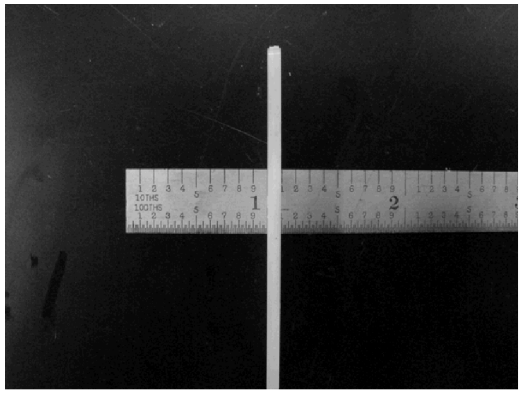




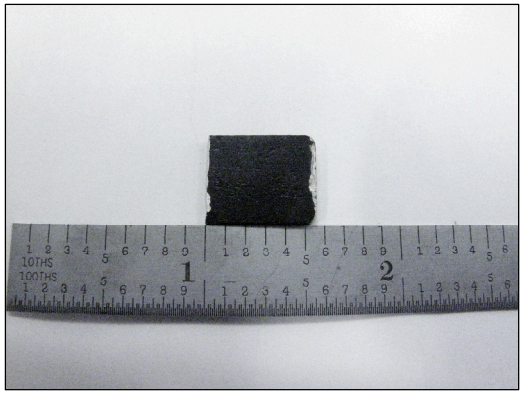
Neat 12k Mw PP electrospinner cartridge

Conductivity test specimens



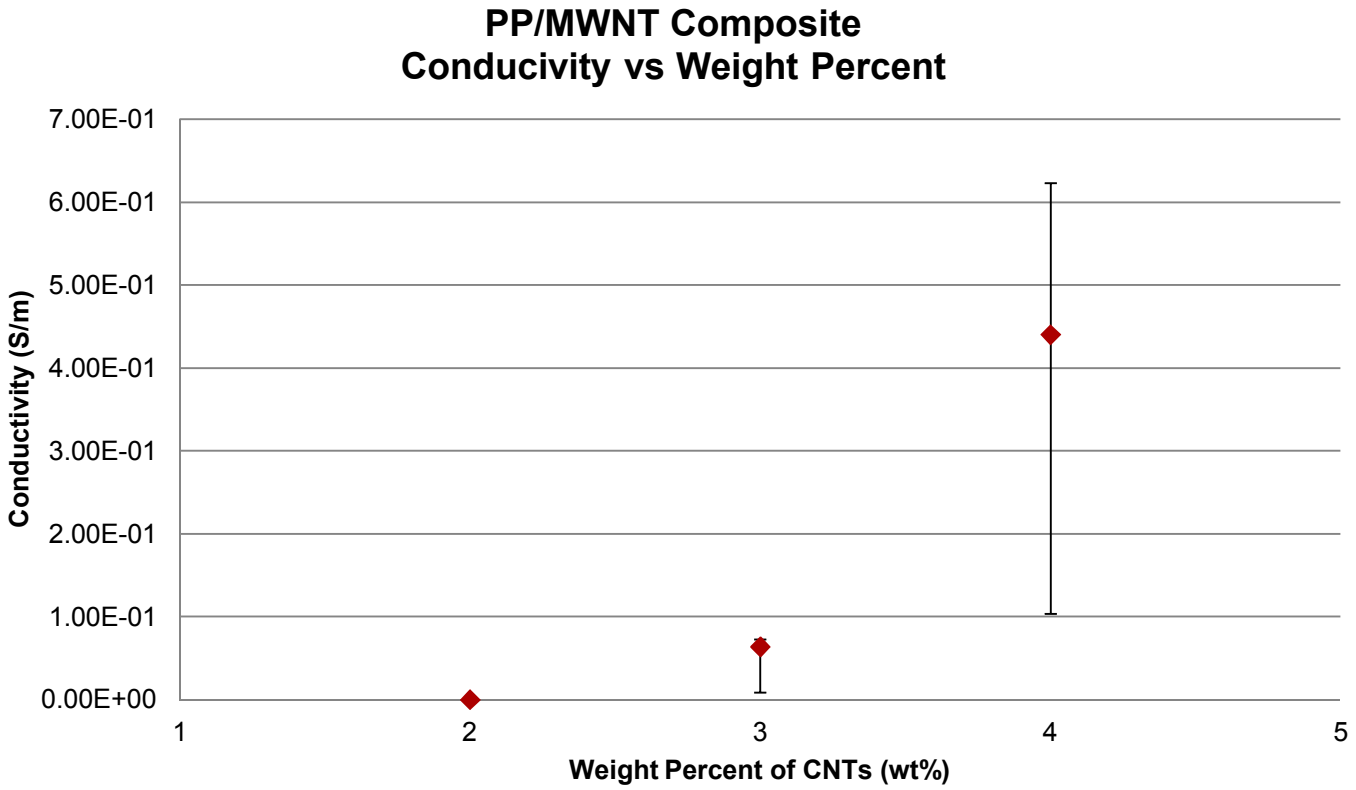


Neat 12k M_w Polypropylene conductivity test sample



12 M_w, 4wt% PP/MWNT conductive sample

Sample Conductivity



Weight Percent CNTs	Conductivity (S/m)							
	1	2	3	4	5	AVG	MAX	MIN
2	2.79E-04	1.22E-04	1.61E-04	9.03E-05	1.94E-04	1.69E-04	2.79E-04	9.03E-05
3	5.92E-02	5.49E-02	6.94E-02	6.30E-02	7.31E-02	6.39E-02	7.31E-02	5.49E-02
4	0.3882	0.623188	0.336738	0.439421	0.415258	4.41E-01	6.23E-01	3.37E-01

Electrospinning

- The Yflow electrospinner is designed for solvent based spinning.
- The solvents that can be used to make PP solutions are not conducive for electro-spinning. [3]
- To electrospin polypropylene modifications were required to convert the electrospinner from solvent based electrospinning to melt electrospinning.

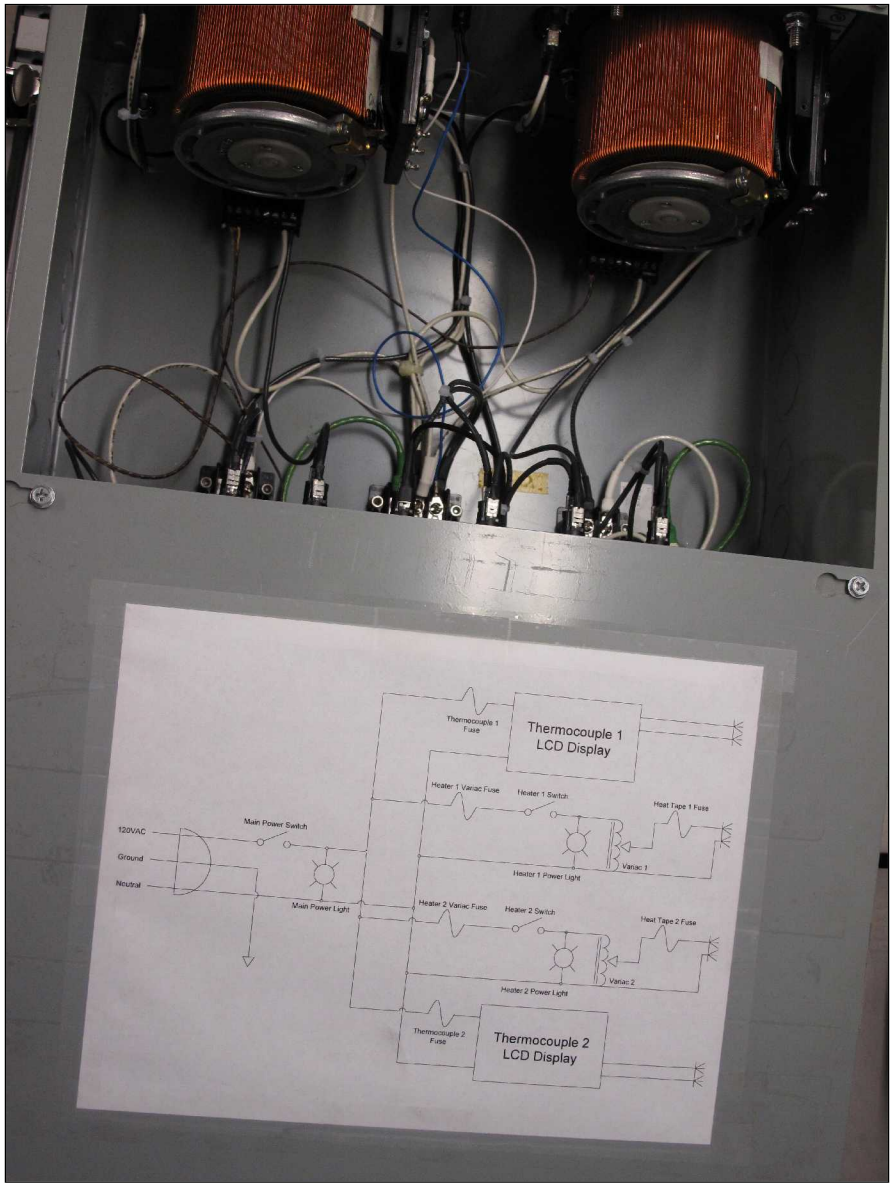
Electrospinner Modifications

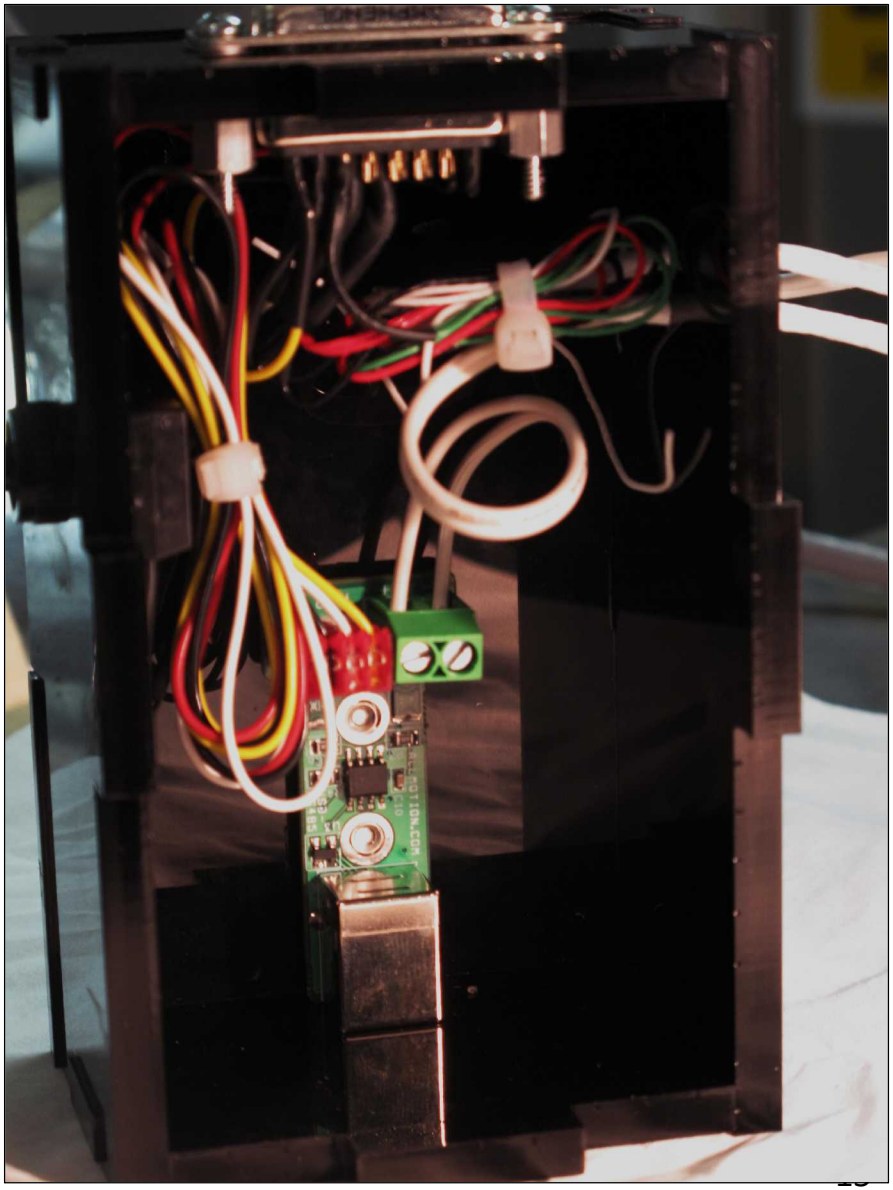
- A capillary connected to a melting pot and linear stage constructed by Henry Korellis was attached to the electrospinner.

- Heating controls were added to the electrospinner for the new modifications.
  - Initial heating controller was constructed by Henry Korellis, extra safety features were later added per ES&H.

Electrospinner Modifications

Electrospinner Modifications



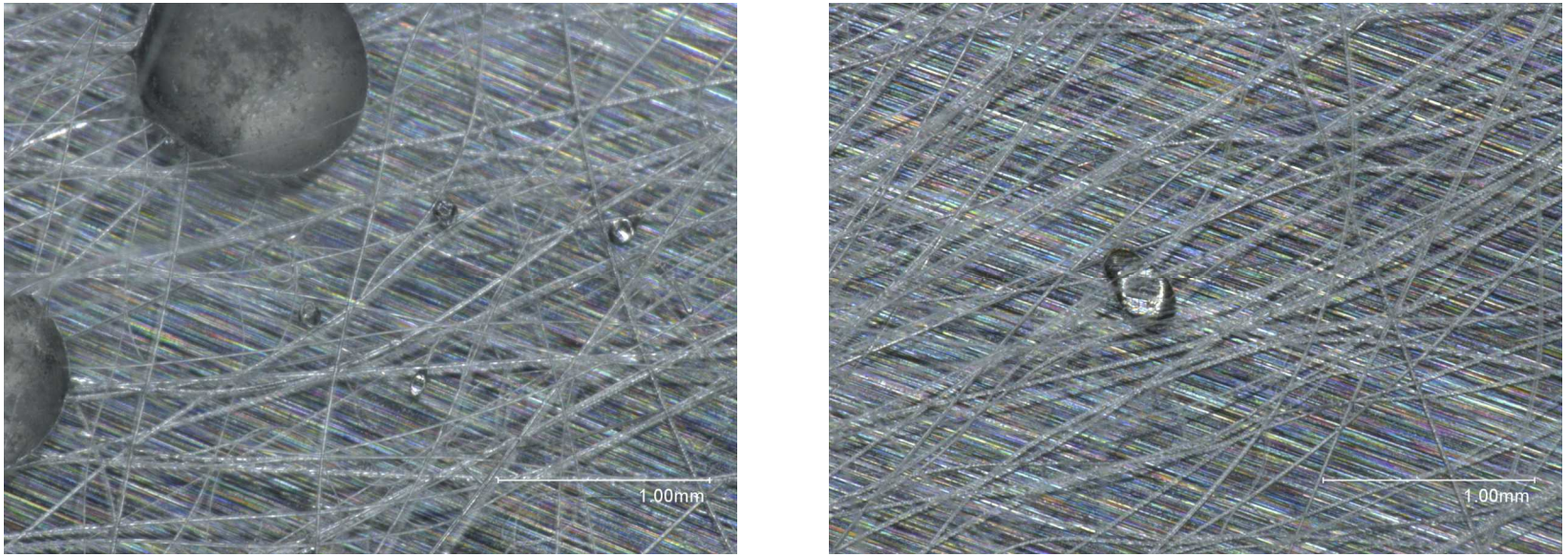


Electrospinning

- Electrospinning of neat 12k Mw PP was accomplished without adequate flow controls under the following parameters*:
  - Cartridge temp: ≈270°C
  - Capillary voltage: 0V (grounded)
  - Collection plate: 15kV (thicker fibers)
  - Collection plate: 18kV (finer fibers)
  - Collection plate to capillary distance ≈3inches

*Parameters are due to change once proper flow control is established and conductive polymer is used.

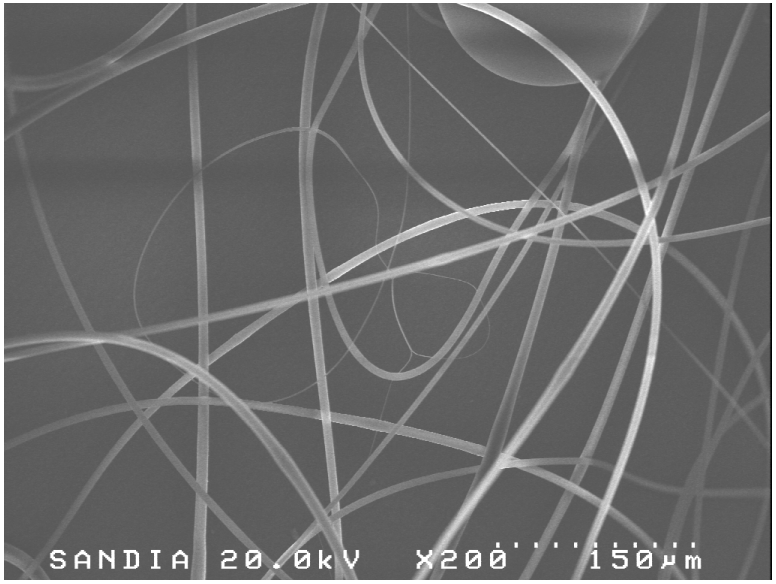
Electrospinning



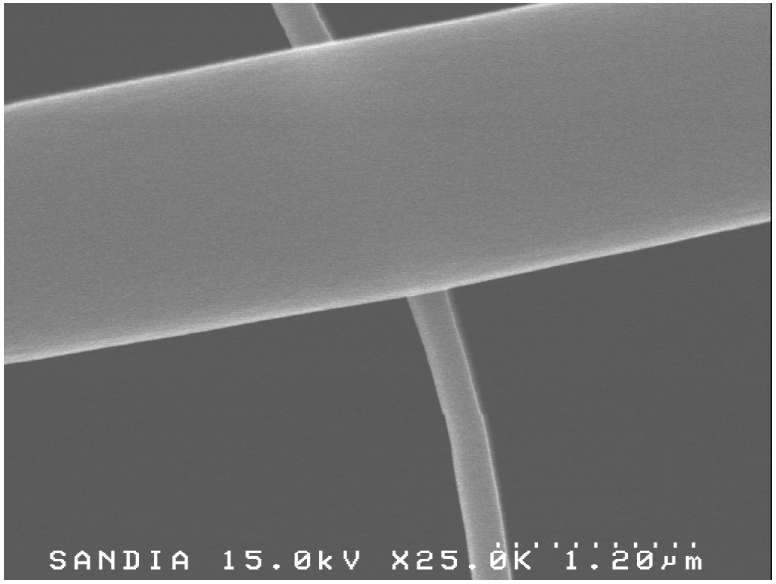
Electrospun fibers viewed under the Keyence digital microscope.

The fiber mat contains large polymer drops due to inadequate flow control

Electrospinning



12k M_w PP fibers of various diameters



Small fiber diameter ≈226nm
Large fiber diameter ≈1.59µm

Electrospinning

- Current method used for flow control needs improvement.
  - The seal around the push rod is not enough to eject polymer through the capillary when the system contains a ball valve to prevent dripping, or to prevent the polymer from completely discharging without the ball valve.
- Melting chamber needs to be hot enough that the end of the capillary is above the melting temperature of the polymer.
  - Due to the high temperatures and slow feed rates needed the use of a ‘sacrificial’ polymer stick could contaminate test samples.
- Without flow control fibers range from ≈226nm to ≈13.8µm with a mean ≈ 6.46µm with a standard deviation ≈ 3.16µm.
- Resulting fiber is highly beaded.

Obstacles

- Melt Mixing
  - Low shear forces acting on the mixture in the LME
- Injection Molding
  - When the mold is at ambient temperature the polymer hardens before the mold can be filled completely
- Electrospinning
  - Linear stage malfunctioned and flow control was lost

Proposed Next Steps

- Melt Mixing
  - Synthesize PP/MWNT composite without agglomerations
    - High shear mixing [1]
    - Ball-milling [4]
    - Ultrasonicating [4]
  - Characterize non-agglomerated PP/MWNT composite
    - Stress
    - Surface and Axial Conductivity
- Injection Molding
  - Create a mold complying to ASTM standards for stress test samples

Proposed Next Steps

- Electrospinning
  - Resolve the flow control issues
    - Seal the flow system to prevent leaks
    - Use a low pressure control system to slowly release the melted polymer
  - Characterize the melt electrospinning process
  - Characterize the resultant fibers

Acknowledgements

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  - Bryan Loyola
  - Marianne LaFord
  - Henry Korellis
  - Delmar Eldredge
  - Chip Steinhaus
  - Matthew Roddewig
  - Greg O'bryan
  - Jack Skinner

Works Sited

[1] Li, Yongjin; Shimizu, Hiroshi “High-shear processing induced homogenous dispersion of pristine multiwalled carbon nanotubes in a thermoplastic elastomer”, *Polymer Communication,* vol.48, no. 8, pp. 2203-2207, 2007

[2] Bousmina, M.; Ait_Kadi, A.; Faisant, J.B. “Determination of shear rate and viscosity from batch mixer data”, *Journal of Rheology*, no. 43,pp. 415-433, 1999

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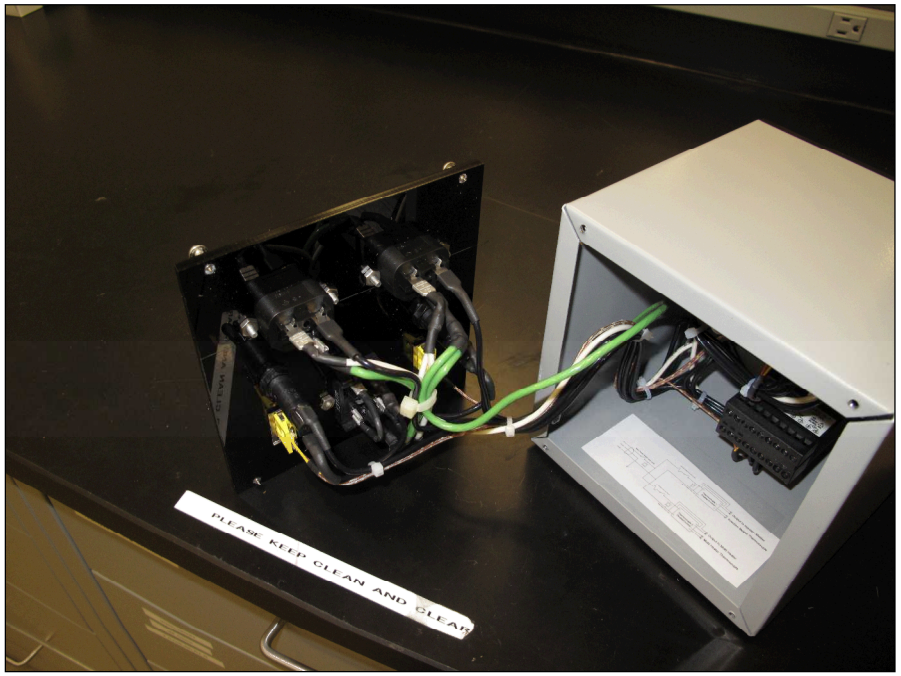
[4] Breuer, O.; Sundararaj, Uttandaraman “Big returns from small fibers: A review of polymer/carbon nanotube composites”, *Polymer Composites*, vol. 25,no. 6, pp. 630-645, 2004

Questions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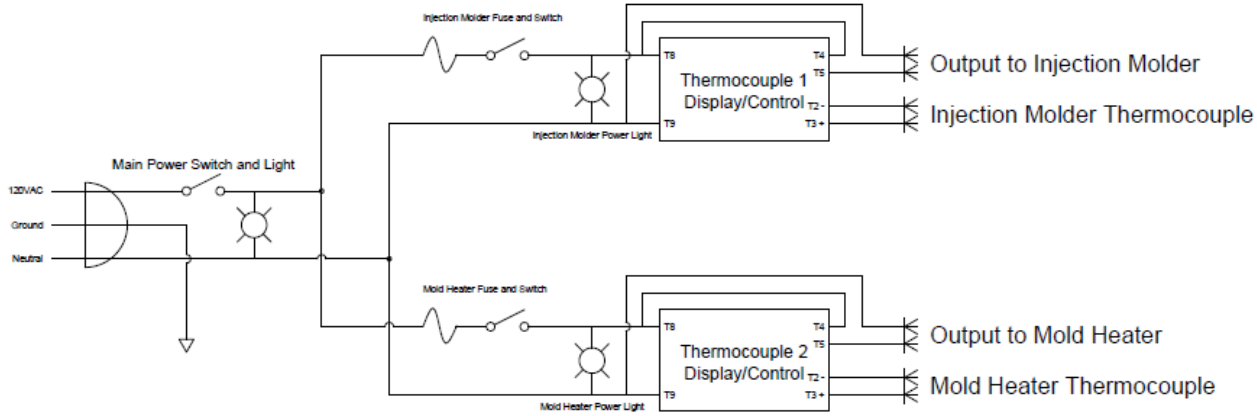
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Display/Control
Injection Molder Power Light
Output to Injection Molder
Injection Molder Thermocouple
Main Power Switch and Light
120VAC
Ground
Neutral
Mold Heater Fuse and Switch
Thermocouple 2
Display/Control
Mold Heater Power Light
Output to Mold Heater
Mold Heater Thermocouple