Electrospun Multifunctional Composite Fibers for Improved Warfighter Insect Protection

WP19-1187

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WP19-1187: Electrospun Multifunctional Composite Fibers for Improved Warfighter Insect Protection

Performers:

Dr. Jeffrey Lundin, Dr. Justin Ryan, & Dr. Riccardo Casalini

Naval Research Laboratory, Chemistry Division

Dr. Joshua Orlicki

Army Research Laboratory

Technology Focus

- *Develop durable, tunable insect repellent composite fibers for enhanced fabrics and textiles.*

Research Objectives

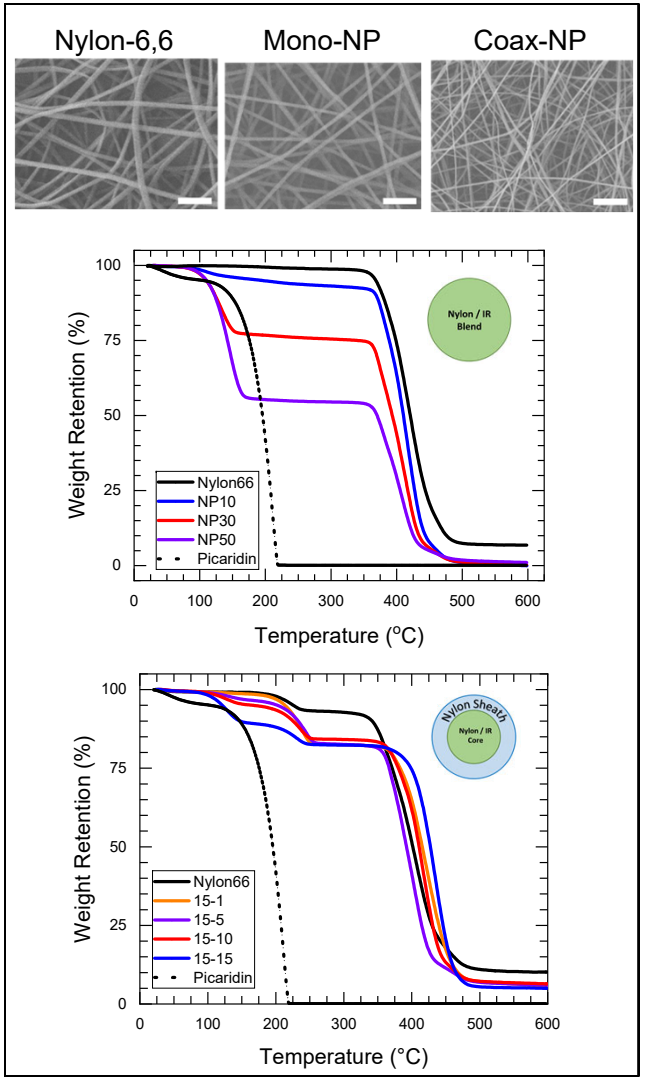
- *Encapsulate volatile insect repellents into the matrix of electrospun polymer fibers.*
- *Utilize coaxial electrospinning to physically control and tune insect repellent release over long time scales.*

Project Progress and Results

- *Fabricated composite fibers with monofilament and core/sheath structures containing different classes of insect repellents.*
- *Demonstrated and characterized the ability to control release rates of repellent fibers through physical and chemical design.*

Technology Transition

- *Filed a provisional patent describing the invention and fabrication of composite repellent fibers with core/sheath structure containing physically encapsulated volatile insect repellents.*



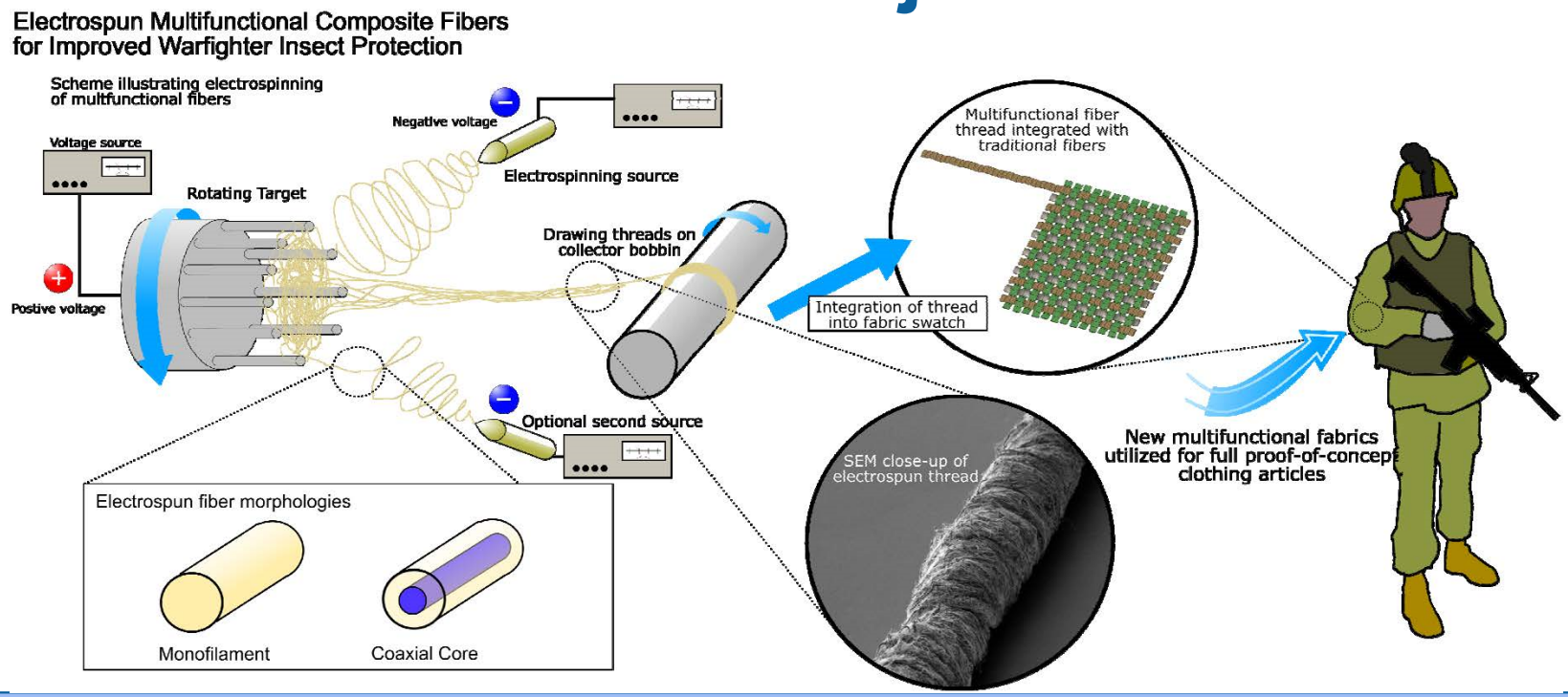
Project Team

- Dr. Jeffrey Lundin – PI; US NRL
- Dr. Justin Ryan – NRC Postdoc; US NRL
- Dr. Riccardo Casalini – Co-PI; US NRL
- Dr. Joshua Orlicki – Perfomer; US ARL

Background

- FY2019 Limited Scope
- SON: WPSON-19-C5
- Multifunctional Fibers and Textiles for Warfighter Integrated Protection
  - "…develop material formulations and processing techniques to examine a variety of novel fibers and textiles for performance."
  - "…novel and alternative fibers, blends of fibers, chemical treatments or processing techniques to impart (a) FR properties and/or (b) insecticide or insect repellant properties to military textiles,.."

Technical Objectives



Objectives

Develop novel multifunctional fibers for the controlled delivery of environmentally friendly, low toxicity insect repellents that exhibit broad spectrum protection.

- DEET, Picaridin, Permethrin

Utilize coaxial electrospinning to tune fiber morphology and release kinetics to control repellency in a variety of environments.

Generate and evaluate durable, high-performance fabric prototypes for field implementation and extend to scalable manufacturing processes.

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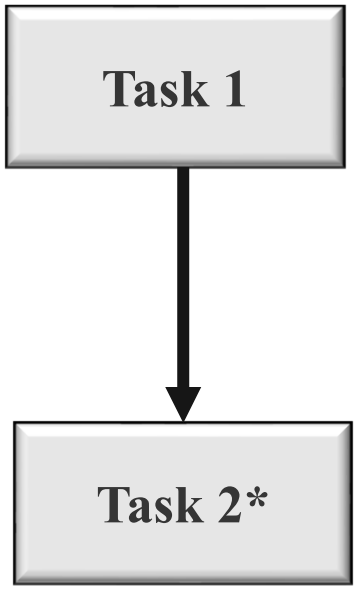
Technical Approach

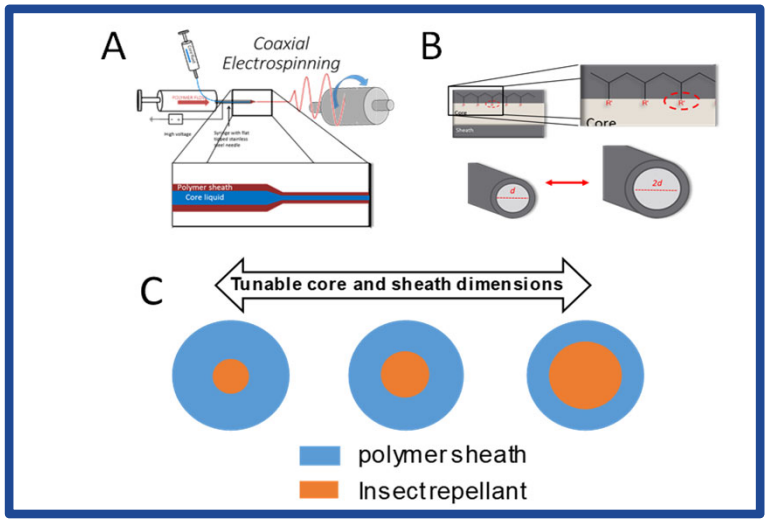


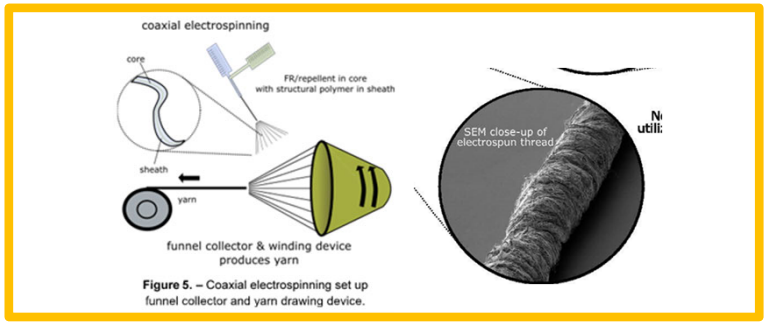
Task 1: Develop insect repellent composite fibers

a. Encapsulate insect repellents in coaxial fibers, control dimensions
b. Optimize permeability of sheath polymer for release kinetics
c. Mechanical optimization of fibers via control of additive dispersion
d. Performance evaluation (repellent release rate, efficacy)
e. Durability challenge (laundering, aging)

Task 2: Evaluation and delivery of prototypes threads

a. Thread production - collection of fibers on spiral target
b. Evaluate thread performance
c. Prototype fabric production and evaluation





Presentation Outline

1. Confirm loading and release of IR Electrospun fibers
   a. DEET Monofilament Fibers
   b. Picaridin Monofilament Fibers
2. Additional control of release behavior
   a. Picaridin Coaxial Fibers
3. Key Points and Future Research

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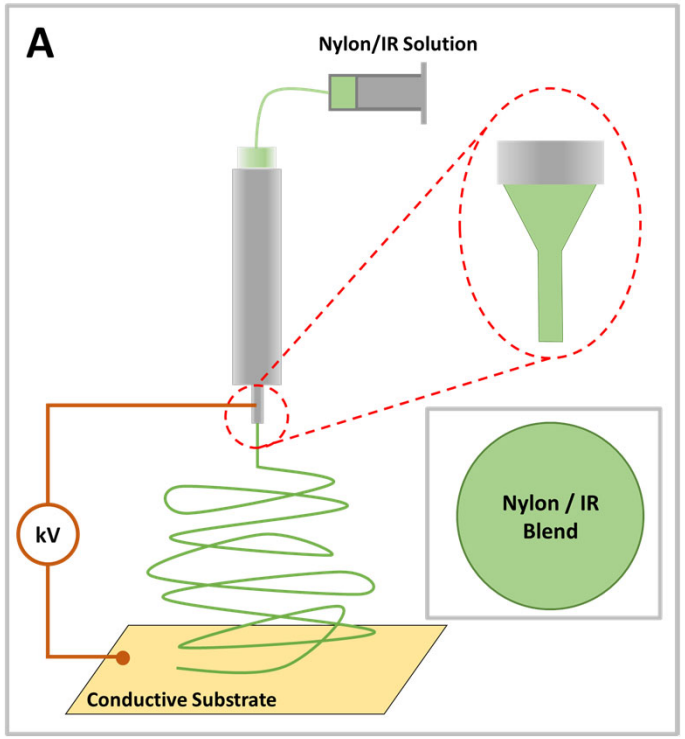
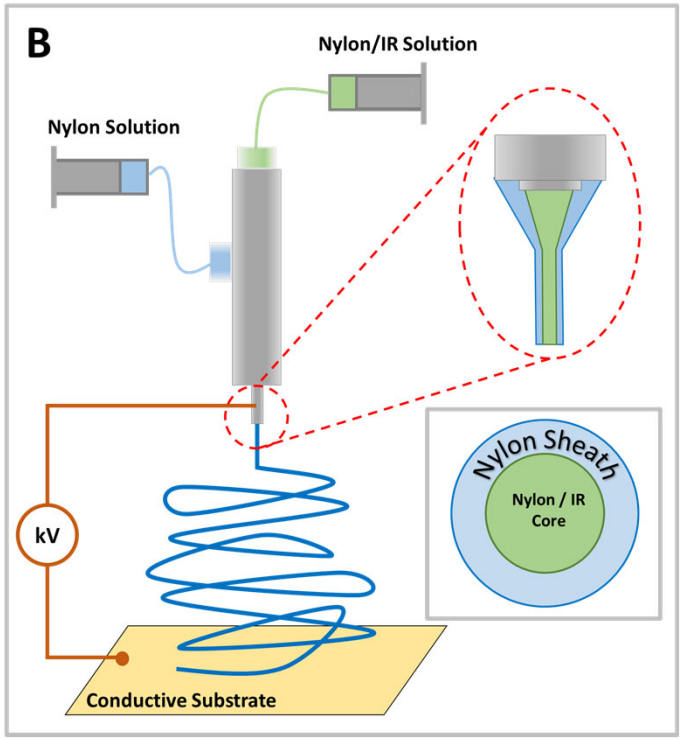
Approach: Electrospinning

Monofilament



Coaxial



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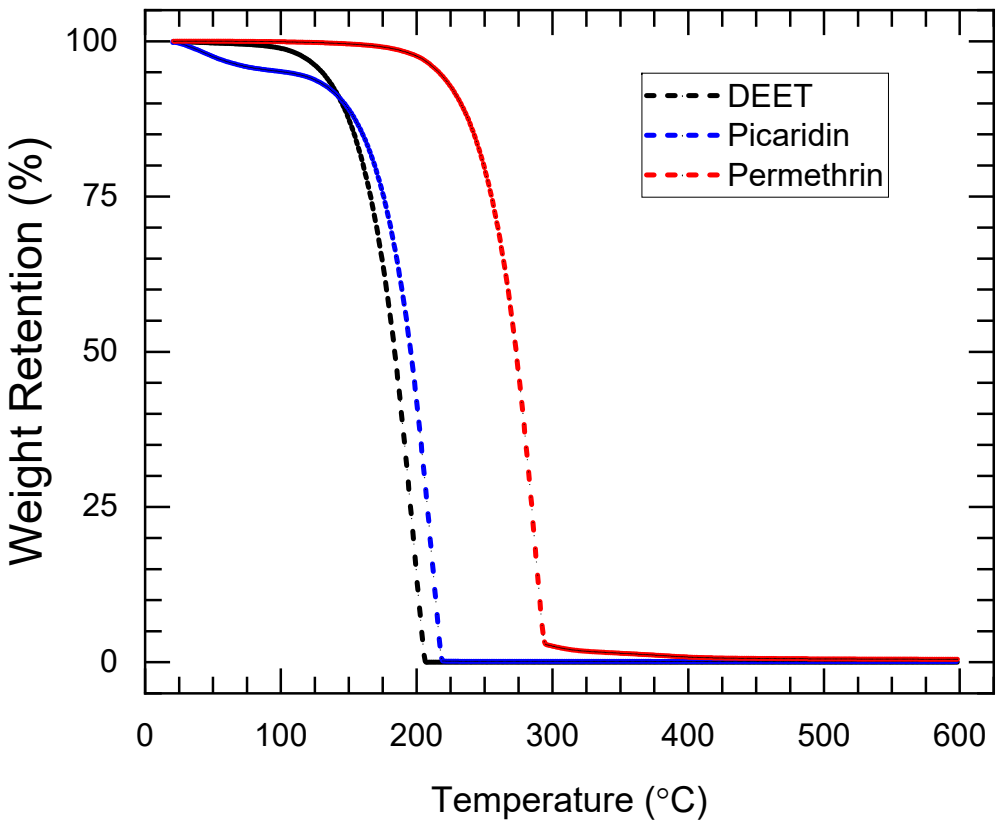
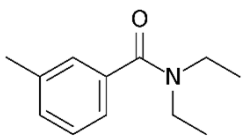
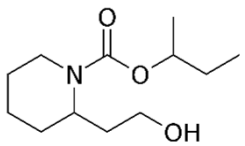
Neat Repellents: TGA

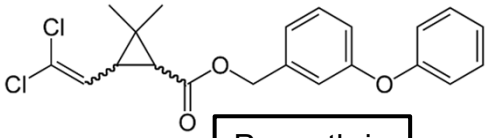




DEET



Picaridin



Permethrin

Repellent	M.P. (°C)	B.P. (°C)	Vapor Pressure @ 20 °C (mmHg)
DEET	-49	~285	5.6×10^{-3}
Picaridin	< -170	296	2.5×10^{-4}
Permethrin	34	~290	2.16×10^{-8} (*cis*) 6.9×10^{-9} (*trans*)

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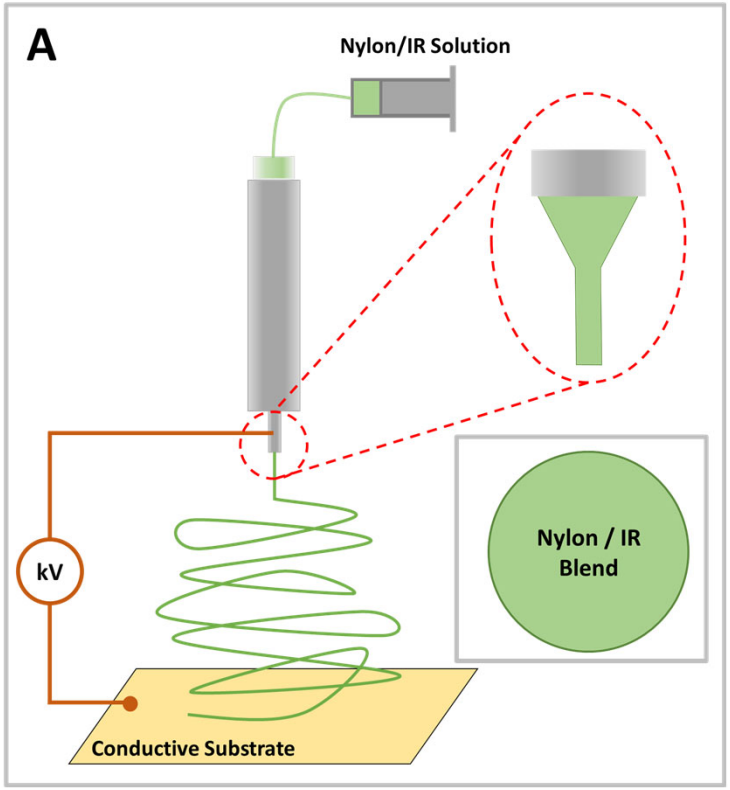
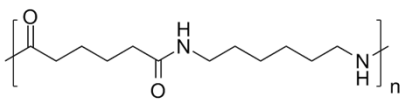
Monofilament Fibers
DEET

- Composition
- Solvent: Formic Acid
- Polymer Concentration: 12.5 wt% Nylon 6,6
  - Nominal DEET Concentrations:
    - 0, 10, 30, 50 wt% (wrt polymer)
      - » ND0, ND10, ND30, ND50, respectively
- Field Strength: 1.5 kV/cm
  - Distance: 10 cm
- Flow Rate: 15 µL/min

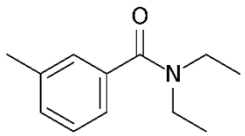


DEET Monofilament Fibers: *Morphology*

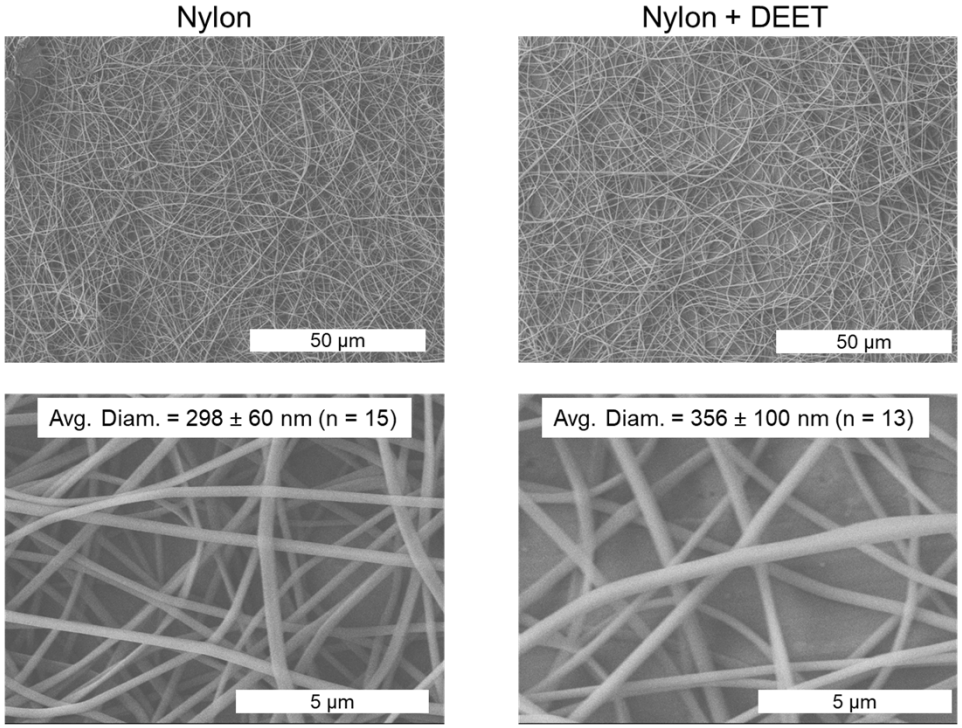
- Electrospinning Parameters
  - Solvent: Formic Acid
  - Polymer Concentration: 12.5 wt%
    - Nominal DEET Concentration: 10wt% (wrt polymer)
  - Field Strength: 1.5 kV/cm
    - Distance: 10 cm
  - Flow Rate: 15 µL/min



Nylon-6,6



DEET



Physical incorporation of DEET into monofilament, composite fibers appears to have little effect on fiber morphology at low concentrations.

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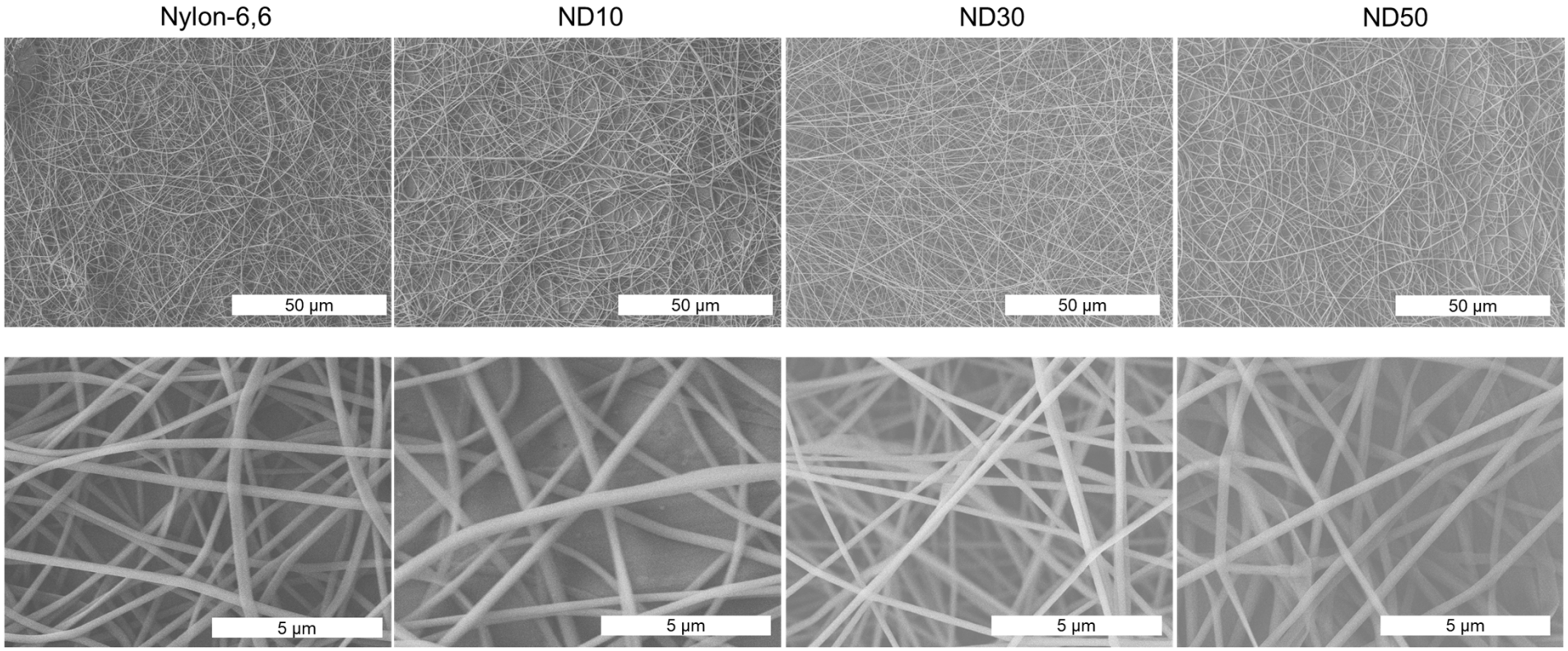
DEET Monofilament Fibers:
Effect of DEET Concentration on Morphology



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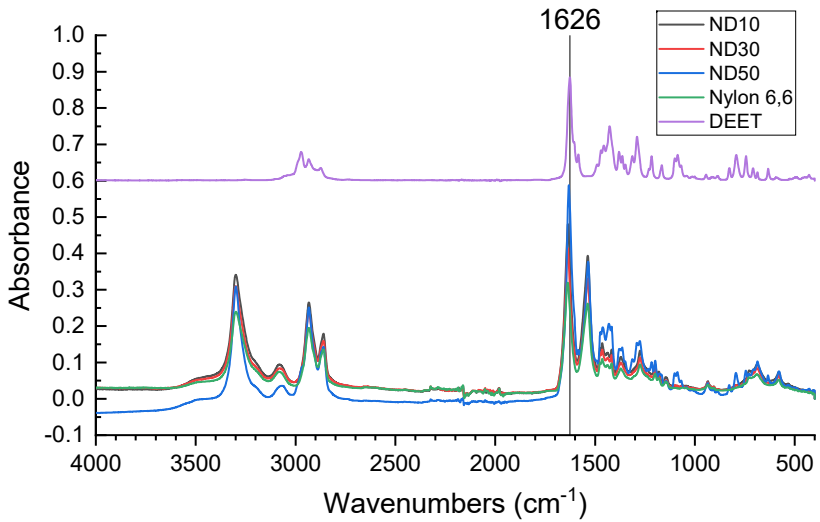
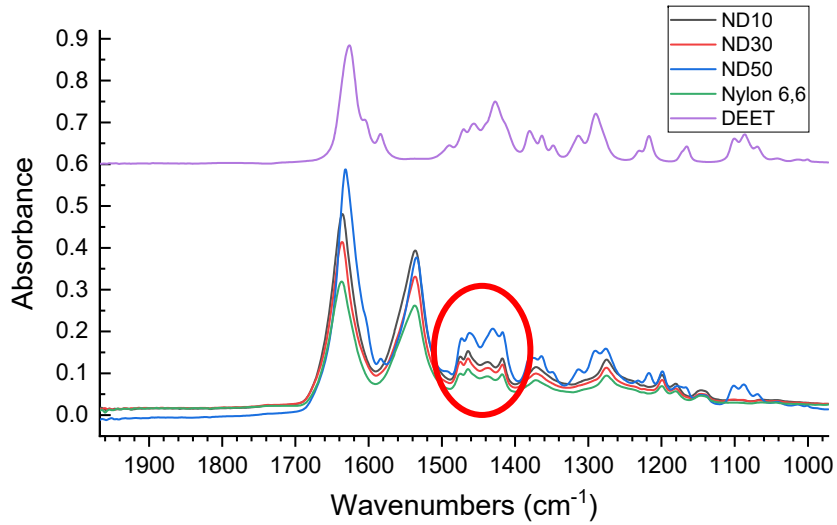
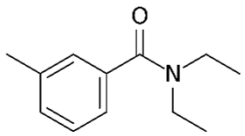
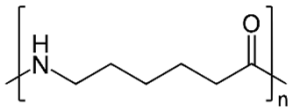
DEET Monofilament Fibers:
ATR-FTIR Characterization







DEET



Nylon 6,6

- 3298 – NH stretch
- 2933/2860 – CH asymmetric/symmetric stretching (*~+10-20 cm-1 -> more CH3*)
- 1635 – C=O (both Nylon and DEET)
- <u>1584 – C-C stretch aromatic DEET ring</u>
- <u>1535 – NH in-plane bend</u>
  - 3100 – NH in-plane bend overtone
- 1427 - $\delta(CH_2)$ DEET

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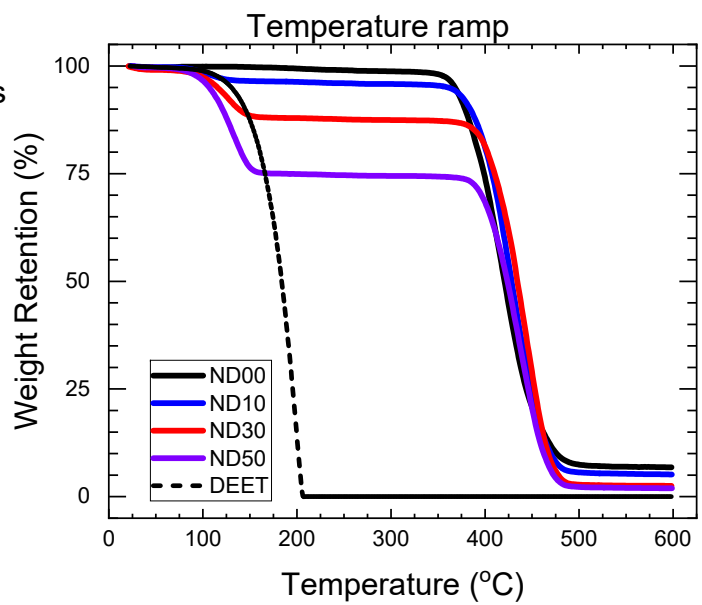
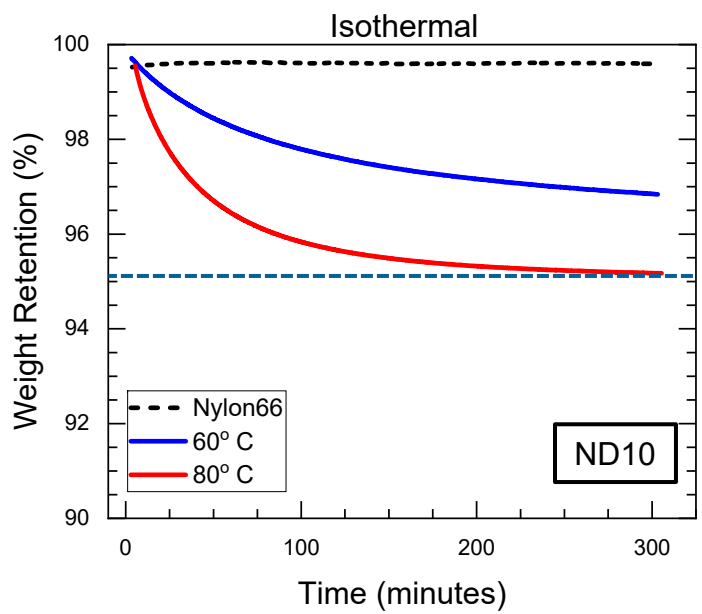
DEET Monofilament Fibers: *Thermal Analysis*

TGA Parameters

- Temperature ramp
  - Heating rate: 10 ° C/min
- Isothermal (T = 60 & 80 ° C)
  - Dwell time: 300 minutes

Sample	Composition (from TGA)
ND10	~4.5 wt%
ND30	~12.5 wt%
ND50	~25.5 wt%





- Significant amount of DEET is lost during the electrospinning process.

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DEET Monofilament Fibers: *Thermal Analysis*

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- Temperature ramp
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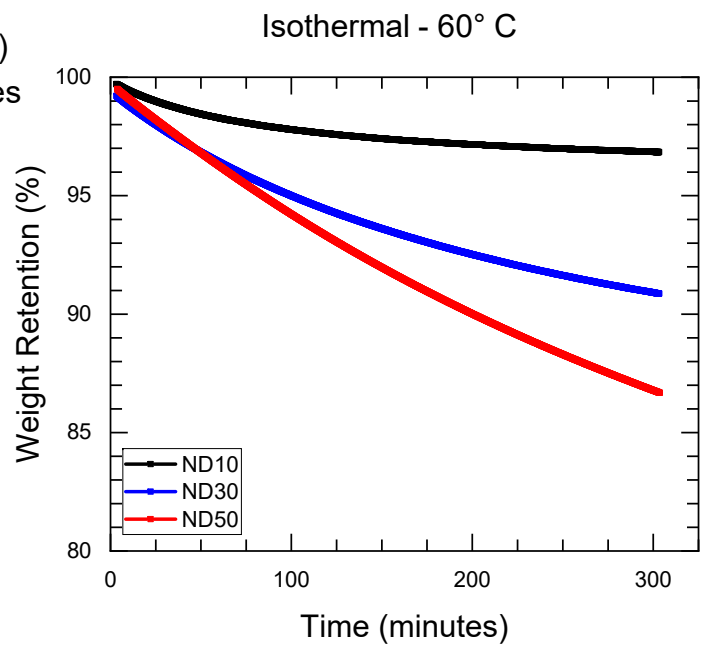

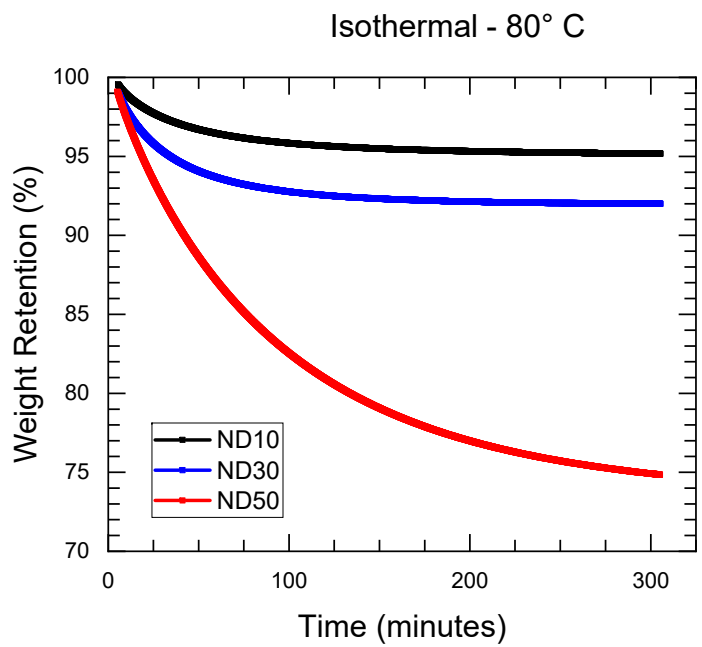

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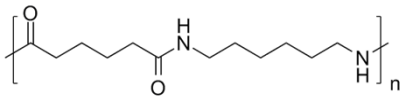
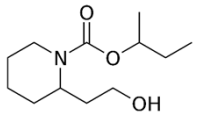
Monofilament Fibers
Picaridin

Composition

- Solvent: Formic Acid
- Polymer Concentration: 12.5 wt% Nylon 6,6
  - ♦ Nominal Picaridin Concentrations:
    - 0, 10, 30, 50 wt% (wrt polymer)
      - NP0, NP10, NP30, NP50, respectively

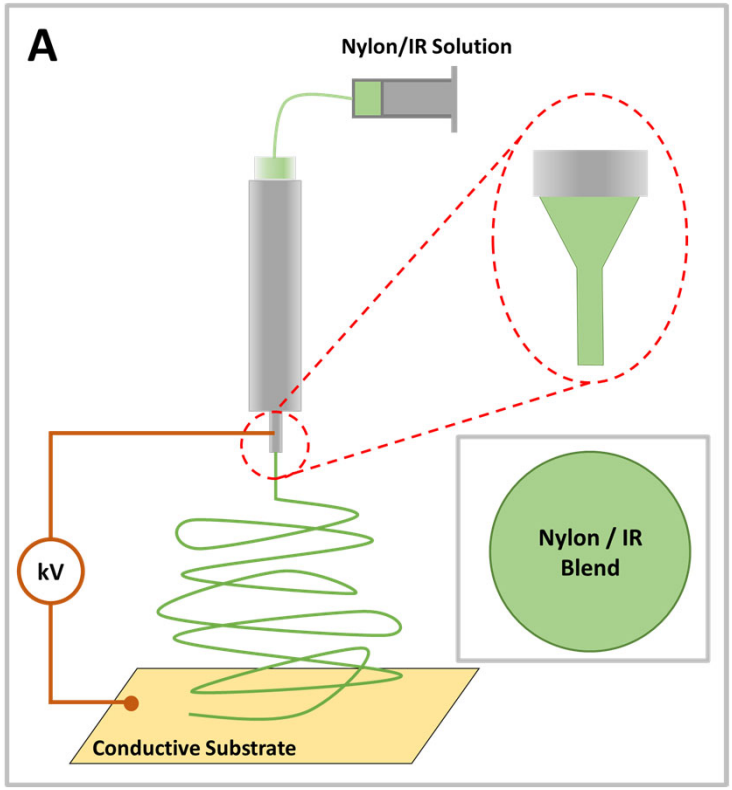


Nylon-6,6

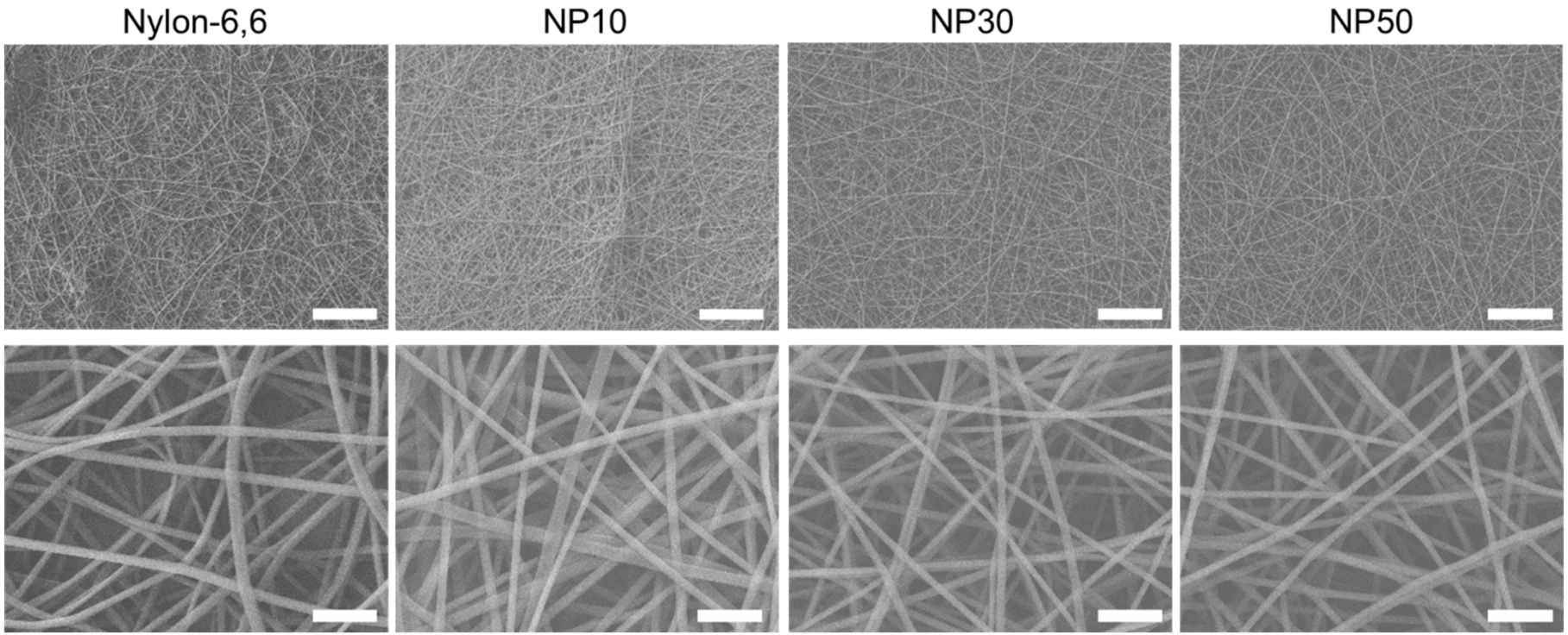


Picaridin

- Field Strength: 1.5 kV/cm
  - Distance: 10 cm
- Flow Rate: 15 µL/min



Picaridin Monofilament Fibers:
Effect of Picaridin Concentration on Morphology



Representative scale bars for top and bottom are 20 µm and 2µm, respectively.

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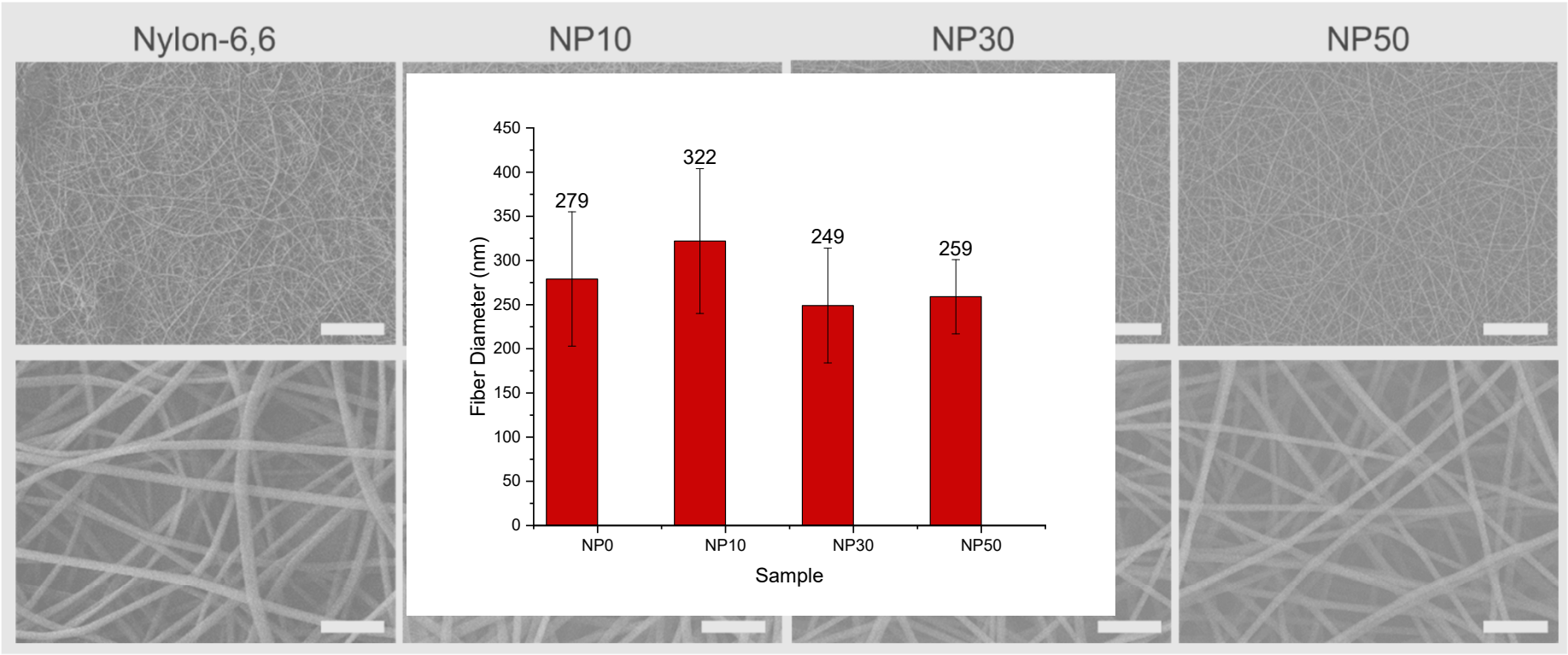
Picaridin Monofilament Fibers:
Effect of Picaridin Concentration on Fiber Diameter



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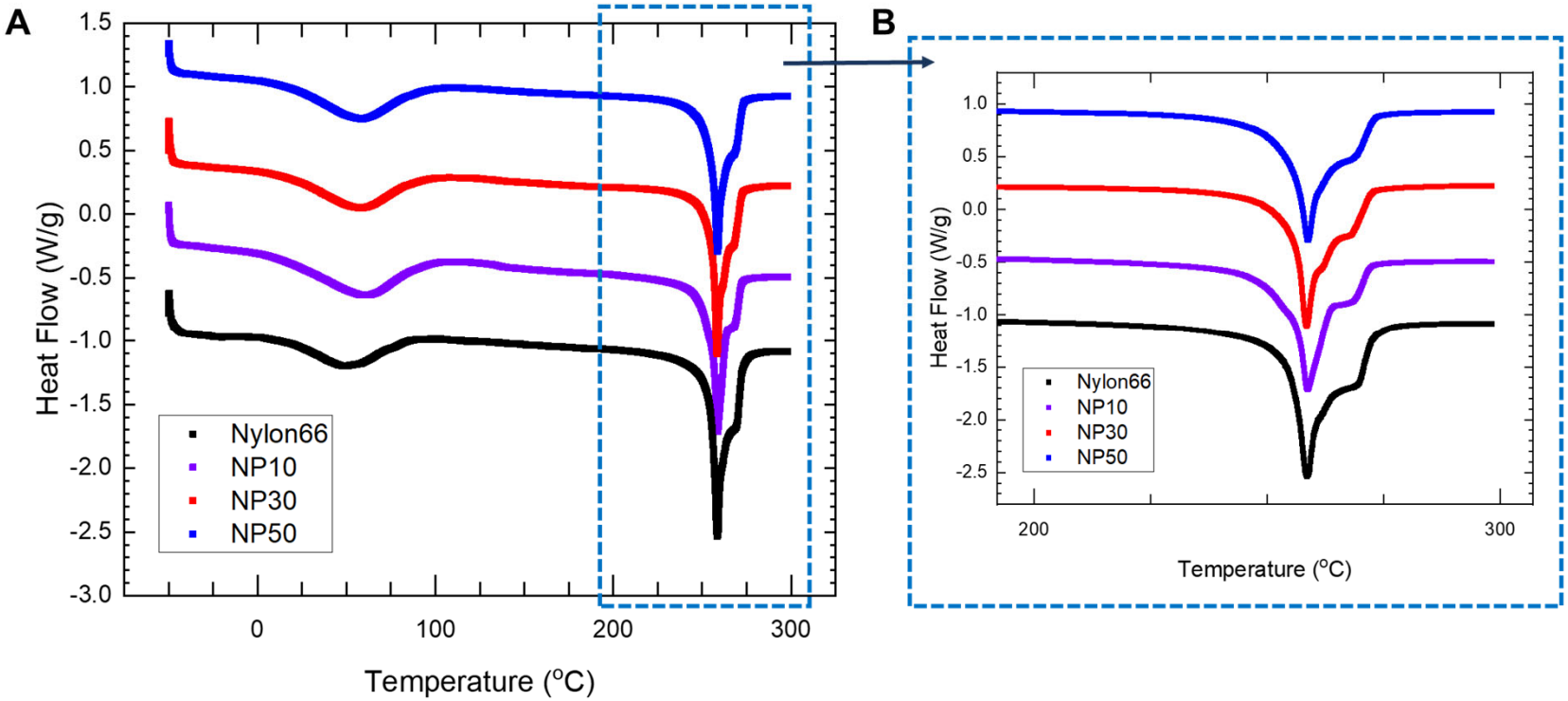
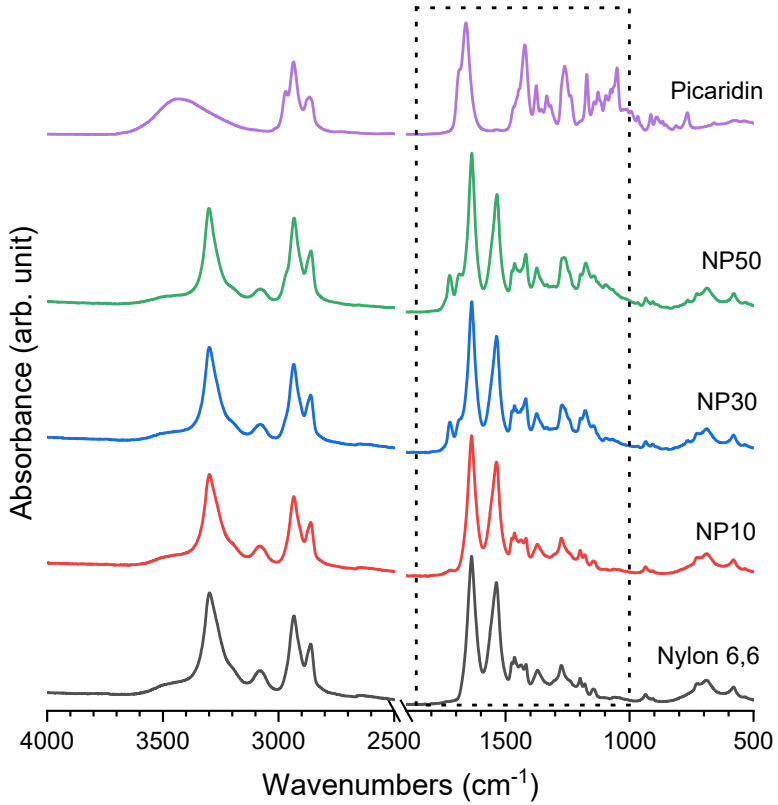
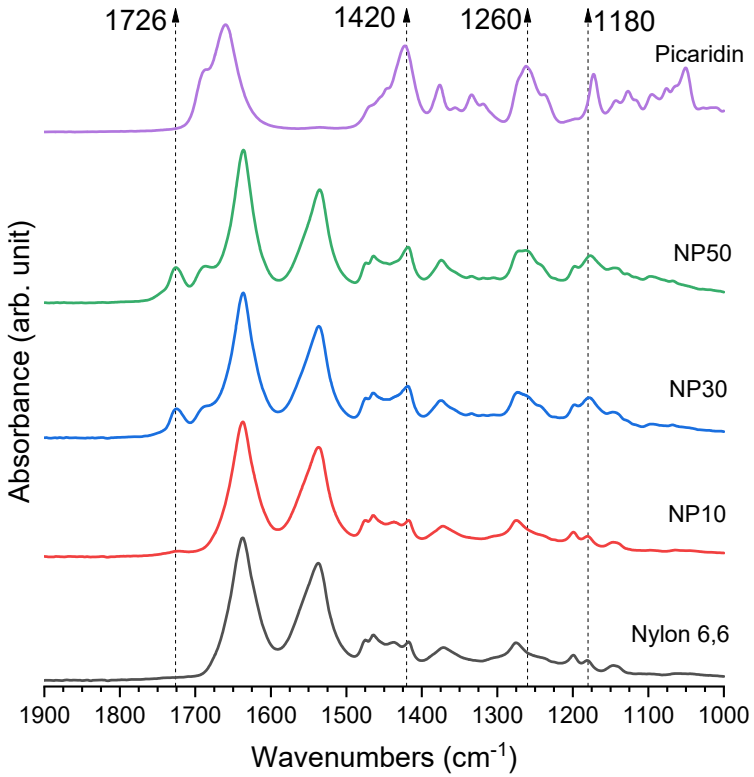
Picaridin Monofilament Fibers: Thermal Characterization *DSC*



Picaridin Monofilament Fibers:
ATR-FTIR Structural Characterization





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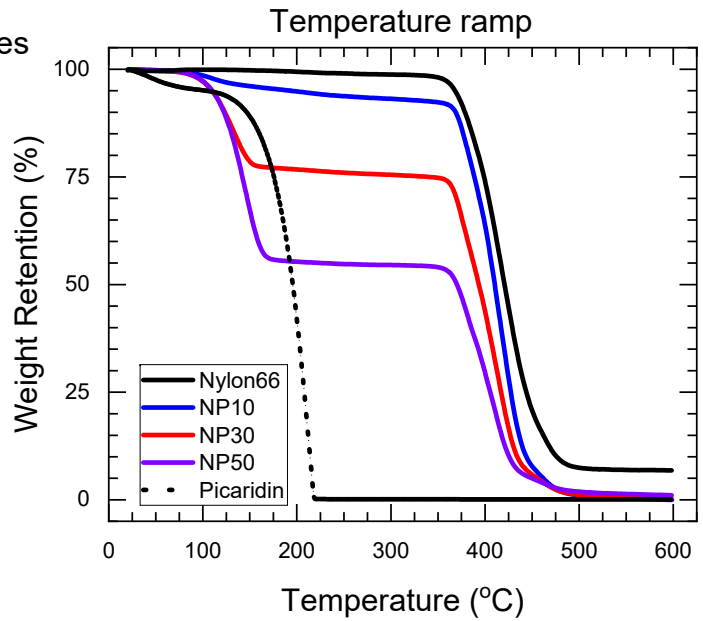
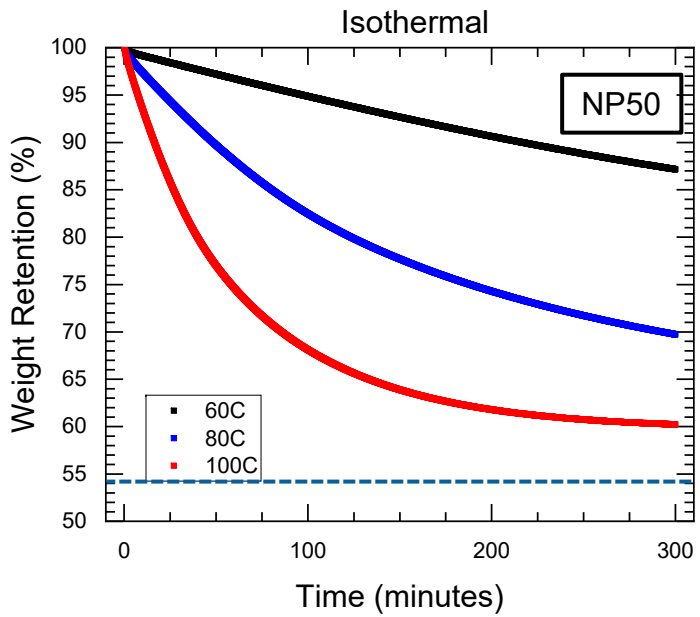
Picaridin Monofilament Fibers: *Thermal Analysis*

TGA Parameters

- Temperature ramp
  - Heating rate: 10 ° C/min
- Isothermal (T = 60, 80, & 100 ° C)
  - Dwell time: 300 minutes

Sample	Composition (from TGA)
NP10	~6.8 wt%
NP30	~25.5 wt%
NP50	~45.5 wt%





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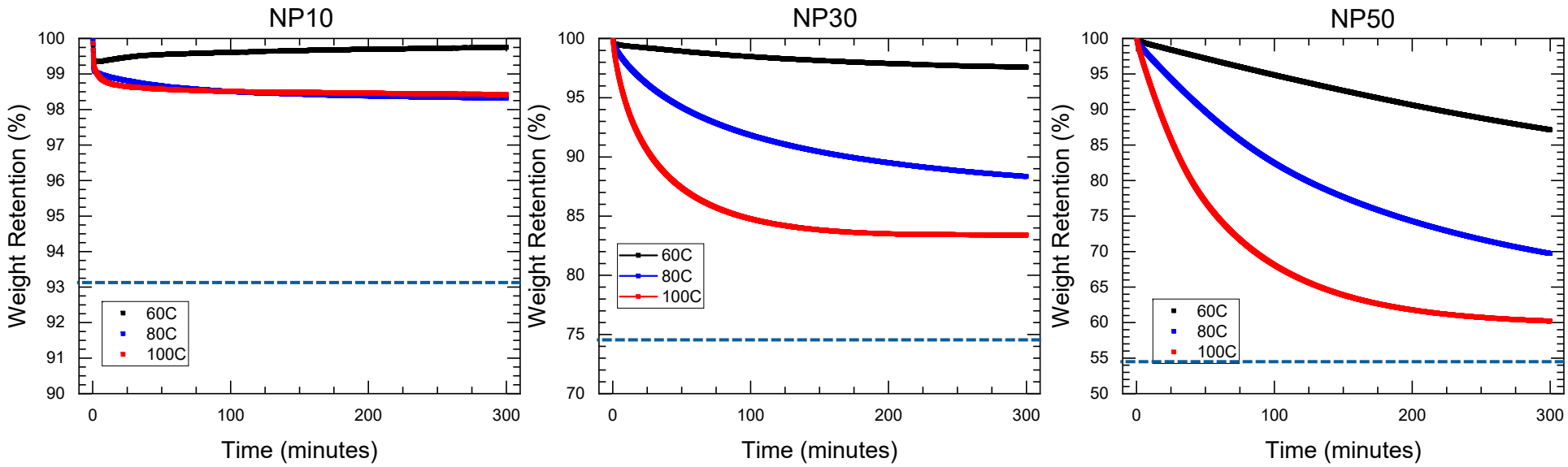
Picaridin Monofilament Fibers:
Isothermal TGA Analysis



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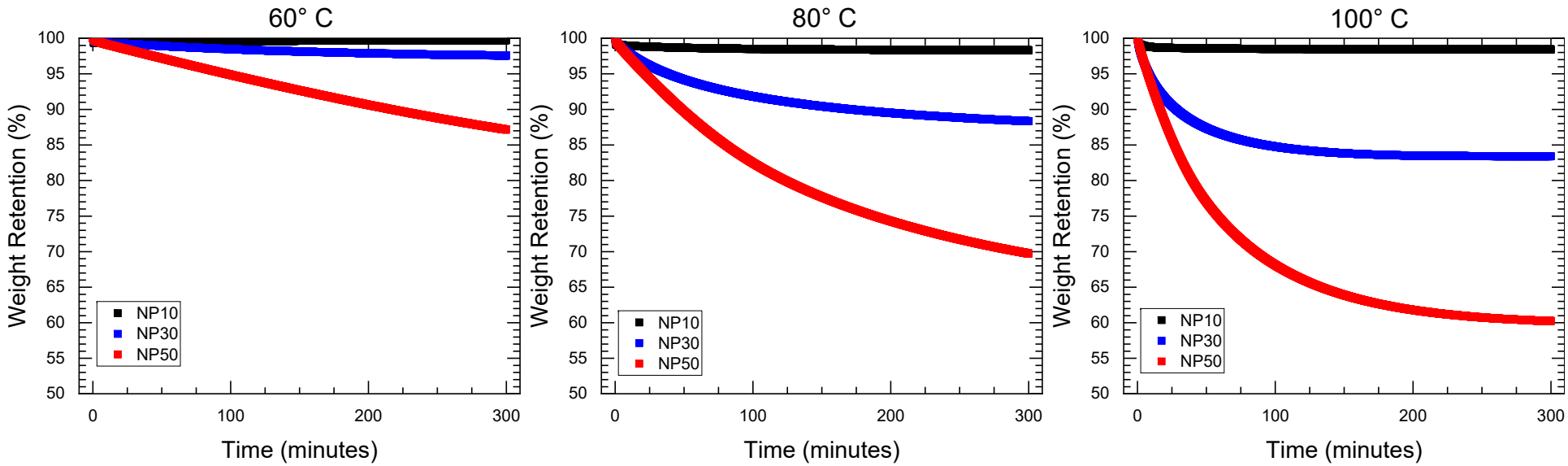
Picaridin Monofilament Fibers:
Isothermal TGA Analysis



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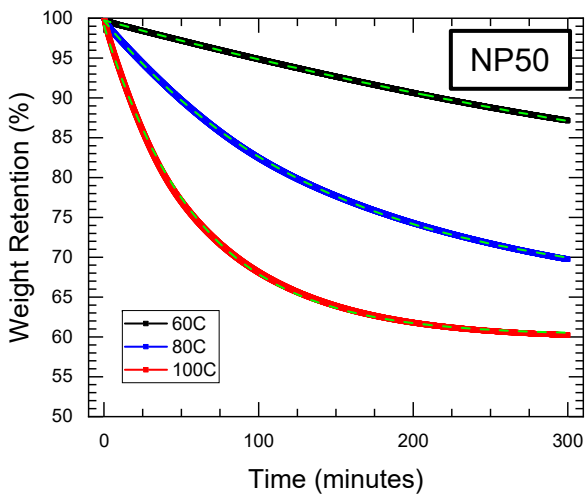
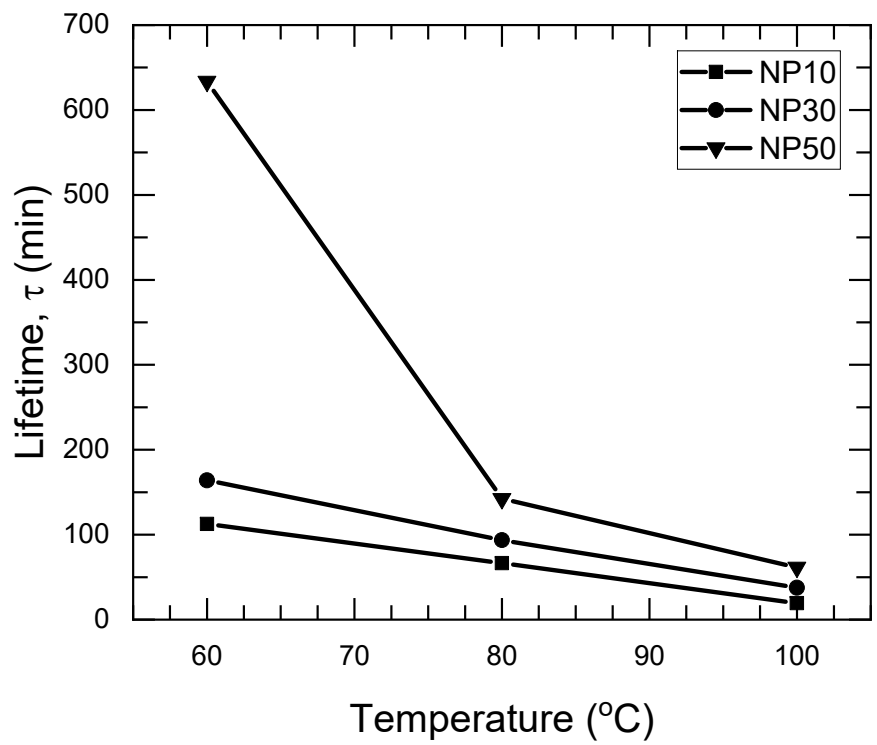
Picaridin Monofilament Fibers:
Release Behavior



Decay Function: $W_t = W_0\, e^{-\frac{t}{\tau}} + 1$

W_t: weight at time=t
W_0: initial weight at time=0
τ: decay lifetime



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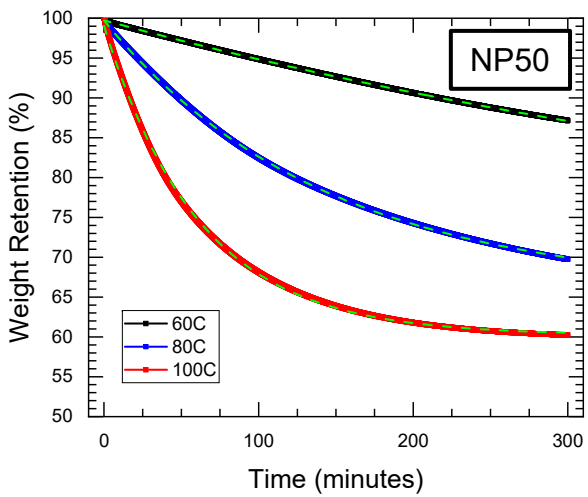
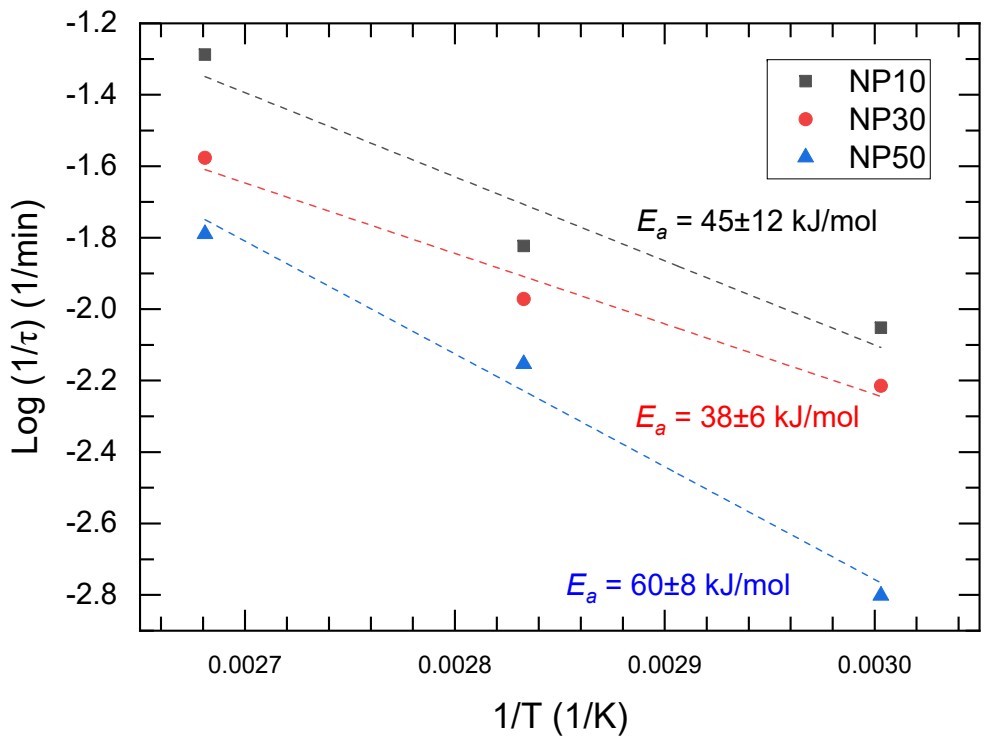
Picaridin Monofilament Fibers:
Release Behavior



Decay Function: $W_t = W_0\, e^{-\frac{t}{\tau}} + 1$

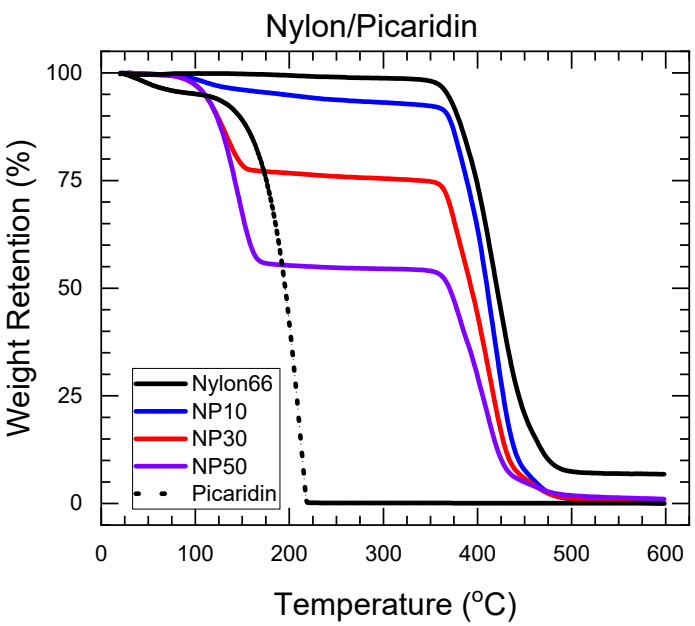
W_t: weight at time=t
W_0: initial weight at time=0
τ: decay lifetime

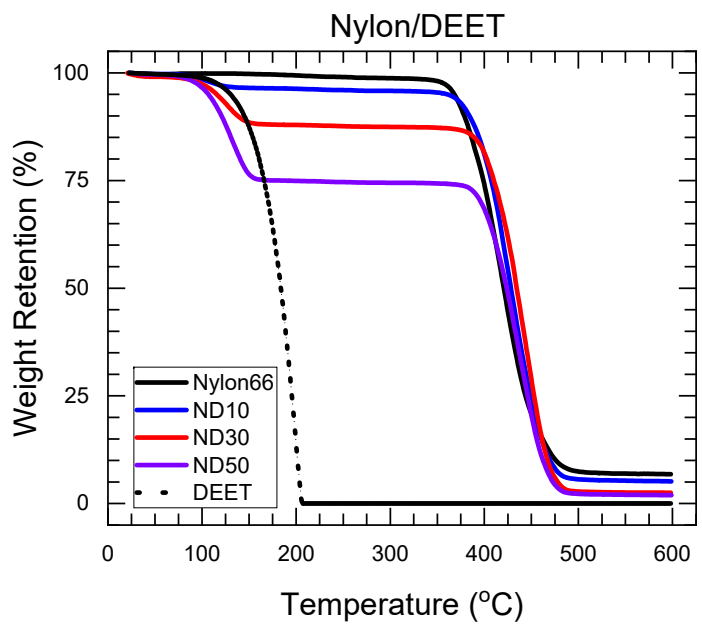


Picaridin Monofilament Fibers:
DEET Comparison

Sample	Composition (from TGA)
ND10	~4.5 wt%
ND30	~12.5 wt%
ND50	~25.5 wt%

Sample	Composition (from TGA)
NP10	~6.8 wt%
NP30	~25.5 wt%
NP50	~45.5 wt%





Repellent	Vapor Pressure @ 20 °C (mmHg)
DEET	5.6×10^{-3}
Picaridin	2.5×10^{-4}

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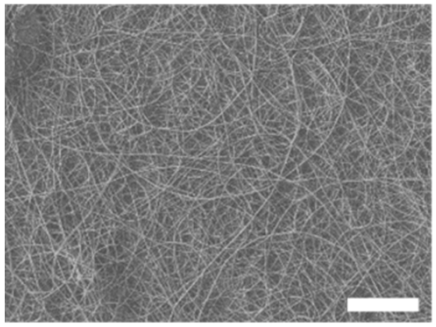
Monofilament Fibers: *Summary*

- Monofilament insect repellent Nylon fibers containing DEET and picaridin were fabricated using a simple electrospinning technique and was shown to be homogenously distributed throughout the fiber matrix via FTIR and differential scanning calorimetry.

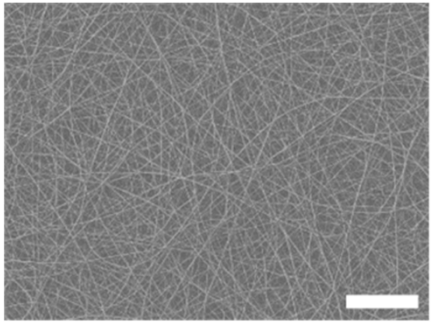
- Diffusion kinetics of encapsulated insect repellents through the semi-crystalline Nylon-6,6 matrix could be tuned by environmental temperature as shown by isothermal thermogravimetric analysis.

- The morphology of repellent fibers was found to be independent of fiber composition, demonstrating the ability to design fibers with defect-free structures at very high repellent loadings for highly durable, performance fabrics.

Nylon-6,6



NP50



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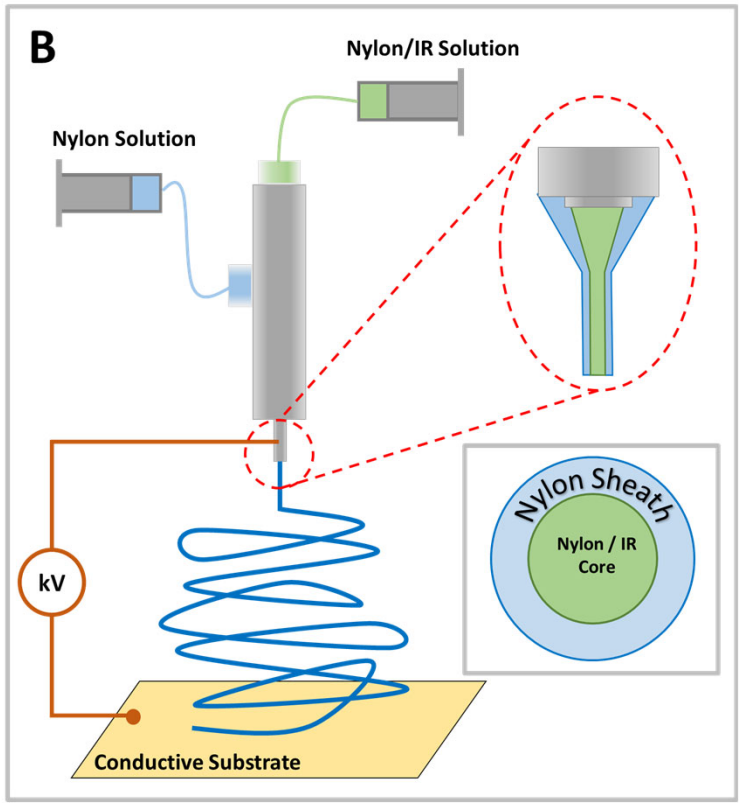
Coaxial Fibers

Sheath

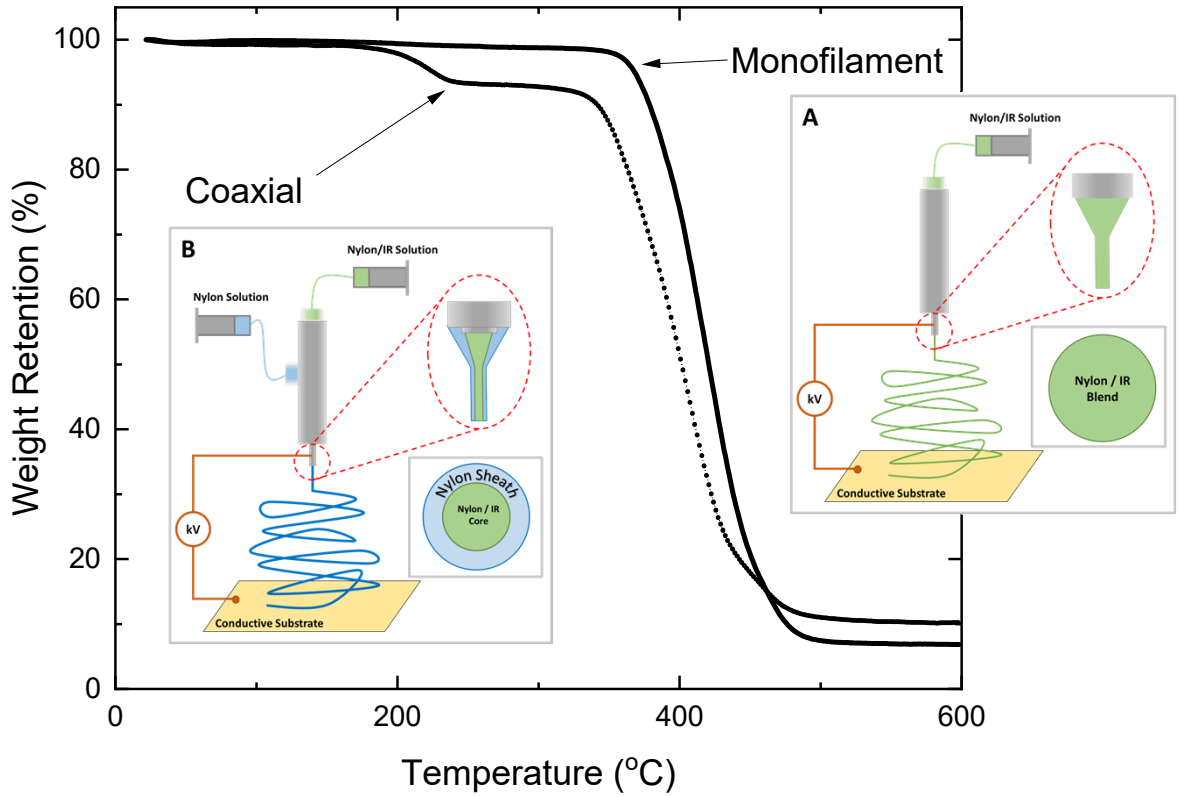
- Nylon/FA solution

Core

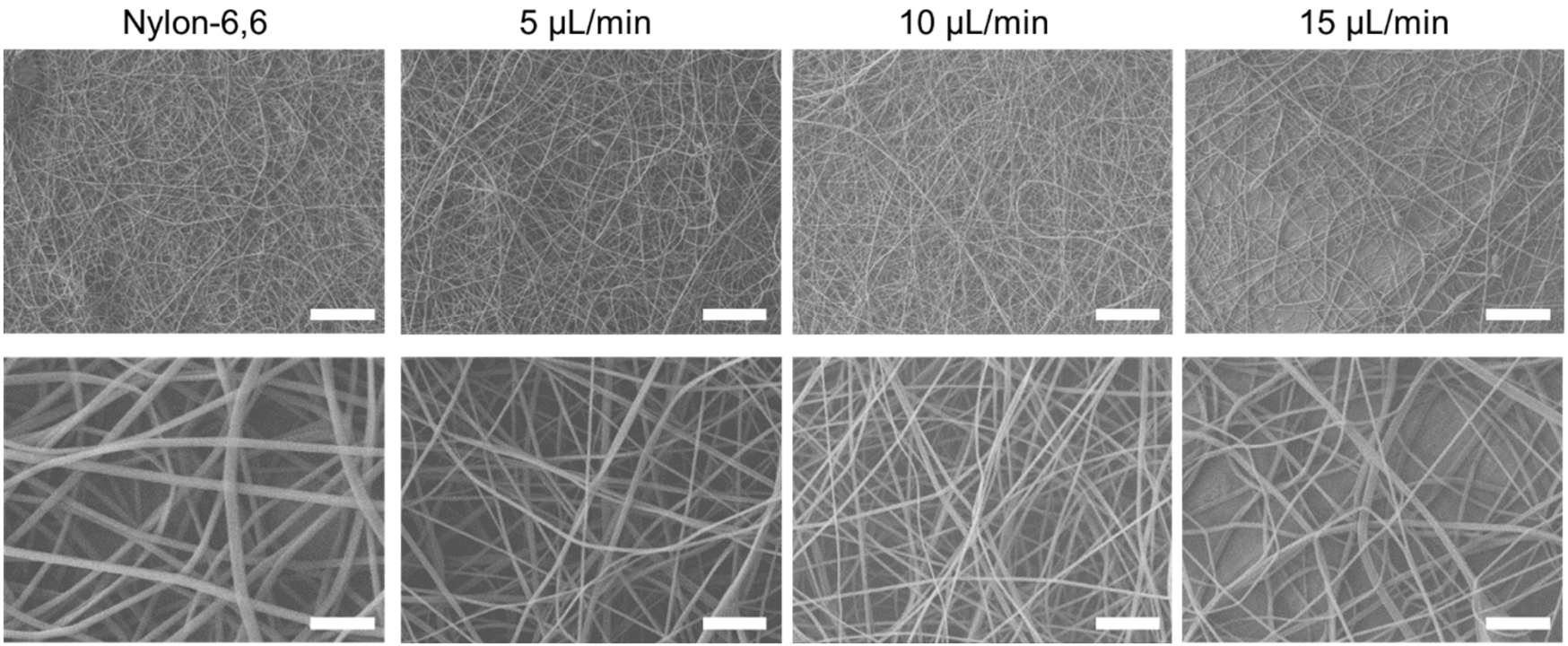
- Picaridin/Nylon/FA solution
  - Modulated core flow rate
    - 5, 10, 15 µL/min



Picaridin Coaxial Fibers: Thermal Analysis Comparison – Nylon 6,6 Fibers



Picaridin Coaxial Fibers:
Morphology



Representative scale bars for top and bottom are 20 µm and 2µm, respectively.

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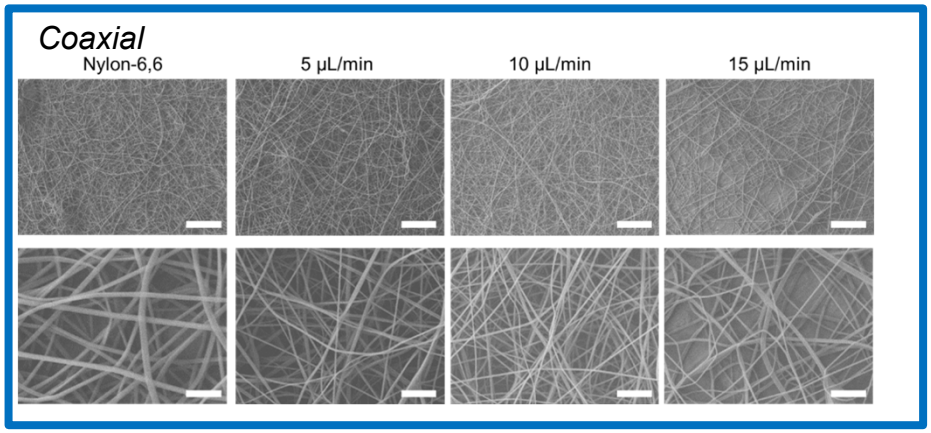
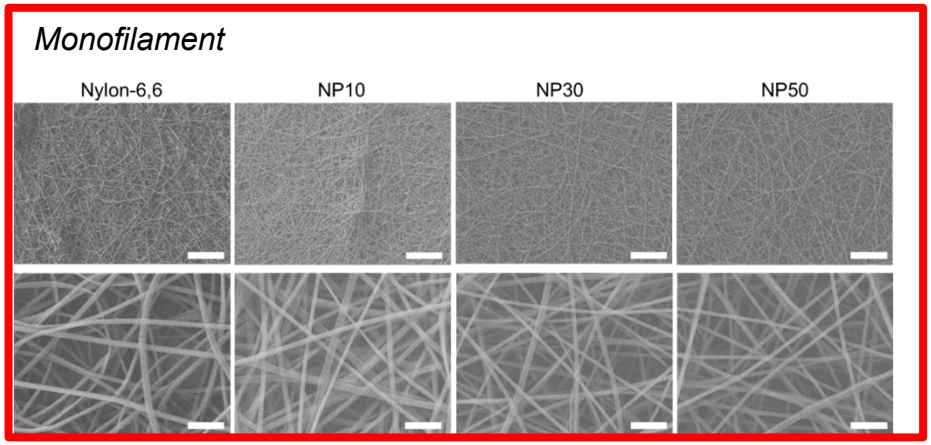
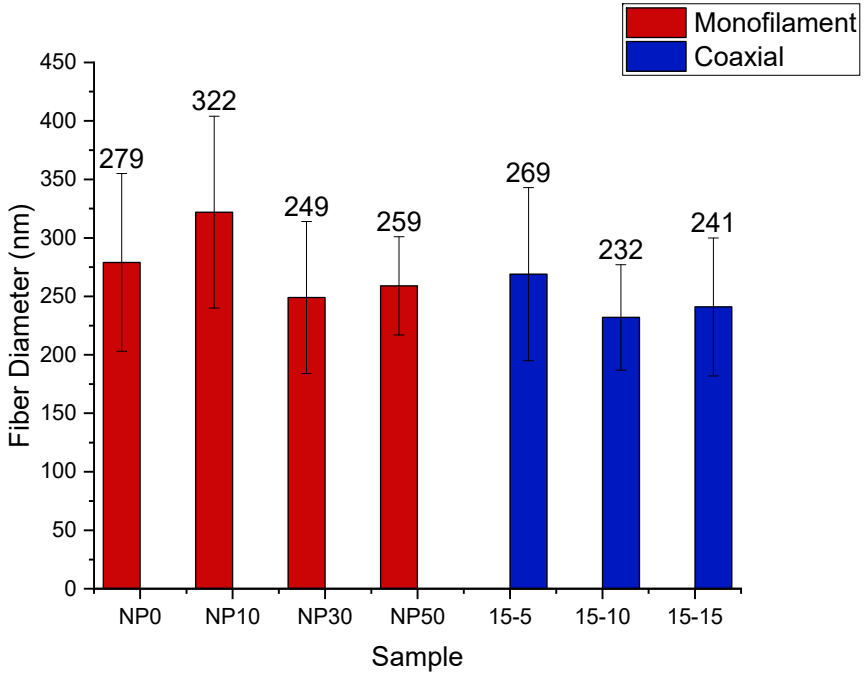
Picaridin Coaxial Fibers:
Morphology & Diameter Comparison to Monofilament







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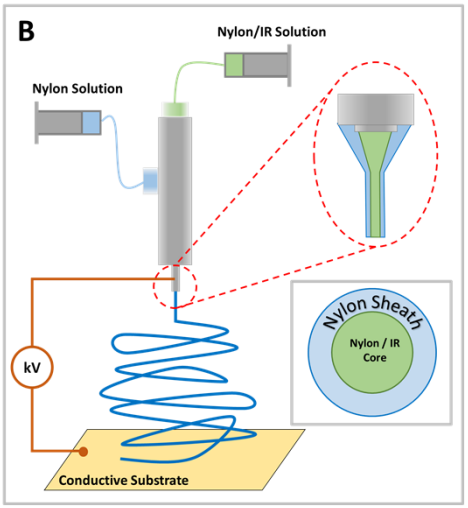
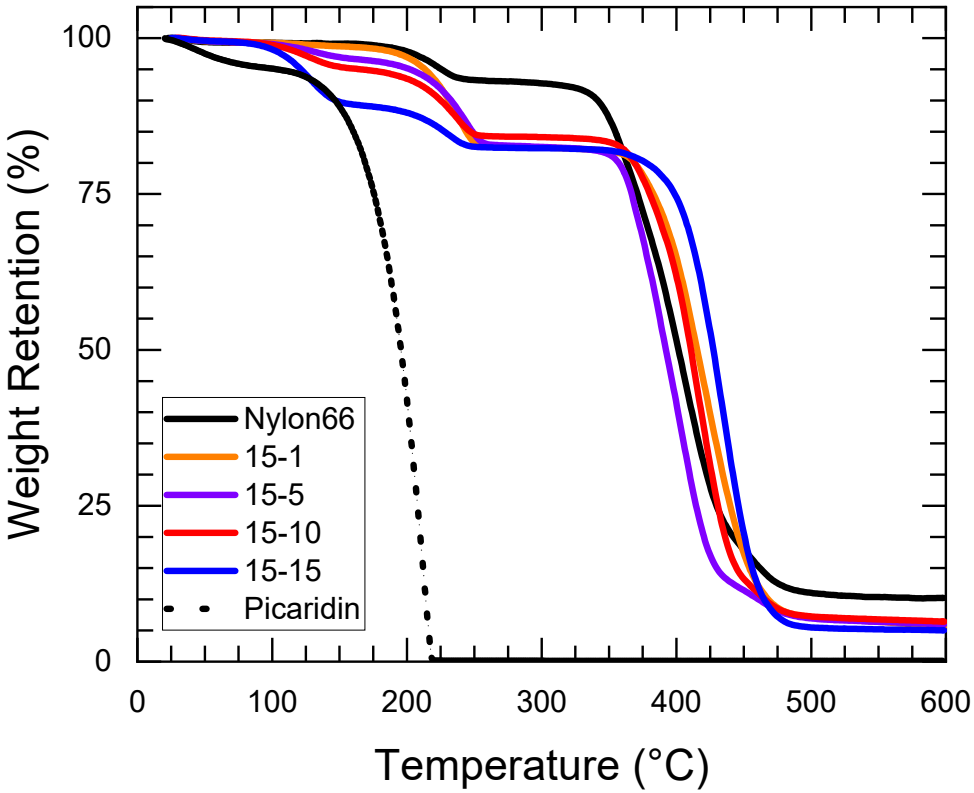
Picaridin Coaxial Fibers:
Thermal Analysis & Release Behavior





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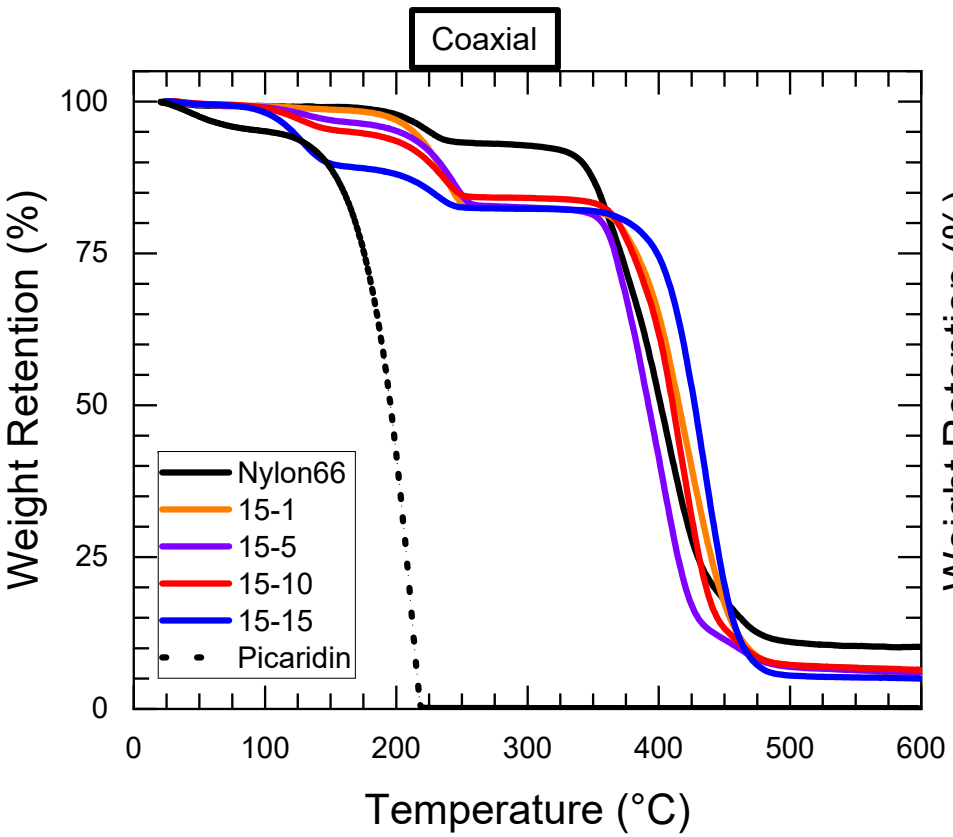
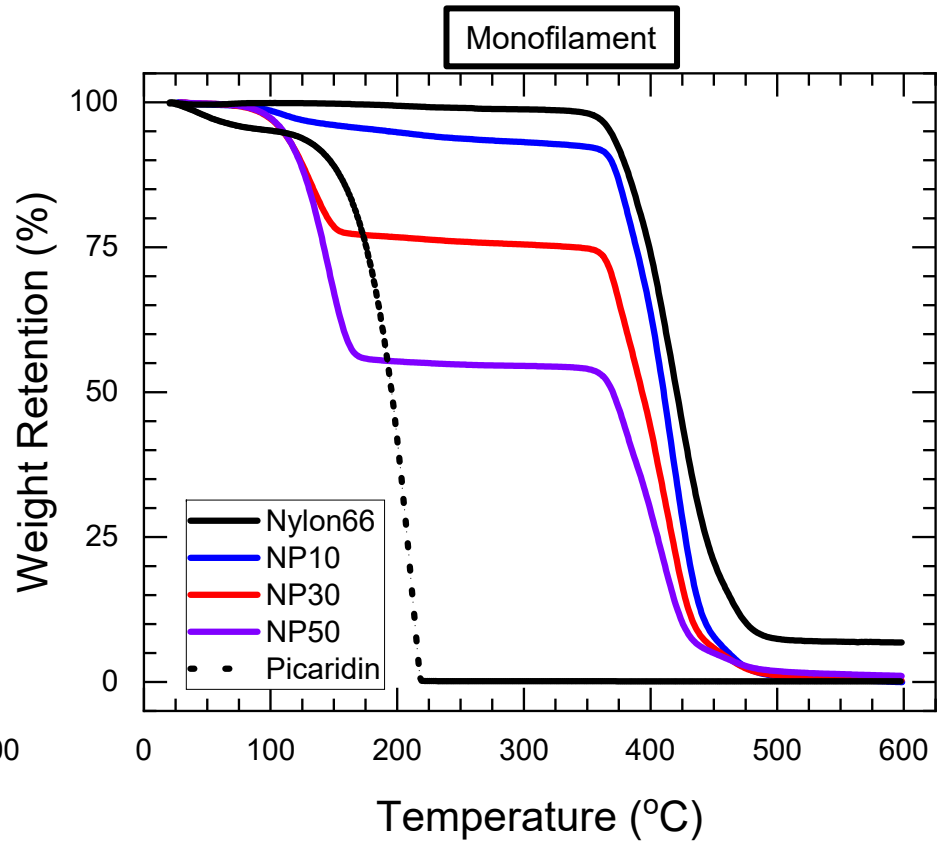
Picaridin Coaxial Fibers:
Thermal Analysis & Release Behavior





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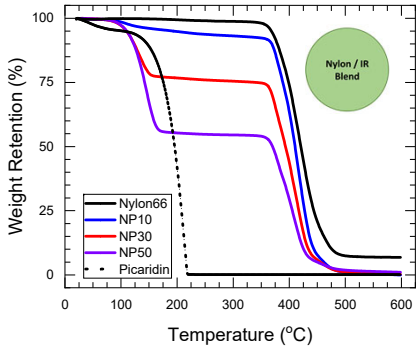
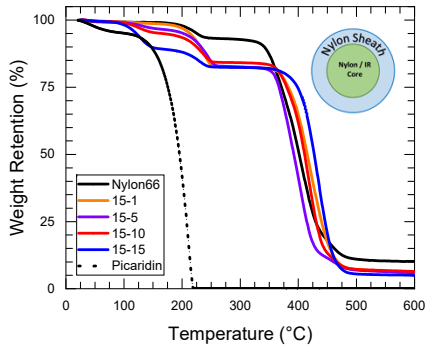
Picaridin Coaxial Fibers: *Summary*

- Coaxial repellent nanofibers were fabricated containing the insect repellent picaridin through a custom-designed core/sheath spinneret.

- Picaridin exhibited a dual-release diffusion mechanism through the Nylon-6,6 matrix as shown by thermogravimetric analysis and was attributed to diffusion of near-surface repellent at low temperature/short times followed by diffusion of core-concentrated repellent at higher temperatures/long times.

- Coaxial repellent nanofiber morphologies, similar to monofilament analogues, were shown to be independent of fiber composition, providing an additional design tool for developing and fabricating tunable composite nanofibers for highly durable, performance fabrics.





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Technical Challenges

- NRL Financial System Transition Delays, Nov 2019 – April 2020 – purchasing freeze (materials, chemicals, supplies, etc.)
- COVID19, March 2020 – present; mandatory Telework

Task 2: Evaluation and delivery of prototypes threads

a. Thread production - collection of fibers on spiral target
b. Evaluate thread performance
c. Prototype fabric production and evaluation

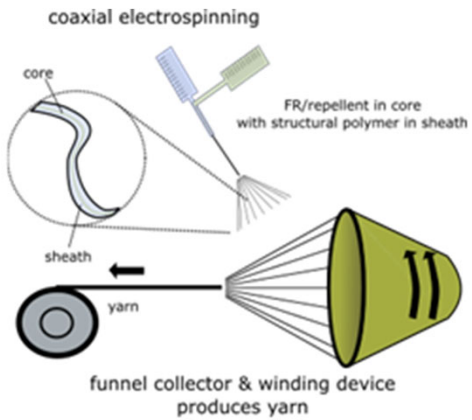

Figure 5. – Coaxial electrospinning set up funnel collector and yarn drawing device.

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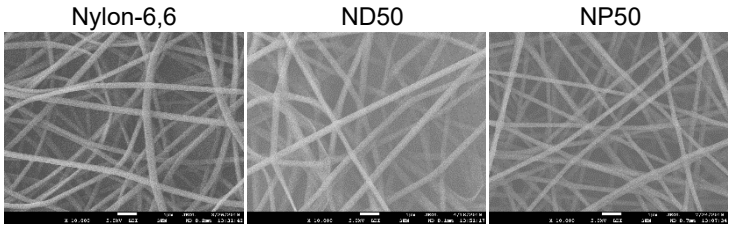
Key Points

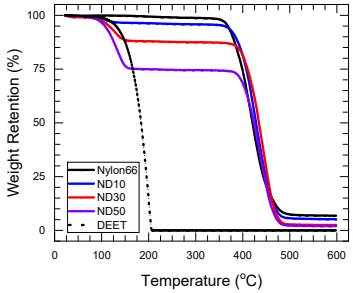
- Incorporation of DEET and Picaridin results in a modest decrease in diameter of Nylon-6,6 nanofibers and does not significantly effect overall spinnability.

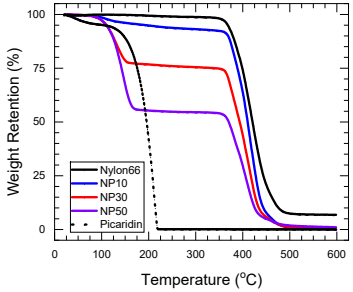
- Vapor pressure/boiling point have a significant impact on the total amount of repellent that can be incorporated into electrospun nanofibers.

- Release **controlled** by insect repellent concentration
- Coaxial design demonstrated enhanced release behavior

- Electrospinning of composite insect repellent nanofibers is a **facile approach** to generate tunable release platforms for textile-based fabrics.
    - Compatible with transition to conventional fiber drawing







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Technology Transfer

IP: Invention Disclosure:

Lundin, J.G; .Ryan, J.J.; Casalini, R.; Orlicki, J.A. ELECTROSPUN COAXIAL POLYMER FIBERS FOR CONTROLLED INSECT REPELLENT RELEASE. *Invention Disclosure*. Navy Case 112377. January 31, 2020

Potential applications/markets:

DoD Applications: Improved insect repellent textiles, reduce transmission of insect (mosquito) borne illness and vaccination burden, Mitigate toxicity and irritation from direct insect repellent spray application

Commercial interest/applications: Potential markets include: military insect repellent textiles, performance textile manufacturers; outdoor recreation companies; medical/infectious disease community.

Transition Pathways:

DOD

- Army Center for Advanced Polymer Processing (ACAPP)
- Natick Soldier Research, Development and Engineering Center houses the Army Fiber Center of Excellence

Commercial (Letter of support)

- SciGenesis – pilot scale capability

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Future Research

Follow-on options:

1. Insect Repellent Yarns, Fabrics, & Demonstration
    1. Deliver –
        1. Repellent efficacy of spun fabrics/yarns.
        2. Mixed Repellent systems
        3. Electrospun Yarns
        4. Transition to conventional Fiber Fabrication
        5. Insect Demonstration
    2. ROM: Y2 ~$210K; Y3 ~$250K

2. Multifunctional Fibers
    1. Demonstrate IR + Fire Retardants or Antimicrobial/Antiviral
        1. Fire retardant
            1. ROM: Y2 ~$260K, ~$290K
        2. Antimicrobial/Antiviral
            1. ROM: Y2 ~$230K, $260K

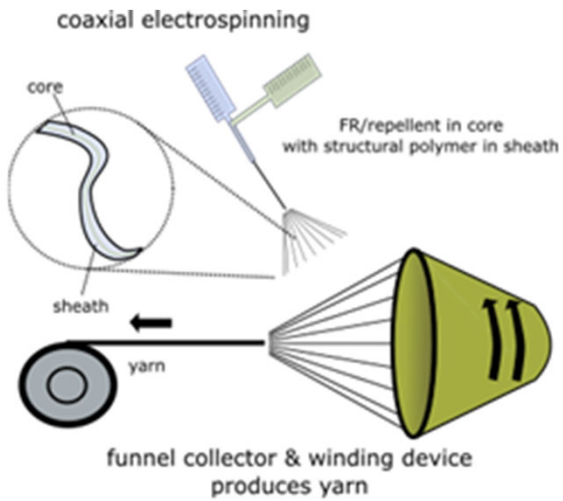
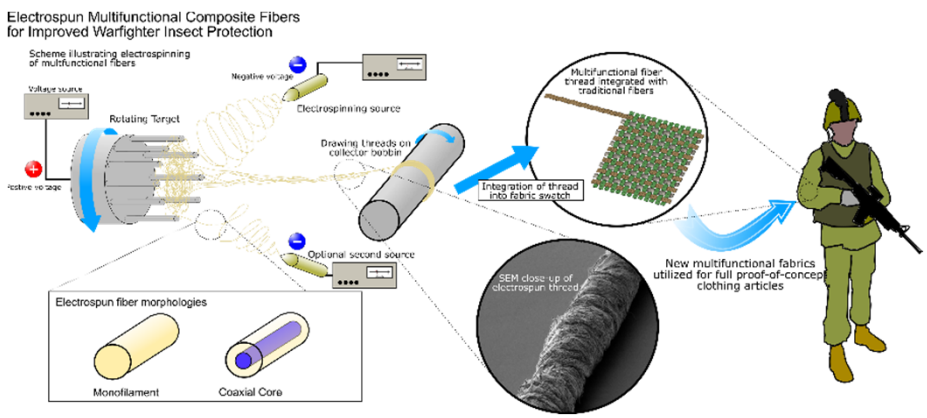


Figure 5. – Coaxial electrospinning set up funnel collector and yarn drawing device.



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Publications

Refereed Journal Article:

1. Ryan, J.J.; Casalini, R.; Orlicki, J.A.; Lundin, J.G. Controlled Release of the Insect Repellent Picaridin from Electrospun Nylon-6,6 Nanofibers: Comparison of Monofilament and Coaxial Structures. *Submitted to Journal of Applied Polymer Science – Jan. 31, 2020*

Invention Disclosure:

1. Lundin, J.G; .Ryan, J.J.; Casalini, R.; Orlicki, J.A. ELECTROSPUN COAXIAL POLYMER FIBERS FOR CONTROLLED INSECT REPELLENT RELEASE. *Invention Disclosure*. Navy Case 112377. January 31, 2020

Memorandum Report:

1. Lundin, J.G; .Ryan, J.J.; Casalini, R.; Orlicki, J.A. Electrospun Multifunctional Composite Fibers for Improved Warfighter Insect Protection. *2020 NRL Memorandum Report. To be published on DTIC*

Conference Presentations:

1. Ryan, J.; Casalini, R.; Orlicki, J.A.; Wynne, J.H.; Lundin, J.G. Insect Repellent Release from Coaxial Electrospun Fibers. *2019 ACS Fall Meeting & Exposition*, San Diego, CA, August 27. POLY 286
2. Ryan, J.J.; Casalini, R.; Orlicki, J.A.; Lundin, J.G. Electrospun Multifunctional Composite Fibers for Improved Warfighter Insect Protection, *2019 SERDP-ESTCP Symposium*, Washington, DC, Dec. 4 2019
3. Ryan, J.J.; Casalini, R.; Orlicki, J.A.; Wynne, J.H.; Lundin, J.G. Electrospun coaxial nylon fibers for controlled insect repellent release. *ACS Spring 2020 National Meeting & Exposition.* Philadelphia, PA. March 24, 2020 PMSE638*

   **cancelled due to COVID travel restrictions*

Project Funding

	FY19
Funds received to date ($K)	197.978*
% Expended	99.5
Funds Remaining ($K)	0.948

**Invoiced expenditures total $158K, discrepancy from processing Post Doc charges*

Status of Funds for Federal Performers

FY2019 Funds			
Directly Funded Federal Performer(s)	**Funds Received**	**Funds Obligated***	**Percent Funding Obligated**
NRL - Reimbursable MIPR	$154,424	$153,487	99.4
ARL - Reimbursable MIPR	$43,554	$43,543	100%

* Funds put on contracts and/or purchase orders that have been issued, and funds associated with internal labor or travel expenses that have been incurred.

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