



# A Simple Surface Functionalization Method for Multifunctional Textiles with Flame and Vector Protection

**Project Number: WP19-1050**

**Dr. Ravi Mosurkal**

**U.S. Army DEVCOM - Soldier Center, Natick, MA 01760**

**28 February 2020**



**REPORT DOCUMENTATION PAGE**

Form Approved  
OMB No. 0704-0188

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<b>1. REPORT DATE (DD-MM-YYYY)</b> 28/02/2020		<b>2. REPORT TYPE</b> SERDP Project Outbrief		<b>3. DATES COVERED (From - To)</b> Feb 2019-Feb 2020	
<b>4. TITLE AND SUBTITLE</b> A Simple Surface Functionalization Methodfor Multifunctional Textiles with Flame and Vector Protection: Multifunctional Fibers and Textiles for Warfighter Integrated Protection				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Ravi Mosurkal and Julie St. Cyr: U.S. Army DEVCOM  Arjan Giaya: LaunchBay LLC  Ramaswamy Nagarajan, Sourabh Kulkarni, and Zhiyu Xia: University of Massachusetts Lowell				<b>5d. PROJECT NUMBER</b> WP19-1050	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army DEVCOM Soldier Center Natick, MA 01760				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> PAO #: U20-1926	
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> SERDP	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> WP19-1050	
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The technical objectives of this project are listed below: <ul style="list-style-type: none"> <li>• Develop safer, durable and cost-effective fire retardant and insect repellent coatings for Nylon/Cotton (50:50 blend) aka Nyco.</li> <li>• Covalent functionalization of safer, bio-derived flame retardant material, Phytic acid on Nyco.</li> <li>• Plasma assisted deposition of permethrin (insect repellent) on Nyco.</li> <li>• Characterization of thermal and flammability properties of FR Nyco.</li> <li>• Evaluation of efficacy of the IR Nyco</li> </ul>					
<b>15. SUBJECT TERMS</b> Multifunctional Fibers, Textiles, Warfighter Integrated Protection, Flame and Vector Protection					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b> UNCLASS	<b>18. NUMBER OF PAGES</b> 26	<b>19a. NAME OF RESPONSIBLE PERSON</b> Ravi Mosurkal
<b>a. REPORT</b> UNCLASS	<b>b. ABSTRACT</b> UNCLASS	<b>c. THIS PAGE</b> UNCLASS			<b>19b. TELEPHONE NUMBER (Include area code)</b> 508-233-5791

# Project Team

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## **Prof. Ramaswamy Nagarajan** (Cooperative Agreement)

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Ph.D. Student

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## **Julie St. Cyr**

ORISE Participant, US Army DEVCOM - Soldier Center, Natick, MA 01760



*Learning with Purpose*

## **Dr. Arjan Giaya** (UML sub-contract using CA)

President, LaunchBay LLC, Chelmsford, MA 01824



# Background

- Period of Project: Feb 2019- Feb 2020
- Addressing WPSO-19-C5
  - ◆ Program Area: Weapons Systems and Platforms (WP)
  - ◆ Project Title: Multifunctional Fibers and Textiles for Warfighter Integrated Protection
  - ◆ Statement of Need (SON): Investigate multifunctional fibers, textiles and/or impregnated fabrics that utilize formulations with environmentally friendly insect repellants, insecticides and/or flame retardants (FR).

# Current State of Art & Limitations

## Flame Resistant Army Combat Uniform (FR-ACU)

### Positive Attributes:

Meets FR requirements

FR-ACU  
Rayon/Kevlar/nylon  
65/25/10

### Challenges:

- Cost prohibitive to issue to every soldier (*not available for soldiers in training, domestic operations, other service members etc.*)
- Poor durability (especially when wet)
- Raw materials are not domestically produced (Berry Amendment!)
- Rayon requires use of toxic solvent, carbon disulfide
- Dying and Colorfastness issues

## Army Aircrew Combat Uniform (A2CU)

### Positive Attributes:

Meets FR requirements

NOMEX

### Challenges:

- Expensive
- Processed with Hazardous solvents/chemicals
- Nomex uniforms are less breathable than traditional ACU

## Army Combat Uniform (ACU)



### Positive Attributes:

Durable  
Inexpensive  
Comfortable

### Challenges:

- No FR protection
- No Insect protection

NYLON-COTTON (50/50)  
NYCO

Army combat uniforms can be made flame retardant

- Without the use of Toxic Solvents
- FR molecules
  - Bio-derived
  - In expensive
  - No Bio-accumulation

# Technical Objectives

Develop safer, durable and cost-effective fire retardant and insect repellent coatings for Nylon/Cotton (50:50 blend) aka Nyco

- ❖ Covalent functionalization of safer, bio-derived flame retardant material, Phytic acid on Nyco



- ❖ Plasma assisted deposition of permethrin (insect repellent) on Nyco
- ❖ Characterization of thermal and flammability properties of FR Nyco
- ❖ Evaluation of efficacy of the IR Nyco

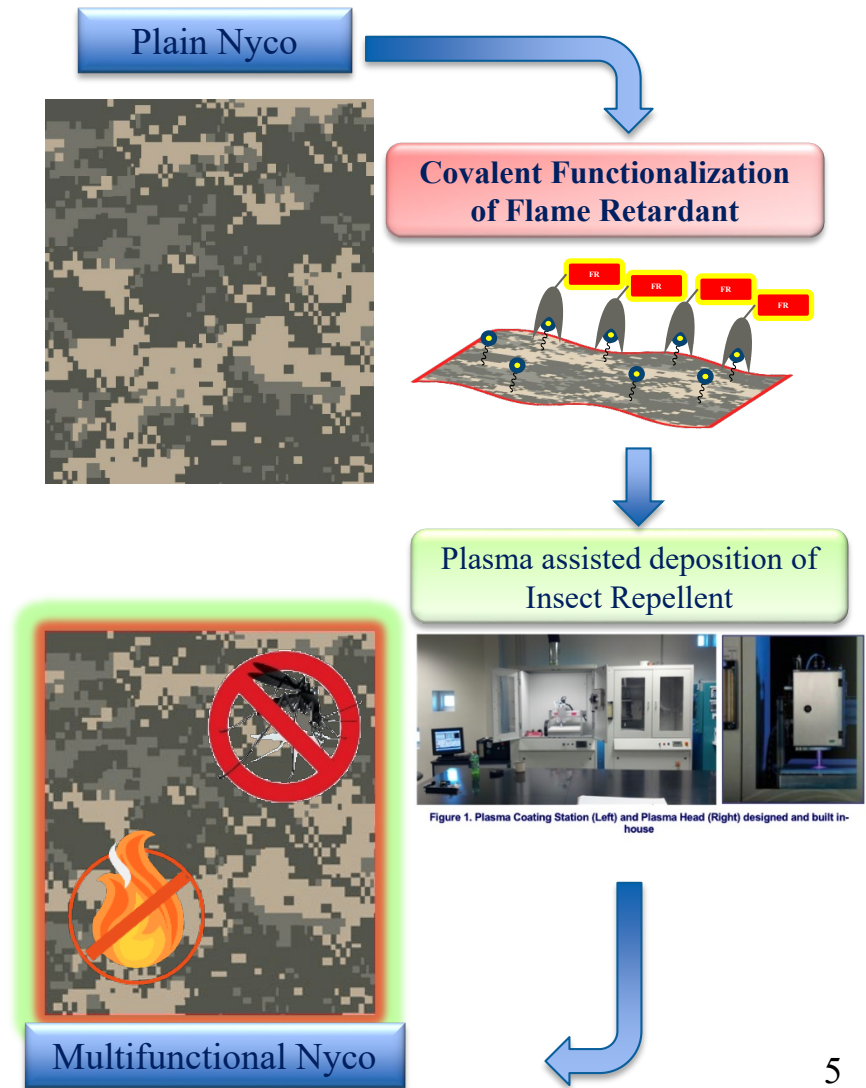


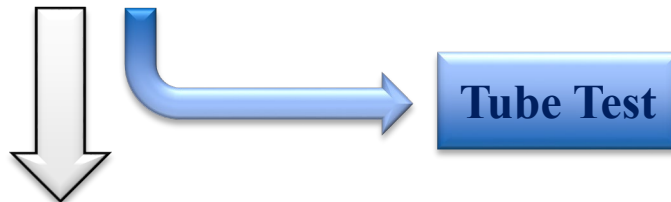
Figure 1. Plasma Coating Station (Left) and Plasma Head (Right) designed and built in-house

# Technical Approach

**Task 1: Chemical Functionalization of Flame Retardant (FR) and Characterization**



**Task 2: Plasma Assisted Deposition of Insect Repellent (IR) and Characterization**

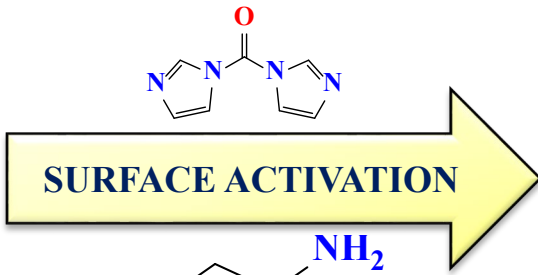
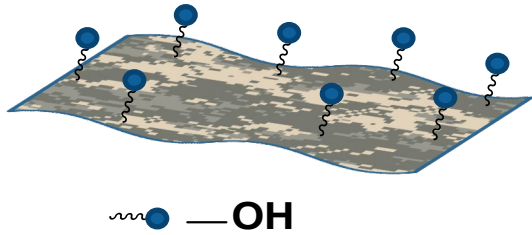


**Task 3: Fabrication of Multifunctional Fabric**

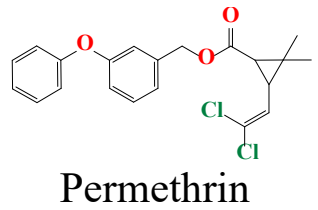
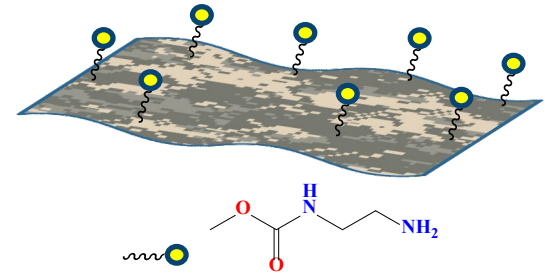


# Schematic of Technical Approach

**Plain Nyco**

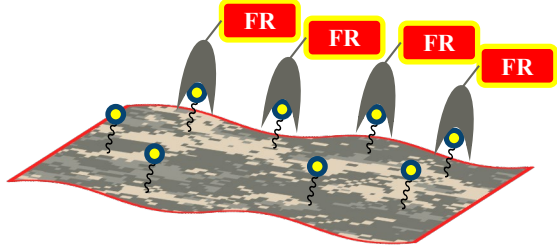
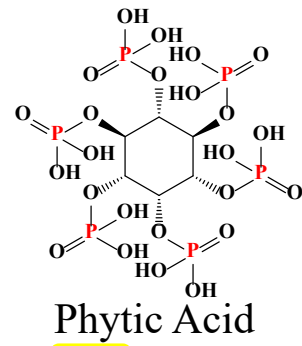


**Surface Activated Nyco**



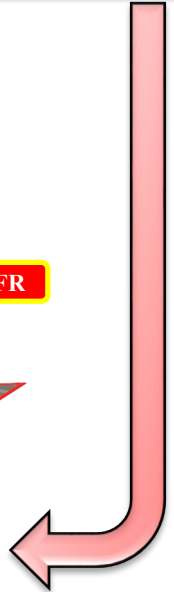
**FR IR Nyco**

**IR TREATMENT**

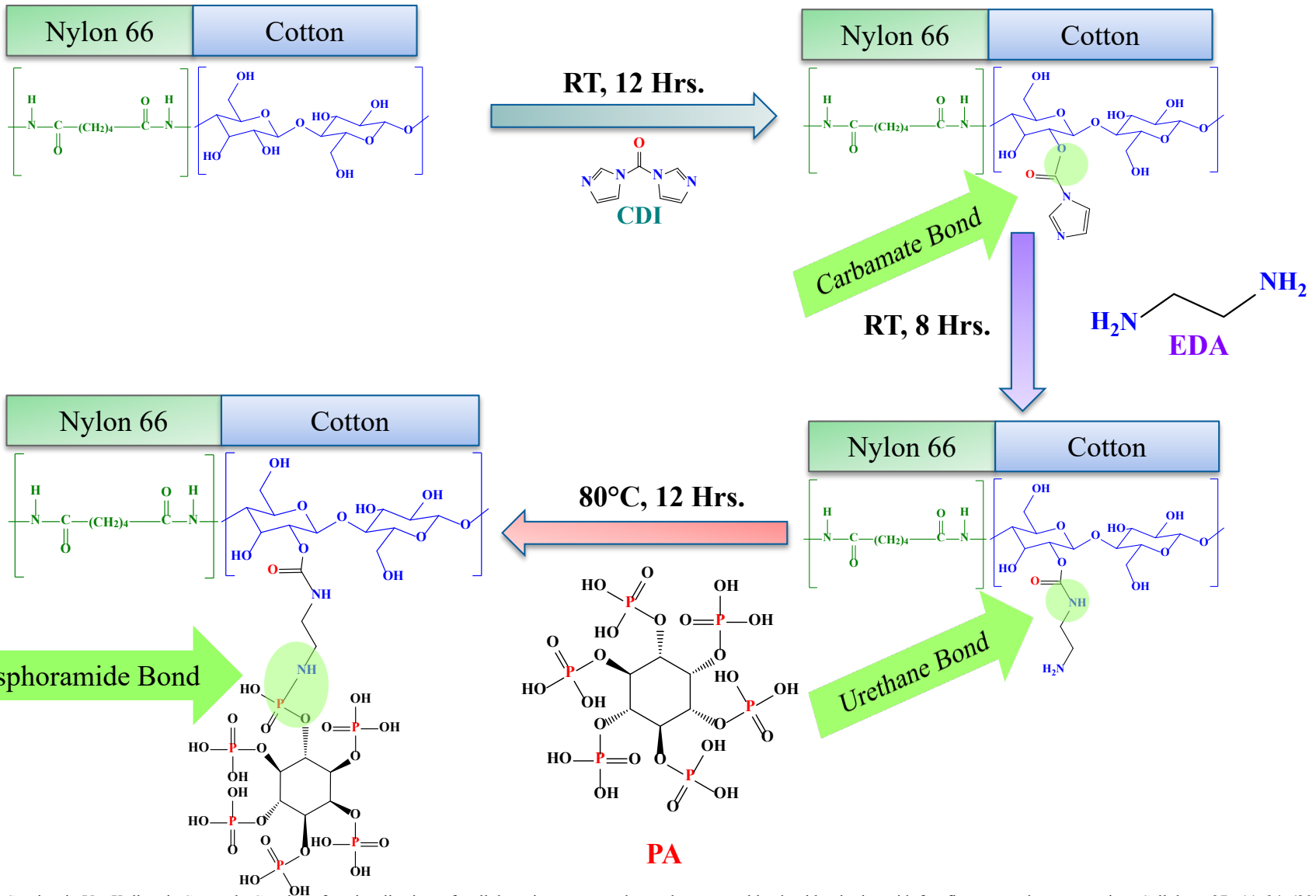


**FR Nyco**

**FR TREATMENT**



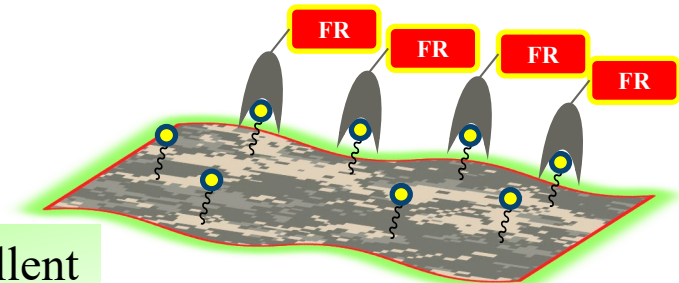
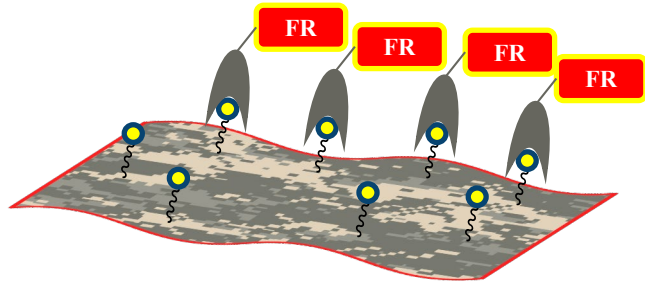
# Chemistry behind FR functionalization



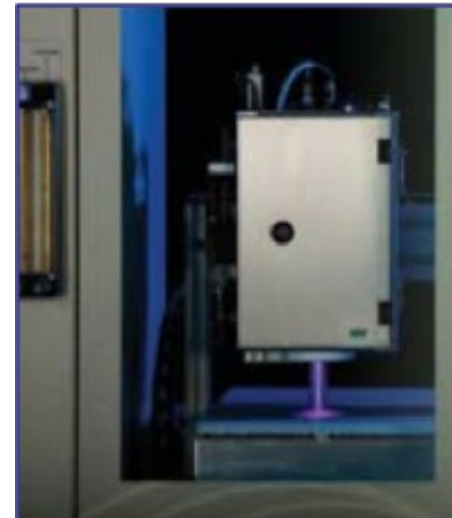
# Plasma Assisted Deposition of Permethrin

Flame Retardant Nyco

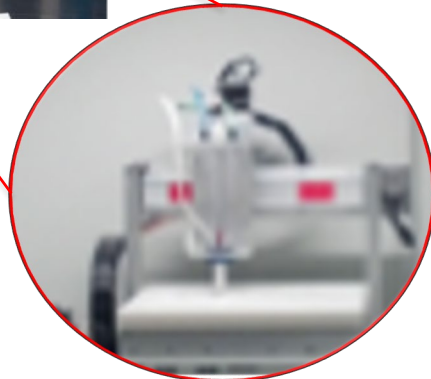
Multifunctional Nyco



Insect Repellent



Active Ingredient  
+  
Acrylic Binder  
+  
Curing Agent



Robotic Coating Arm



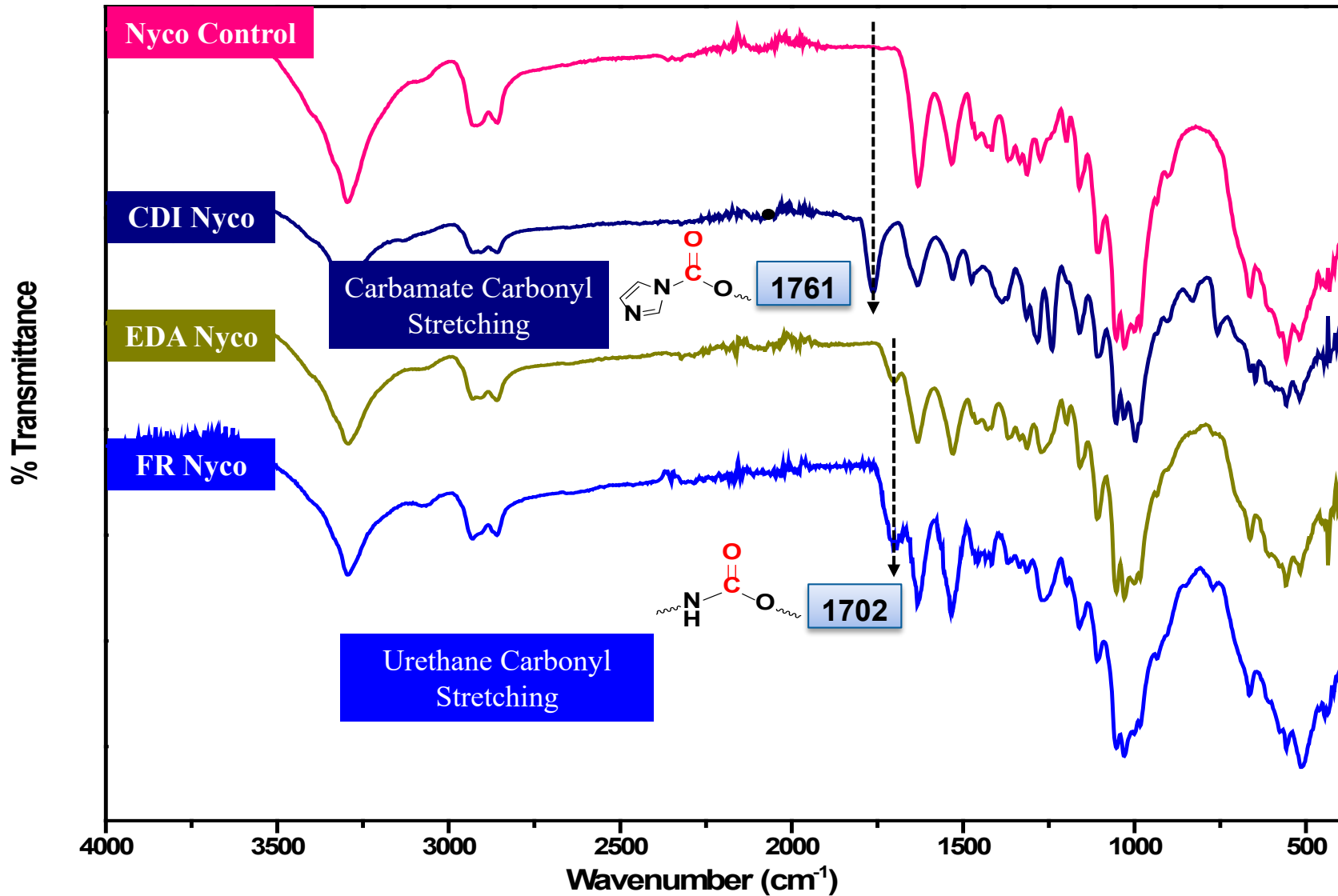
# Results Overview

- Surface Characterization: ATR-FTIR

Evaluation of:

- Thermal Stability & Char Formation: TGA
- Heat Release Properties: MCC
- Flammability Properties: Vertical Flame Test
- Insect Repellency: WHO Tube Test
- Air Permeability: ASTM D737

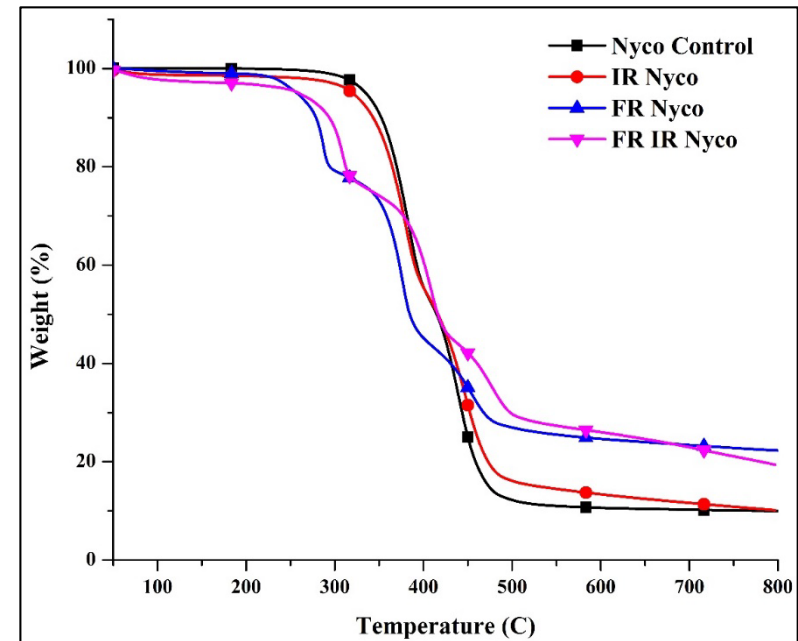
# Characterization of FR Functionalization using FTIR



# Thermogravimetric Analysis

- Performed under N<sub>2</sub>
- Temperature Range: RT- 800° C

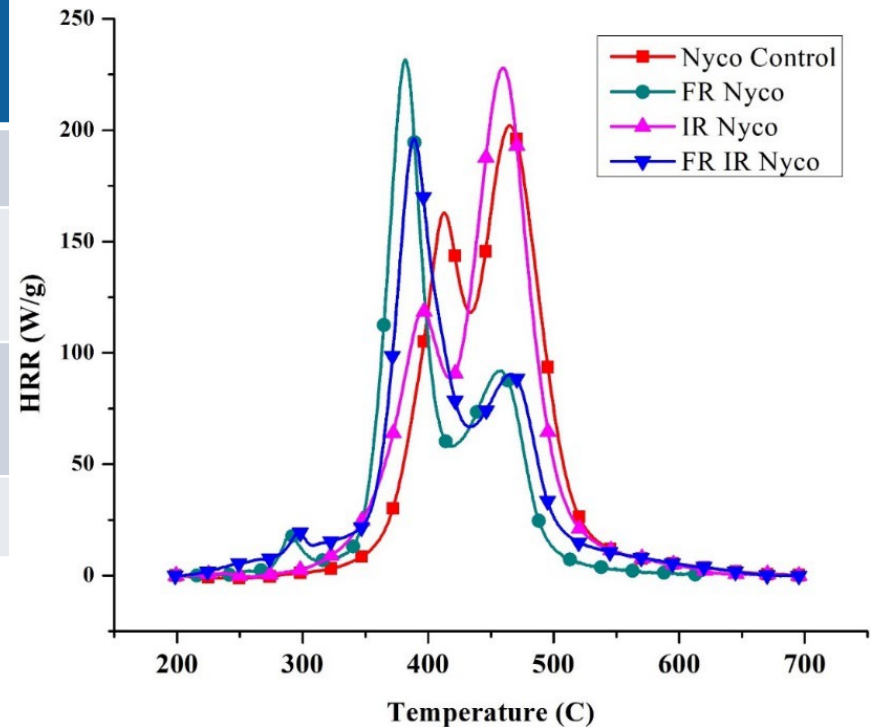
Fabric Type	Char at 700°C
Nyco Control	10%
IR Nyco	11.6%
FR Nyco	23.4%
FR IR Nyco	22.4%



✓ Char forming ability of FR Nyco and FR IR Nyco has been improved significantly from 10 to ~22% compared to Nyco control

# Microscale Combustion Calorimetry

Fabric Type	Heat Release Capacity (J/g-K)	Total Heat Release (KJ/g)
Nyco control	325	19.6
Nyco with FR only	229 (-35%)	15.1 (-23%)
Nyco with IR only	294	20.0
FR IR Nyco	252 (-23%)	16.5 (-16%)



- Test Method: ASTM D7309
- Gas Blend: 80:20- N<sub>2</sub>:O<sub>2</sub>
  - ◆ This combination is used to mimic the atmosphere

# Vertical Flame Test

## Nyco Control

- Burns Away completely
- After Flame: ~40 sec
- No melt Dripping

## FR IR Nyco

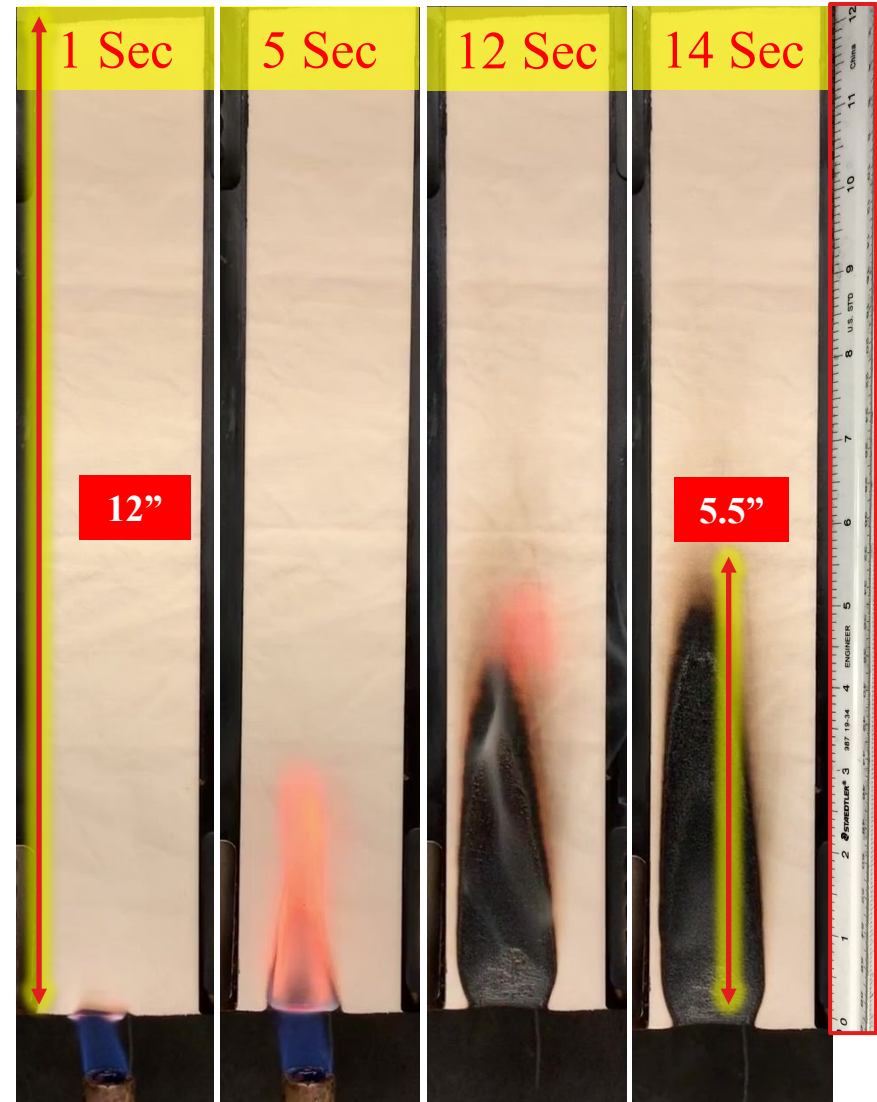
- Self Extinguishing
- Char Length: <5.5"
- After Flame: < 2 sec
- Significant Char formation
- No Melt Dripping

## Test Specifications

- Test Method: ASTM D6413
- Flame Height: 1.5"
- Ignition Time: 12 sec



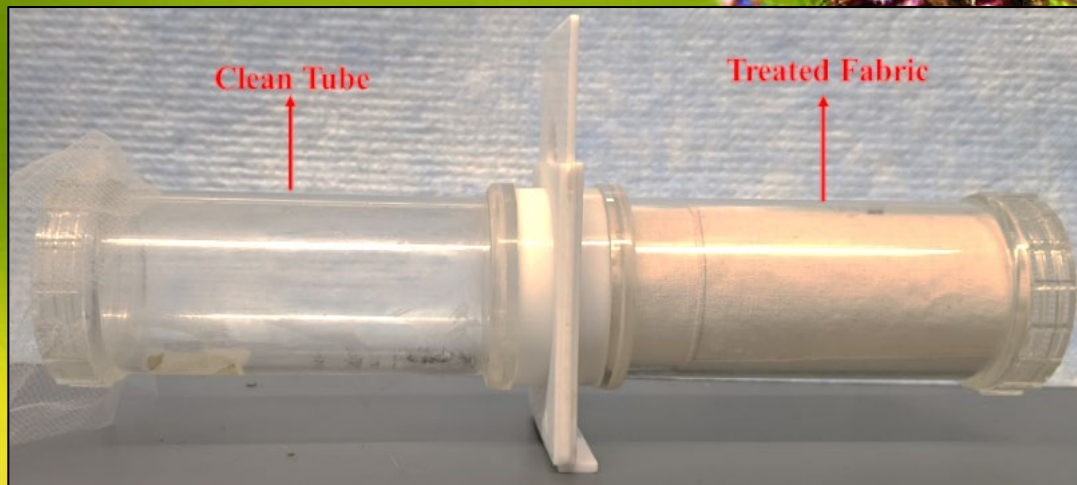
Control



FR IR Treated Nyco

# Insect Repellency Testing

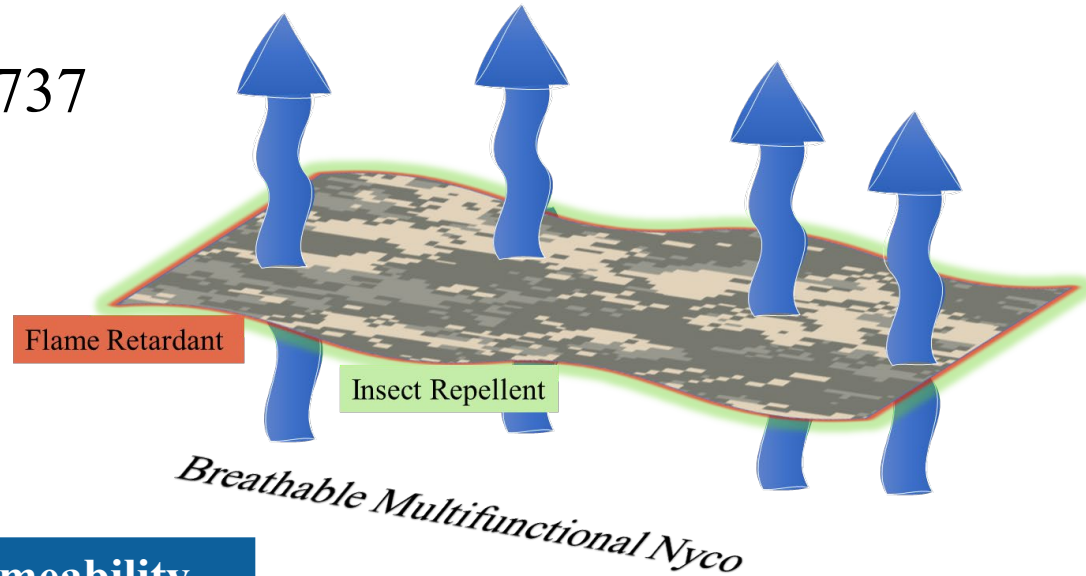
- WHO Tube Test for Mosquito Susceptibility
  - ◆ Mosquito Type: Female Aedes Aegypti
  - ◆ Exposure Time: 2 mins
  - ◆ Residence/ Observation Time: 24 hrs.
  - ◆ Incapacitated the mosquitos within first 2 hrs
  - ◆ Test results reported here are average of 3 tests



Sample	Mortality
Nyco Control	0%
Nyco with FR only	0%
Nyco with IR only	98± 2%
FR IR Nyco	98± 2%

# Air Permeability Studies

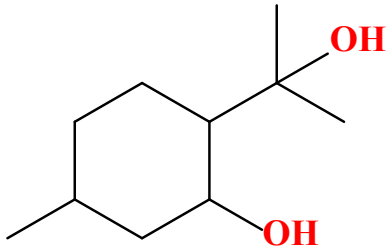
- Test Method: ASTM D737
- Test Pressure: 200 Pa
- Test Area: 20 cm<sup>2</sup>
- Average of 4 runs



Fabric Type	Air Permeability (ft <sup>3</sup> /min/ft <sup>2</sup> )
Nyco Control	6.1
FR IR Nyco	5.3 <b>(-14%)</b>

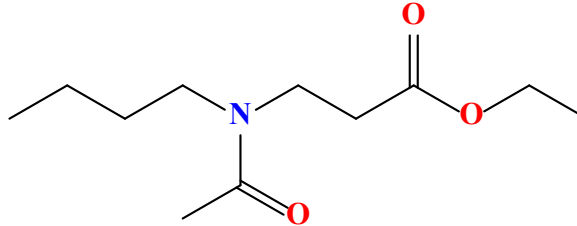
# Current State of Research

- Launder Durability studies: AATCC 135 Test Method (at least 25 laundry cycles)
- Grafting of Ethyl Chrysanthamate was carried out on Nyco and the IR testing results were not very promising.
- Alternative safer, bio-derived/ bio-inspired Insect repellents are under investigation



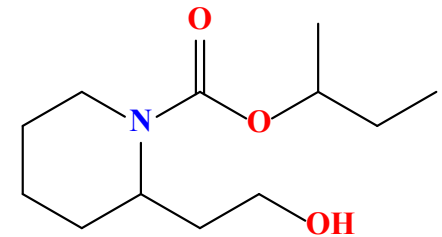
**p-Menthane-3,8-diol**

- ✓ Bio-Derived
- ✓ Commercially available
- ✓ No Skin Irritation
- ✓ Performance comparable to DEET



**IR 3535- Ethyl 3-(N-butylacetamido)propionate**

- ✓ Commercially available
- ✓ No Skin Irritation
- ✓ EPA approved



**picaridin**

- ✓ Bio-Derived
- ✓ Commercially available
- ✓ No Skin Irritation
- ✓ Performance comparable to DEET

Donald R. Barnard, Ulrich R. Bernier, Kenneth H. Posey, Rui-De Xue, Repellency of IR3535, KBR3023, para-menthane-3,8-diol, and Deet to Black Salt Marsh Mosquitoes (Diptera: Culicidae) in the Everglades National Park, Journal of Medical Entomology, Volume 39, Issue 6, 1 November 2002, Pages 895–899, <https://doi.org/10.1603/0022-2585-39.6.895>

Stafford III, Kirby C. "Tick bite prevention & the use of insect repellents." risk 60.80 (2006): 100.

# Status of Funds for Federal Performers

FY2019 Funds			
Directly Funded Federal Performer(s)	Funds Received	Funds Obligated*	Percent Funding Obligated
Federal Performer - Direct Cite MIPR	199,908.00	199,908.00	100%

## Project Funding

	FY18	FY19	FY20
Funds received to date (\$K)	94,074	105,834	-
% Expended	80,812	105,834	-
Funds Remaining (\$K)	13,262	0	-

## Key Points

- ◆ Safer, Bio derived material, Phytic Acid is used as a Flame Retardant by covalent linkage
- ◆ Permethrin was used as Insect Repellent and was locked in place using acrylic monomers and polymerizing them using Atmospheric pressure plasma treatment to avoid leaching.

- ◆ ***The multifunctional Nyco fabric with:***

- ✓ *Increased the thermal stability by improved char formation of FR IR Nyco from 10 to >20% compared to Nyco control*
- ✓ *Reduced the heat release rates by >23%*
- ✓ *Efficacy of the insect repellent >98%*
- ✓ *Self-extinguishing during vertical flame test <2 sec*
- ✓ *Nyco remains breathable even after treatment*

# Technology Transfer

## ▪ **Publications**

- ❖ Covalent functionalization of cellulose in cotton and a nylon-cotton blend with phytic acid for flame retardant properties. *Cellulose*, 27(1), pp.11-24.
- ❖ Multi-functional Nylon/cotton fabric with Flame and Vector Protection, *ACS Sustainable Chemistry and Engineering* (Manuscript Submitted).

## ▪ **Presentations**

- Poster presented at the **SERDP Symposium 2019**, held in DC
- Poster presented at the *Sukant Tripathy Annual Memorial Symposium 2019*, Lowell, MA, December 6, 2019.
- Presented at ACS Fall 2020 National Meeting & Expo, which was held virtually in August 2020.
- ❑ Worked with Technical Program Manager, Claire LePont to establish a collaboration with Milliken (POC: Warren Gerhardt). Milliken is interested to work on the scale-up efforts in future.

# Technology Transition Plan

- ✓ Transition this promising multifunctional coating technology with the help of **SERDP and DEVCOM SC (6.2/6.3) programs**
- ✓ Industrial collaborators – **LaunchBay LLC., and Milliken and Company**
- ✓ Transition to higher TRL levels through an **ESTCP** program.



*Roll to Roll fabric treatment equipment (LaunchBay LLC)*

## Proposed Future Work

- Launder Durability studies of multifunctional nyco fabric
- Process Optimization to reduce treatment times using Microwave assisted grafting of flame retardants
- Replacement/reduction of existing solvents with safer solvents
- Plasma assisted deposition of proposed safer and natural insect repellents
- Scale up efforts in collaboration with industry partners, LaunchBay and Milliken



Microwave Reactor

# Scope of Work: Follow on Research

**Task 1 - Chemical activation of fabric using Microwave Reactor, Testing & Characterization**

**Task 2 - FR functionalization, testing and Characterization**

**Task 3 - Plasma assisted incorporation of safer, natural insect repellents on Nyco**

**Task 4 - Plasma assisted incorporation of insect repellent on FR Nyco**

**Task 5 – Testing of Multifunctional Nyco**

## Cost Estimate/Year: Follow On Research

	<b>FY22</b>	<b>FY23</b>
Total budget estimate (includes in-house labor, contracts/sub-contracts, indirect charges, overhead, supplies, travel)	450k	450k

# WP19-1050: A Simple Surface Functionalization Method for Multifunctional Textiles with Flame and Vector Protection

## Performers:

Lead - **Dr. Ravi Mosurkal**, *US Army DEVCOM Soldier Center*

**Prof. Ram Nagarajan**, *University of Massachusetts Lowell*

## Technology Focus

Development of Durable, safer, low cost multifunctional Nylon/Cotton (Nyco) fabric through covalent functionalization and Plasma assisted deposition

## Research Objectives

- *Covalent attachment of Safer, Low cost & bio-derived material, Phytic Acid as flame retardant*
- *Plasma assisted deposition of Permethrin as insect repellent*
- *Testing, characterization and scale-up*

## Project Progress and Results

- *Multifunctional Nyco with promising flame retardancy and insect repellency properties has been developed, characterized and tested on Lab Scale.*

## Technology Transition Plan

- *The plan is to transition this promising multifunctional coating technology with the help of SERDP/ESTCP and DEVCOM SC (6.2/6.3) programs to higher TRL levels.*
- *Industrial collaborations are planned for possible scale up studies and manufacturing requirements.*

