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

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14. ABSTRACT
The proposed research effort directly addresses the immediate need for developing safer multifunctional textiles through a simple and versatile combination of surface chemical functionalization, plasma deposition processes involving more sustainable materials. Nylon/cotton (Nyco) is one of the widely used fabric for soldiers Army combat uniforms ACU). Nyco combines excellent mechanical properties, abrasion resistance and comfortable to wear. However, Nyco is not flame resistant and does not provide adequate vector protection. There are very few reliable cost-effective solutions that impart durable flame retardancy and vector protection to Nyco. Current flame retardant (FR) protective materials (e.g. FRACU) are expensive have deleterious environmental impacts and in many cases, are not produced in the US. Although permethrin is used for vector protection, lack of durability of the coating and safety is still of concern. In this work, cost-effective and environmentally benign waste byproducts such as phytic acid are utilized to introduce durable flame retardancy. In addition, plasma-assisted deposition of insect repellents such as permethrin to make a multifunctional Nyco fabric is demonstrated.

15. SUBJECT TERMS
Nyco, Nylon cotton blend, Biobased flame retardants, Phytic Acid, Carbonyl diimidazole, Insect Repellent, Permethrin, Multi-functional fabric

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List of Acronyms

AATCC: American Association of Textile Chemists and Colorists

ASTM: American Society for Testing and Materials

ATR: Attenuated total reflectance

CDI: 1 1 Carbonyl diimidazole

DEET: N, N-Diethyl-meta-toluamide

EDA: Ethylene Diamine

DMF: Dimethylformamide

FR: Flame retardancy/ Flame Retardant

FRACU: Flame retardancy Army Combat Uniform

FTIR: Fourier transform infrared

HRC: Heat release capacity

IR: Insect Repellent

MCC: Microscale combustion Calorimetry

NYCO: Nylon/cotton blend

PA: Phytic acid

PCFC: Pyrolysis-combustion flow calorimetry

PEO: Program Executive Office

PPM: Personal protective measures

TGA: Thermal-gravimetric analysis

THR: Total heat release

VFT: Vertical flame test

WHO: World Health Organization

Keywords

Nyco, Nylon cotton blend, Biobased flame retardants, Phytic Acid, Carbonyl diimidazole, Insect Repellent, Permethrin, Multi-functional fabric

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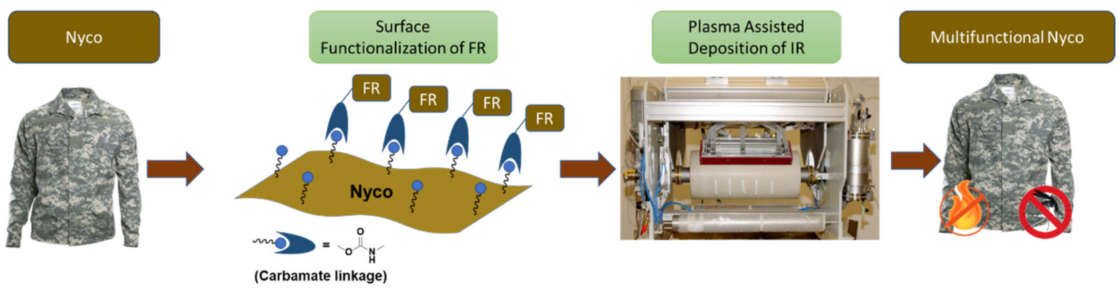
Abstract

The proposed research effort directly addresses the immediate need for developing safer multifunctional textiles through a simple and versatile combination of surface chemical functionalization, plasma deposition processes involving more sustainable materials. Nylon/cotton (Nyco) is one of the widely used fabric for soldiers Army combat uniforms ACU). Nyco combines excellent mechanical properties, abrasion resistance and comfortable to wear. However, Nyco is not flame resistant and does not provide adequate vector protection. There are very few reliable cost-effective solutions that impart durable flame retardancy and vector protection to Nyco. Current flame retardant (FR) protective materials (e.g. FRACU) are expensive have deleterious environmental impacts and in many cases, are not produced in the US. Although permethrin is used for vector protection, lack of durability of the coating and safety is still of concern. In this work, cost-effective and environmentally benign waste byproducts such as phytic acid are utilized to introduce durable flame retardancy. In addition, plasma-assisted deposition of insect repellents such as permethrin to make a multifunctional Nyco fabric is demonstrated.

Technical Approach: Combination of activation of hydroxyl groups on cotton to facilitate chemical surface functionalization followed by plasma assisted deposition of an insect repellent (permethrin) was the approach successfully developed over the course of the project. The insect repellent is locked in position using acrylic monomers followed by crosslinking it under plasma. Extensive characterization of functionalization, thermal and flammability behavior of the multifunctional fabric as well as an assessment of the efficacy of insect repellency of the fabric have been carried out to demonstrate the success of the approach.



Illustrative scheme of technical approach for multi-functionalized fabric

Results: Multifunctional Nyco fabric with combination flame retardant properties and insect repellency was successfully demonstrated. The flame retardancy was imparted to the fabric by covalently functionalizing bio-based phytic acid. The treated Nyco fabric successfully passes the standard vertical flame test in accordance with ASTM D6413. The multifunctional fabric also exhibits excellent thermal stability, improved char formation and a significant reduction in heat release characteristics. The plasma deposited permethrin coating imparts excellent insect repellency with >98% mosquito mortality rate in the WHO Susceptibility Test for Adult Mosquitoes.

Benefits: This research has provided proof-of-concept data on the efficacy of novel low cost, safer and durable multifunctional coatings for Nyco fabric that imparts both Flame retardancy and insect repellency. This multifunctional fabric will have a direct impact the safety, comfort and operational success of the US Soldiers in harsh environments. These functionalization techniques described are simple, sustainable and readily scalable to large scale manufacturing.

1.0 Introduction

Nyco, a blend of 50% nylon 66 and 50% cotton is a widely used fabric for soldiers' uniform in the US Armed forces. Nyco being a blend of nylon and cotton has good mechanical strength, abrasion resistance and comfortable to wear. However, Nyco is inherently combustible and does not provide flame protection and does not have any insect repellency effects. There are very few reliable solutions that provide durable flame retardancy to Nyco[1,2].

Current flame retardant (FR) protective materials (e.g. FR ACU) do not always provide optimum protection against existing and emerging battlefield threats and have inadequate durability [3]. Some of these FR's are expensive, have adverse environmental impacts and in many cases, cannot be produced in the US. In addition to the threats from the fires, vector-borne diseases, and pests are of great concern to the US military. The health of troops engaged in combat operations, peacekeeping efforts or humanitarian relief can be adversely affected which compromises the success of the mission. Of 80 diseases of military importance, over two-thirds are caused by pathogens transmitted by arthropods [4–8]. Despite continual progress in the technology of vector control during the last century, US military forces remain vulnerable to many serious diseases caused by pathogens transmitted by mosquitoes, ticks, and other arthropods that cause considerable morbidity and mortality. Annoyance from persistent pests, itching bites, and loss of sleep can also erode morale. Hence arthropod-borne disease prevention is a top priority for force health protection of the US military.

Personal protective measures (PPMs) are the most effective means of protecting soldiers from these threats, a key component of which is insect repellent treated clothing. Although most arthropods cannot bite through the standard uniform fabric material unless it is tightly stretched against the skin, protection would be improved by treating the uniform with a repellent. An effective clothing repellent based on the synthetic pyrethroid, permethrin, was fielded in 1991 and is still in use today as the standard military clothing repellent. Permethrin is a Type I pyrethroid that knocks down and kills insects by contact or ingestion. Permethrin is effective against various species of crawling and flying insects, including mosquitoes, ticks, fleas, bedbugs, chiggers, and flies. These insects often avoid such pyrethroids, hence giving Permethrin its repellent effects. Currently, permethrin is only approved for use on outer garments, because direct exposure to permethrin can cause skin irritation and rash. It is also persistent in the environment and is toxic to multiple aquatic and terrestrial species, including fish (fresh and saltwater), bees and other beneficial insects and birds. Due to the toxic environmental effects of permethrin, an environmentally friendly alternative is needed. However, permethrin is currently the only insecticide that is approved by the EPA for use as textile treatment and has been shown to persist on the textile even after extended laundering. Furthermore, currently used spatial insect repellents, such as N, N-diethyl-m-toluamide (DEET), possess toxic effects on humans and the environment [9].

2.0 Objectives to Demonstrate the Proof-of-Concept

The primary objective of this effort is to develop and prove the concept of a simple, versatile, sustainable and cost-effective approach to impart safer and durable fire retardant (FR) characteristics and insect repellency to Nylon/cotton (Nyco) based Army Combat Uniform (ACU) fabrics using a unique combination of chemical surface functionalization and atmospheric pressure plasma treatment techniques. To achieve the multifunctionality in Nyco fabrics, bio-derived flame retardants and insect repellants have been employed.

The technical objective of this effort is divided into several tasks as follows

(1) Chemical functionalization of Nyco fabric with proposed flame retardant through CDI chemistry and characterization

(2) Attachment of insect repellent onto FR treated fabric (prepared in the first step) by plasma-assisted deposition and characterization

(3) Evaluate the FR action of the multifunctional fabric & it's thermal characteristics

(4) Evaluate the efficacy of the multifunctional fabrics to mosquitoes

(5) Optimize both the chemical functionalization reaction and plasma treatment conditions to achieve durable multi-functionality for the treated Nyco.

3.0 Technical Approach

3.1 Background

The proposed research effort directly targets the need for developing multifunctional textiles through a simple and versatile surface chemical functionalization of nylon/cotton (Nyco) fabrics along with plasma-assisted deposition. In this work, cost-effective and environmentally benign materials such as phytic acid will be utilized to introduce durable flame retardancy onto the fabric surface by the reaction of hydroxyl functional groups in Nyco. Current flame retardant (FR) protective materials (e.g. FRACU) are either produced using toxic methods or have durability issues. The production methods also have adverse environmental impacts and, in many cases, cannot be produced in the US.

Surface chemical modification of the existing nylon/cotton blends with bio-based flame retardants and chemically modified contact insecticide molecules would provide an environmentally safe and cost-effective solution to fire retardance and vector protection in fabrics.

Phytic acid is the major storage form of phosphorus in many sustainable resources such as cereal grains, beans and oilseeds. Phytic acid has been reported as a naturally occurring environmentally friendly flame retardant on various substrates including wool, cotton and poly(lactic acid) due to its high phosphorus content (28 wt.%)[10–13]. The limited oxygen index (LOI) value of phytic acid-treated cotton fabric was as high as 43% even after 30 laundering cycles [12]. Figure 1 shows the chemical structure of the PA.

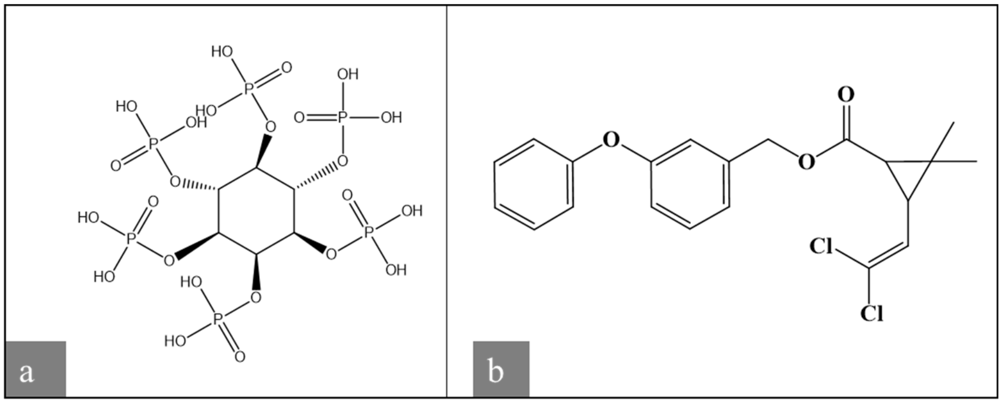


Figure 1. Chemical Structures of (a) Phytic acid and (b) Permethrin

Pyrethroids are one of the most commonly used low-toxic insecticides that were first found in the extraction of pyrethrum flowers [14,15]. In this work, pyrethroids including permethrin (figure 1b) and chrysanthemate will be deposited or covalently grafted onto the fabric for insect repelling purpose. Covalently attaching insecticides will lower the possibility of leaching out during laundering and therefore minimize their impact on health and environment. The covalent bonds provide stability because bonds are scarcely affected by ageing, ultraviolet light (UV) exposure or other environmental effects.

LaunchBay has developed a proprietary surface treatment technology, Invexus®, applicable to fabric rolls or rigid substrates. Their atmospheric pressure plasma surface treatment process is based on a technology that combines a liquid precursor (in the form of a fine aerosol) with an atmospheric pressure inert gas plasma to deposit a very thin (hundreds of nanometer-thick) coating onto a substrates' surface to alter its surface properties. Polymerization and binding of the applied treatment on the substrate surface occur due to interaction of the chemical precursor and substrate surface with the energetic ions, activated molecules and metastable species within the plasma.

This treatment typically uses monomers or precursor chemicals that have a functional group that can be activated by the energetic species within the plasma to initiate polymerization, grafting and/or chemical reactions. These are typically unsaturated molecules (such as acrylates, methacrylates, vinyl etc.), cyclic ring structures that can undergo ring-opening (such as glycidyl, cycloaliphatic compounds, and cyclic siloxanes) and compounds with easily hydrolyzable groups such as alkoxides (e.g. silanes, organometallic compounds, siloxanes).

3.2 Materials and Methods

3.2.1 Materials

All chemicals and solvents purchased were used without further purification. 1,1'-carbonyldiimidazole (CDI) was purchased from TCI America, Ethylenediamine (EDA), aqueous 50% phytic acid solution (PA), and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Cotton and Nyco fabrics were obtained from US Army combat capabilities development command soldier center (Natick, MA, USA).

3.2.2 Methods

3.2.2.1 Chemical Functionalization

Activation of hydroxyl groups on the cellulose-based fiber such as Nyco is the focus in the chemical surface functionalization. The most adopted and well-established approach for the surface modification of cellulose is through condensation reaction taking place involving the hydroxyl groups available on the surface.

The surface functionalization of fabric consists of a two-step process as shown in figure 2 below. The fabric will at first chemically activated and then grafted with appropriate functionality such as (flame retardancy in this case). In the activation step, we will introduce a versatile linker, 1,1-carbonyldiimidazole (CDI), to the hydroxyl functional groups of cellulose. A bifunctional amine, ethylenediamine (EDA), will then be used to replace the imidazole part of the linker thus amine groups will be introduced onto the fabric surface as shown in Figure 2 [16–18].

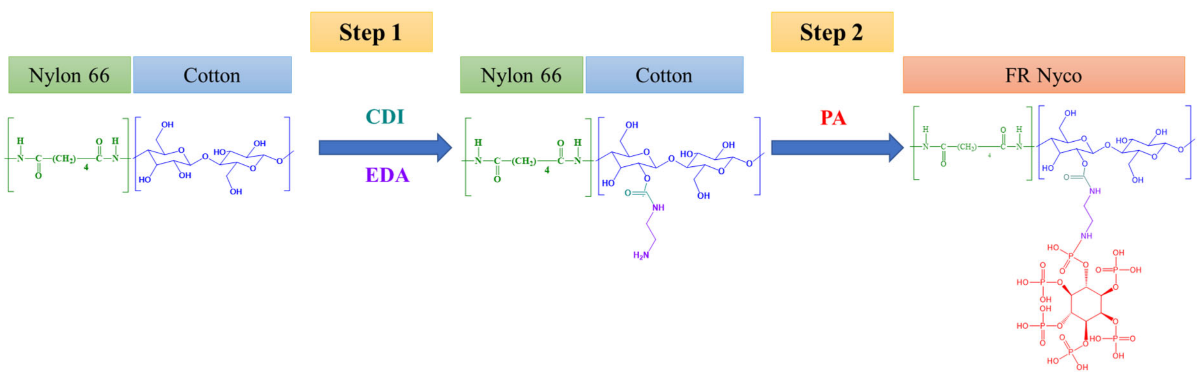


Figure 2. Schematic of Chemical Functionalization Process

These newly introduced amines are very reactive towards many functional groups such as acids, ester, aldehydes, and ketones. Therefore, in the second step of the chemical functionalization, phytic acid was introduced to form a phosphoramide bond by the reaction of amines on the surface of the fabric. By covalently attaching PA onto cotton part of Nyco through the introduced amine, the fabric gained durable flame retardancy.

In a typical procedure, for treating two pieces of 3”x12” fabric samples weighing approximately 10 gm, a solution of CDI was made in DMF having a concentration of 0.03 g/mL which contained 300 mL of DMF as a solvent in a conical flask. To this reaction mixture, the Nyco fabric was then added and left for 12 hours at room temperature for the reaction to occur. At the end of this reaction time, DMF solvent was decanted and the fabric was washed with acetone (2 x 100 mL) to remove unfunctionalized CDI followed by drying the fabric samples at 90 °C for four hours to obtain CDI functionalized Nyco fabric. This CDI functionalized fabric was then taken into another conical flask containing 300 mL of DMF solvent. To this mixture, 5 mL of ethylenediamine was added followed by stirring the reaction mixture in the first two hours of reaction then left it for five hours at room temperature. Then the solvent was decanted, and the fabrics were washed with acetone (2 x 100 mL) followed by drying the samples at 90 °C for four hours to yield the EDA functionalized Nyco fabrics. EDA functionalized fabrics were then dipped in 25% aqueous phytic acid solution for five minutes, followed by drying in an oven at 80 °C for 12 hours. At the end of the drying period, the fabric swatches were cooled down to room temperature and then washed with distilled water (3 x 100 mL) followed by drying of the fabric sample at 90 °C for four hours to obtain PA functionalized Nyco fabric. The details on the average weight gains of the fabric samples before and after treatment with FR are tabulated in table 1 below.

Table 1: Summary of average weight gains after FR Treatment

Fabric	% Gain after CDI	% Total Gain after phytic acid functionalization
Nyco	6±0.6	12±1

3.2.2.2 Plasma assisted deposition of Insect Repellent

In collaboration with LaunchBay, the atmospheric pressure plasma process was explored. This process is a scalable and commercially viable method for deposition of insect repellants. In a typical coating procedure, a solution of permethrin and an acrylate binder was made in distilled water. This solution contained 2.5% by weight of permethrin active ingredient. The coating was performed by aerosolizing the solution followed by applying this solution onto the fabric substrate as a fine spray using an x-y-z traversing robotic coating head. The head speed was maintained at 1000 mm/min and a step distance of 5mm was used. The aerosol spray was set to 375µL/min to target 0.5% permethrin on the treated fabric. Fabric swatches of sizes 3”x6”, 3”x12” & 6”x12” were fabricated and tested. The schematic of the chemistry for both the FR and IR treatments are shown below in figure 3.

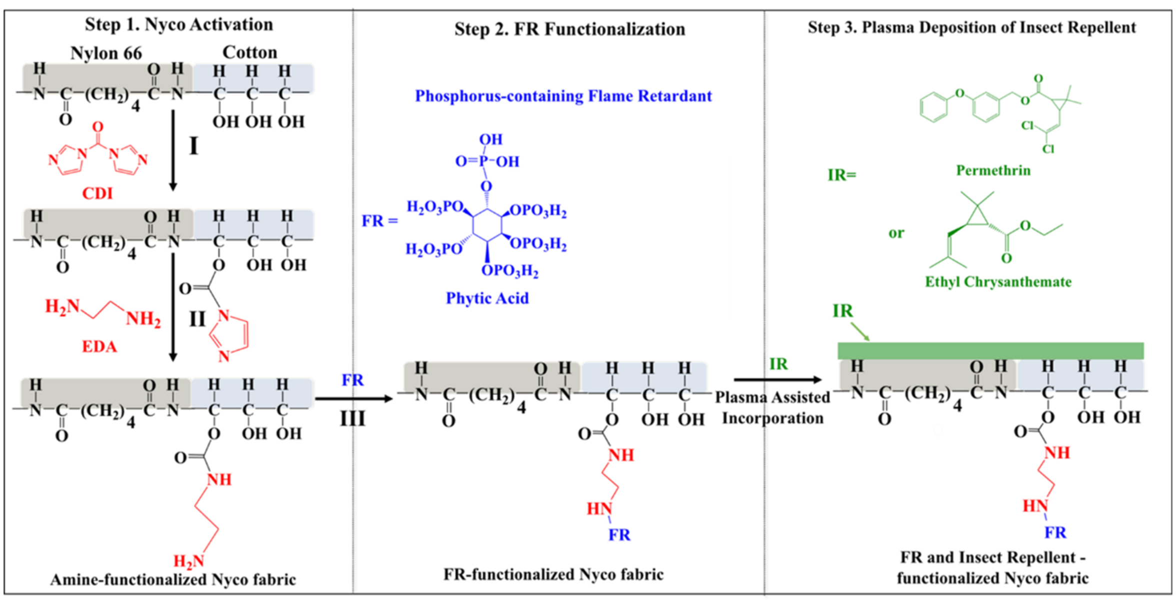


Figure 3. Reaction scheme to achieve Multifunctional Nyco Fabric

4.0 Results and Discussions

4.1 Key Results from successful completion of Limited scope proposal

- The scalable chemical functionalization of Nyco fabric was successfully demonstrated and the attachment of the flame retardant moieties was confirmed using spectroscopy.
- The attachment of these FR moieties also increased the thermal stability of nyco and reduced the heat release rates as confirmed by Thermogravimetric Analysis and Microscale combustion calorimetry.
- The fabric that was covalently linked with the FR was then used to attach IR through plasma assisted deposition. The attachment of IR moieties on the fabric was in very low concentrations and was could not be detected by ATF-FTIR.
- The multifunctional fabric thus made was tested for its thermal stability, heat release rate and insect repellency using TGA, MCC and World health Organization Tube Test respectively.
- The multifunctional fabric and the FR treated fabric had similar results when tested in a vertical flame test, (both were self-extinguishing). This proves that the presence of IR on the FR treated fabric did not interfere with the FR action.
- The presence of the FR did not interfere with the action of insect repellency.

4.2 Surface Characterization using ATR-FTIR

The functionalization of Nyco fabric was carried out through three consecutive reaction steps. As shown in synthesis scheme (Figure 3), in the first step, the reaction occurred between hydroxyl groups of cotton part of Nyco fabric and the reactive carbonyl group of CDI resulted in the formation of carbamate bonds on the surface of the fabric. In this reaction, some of the hydroxyl groups of the cotton fabric (and cotton part of Nyco fabric) were substituted by one of the imidazole groups of CDI. Successful formation of carbamate in the fabrics was confirmed by the ATR-FTIR spectra (Figure 4), with the appearance of newly formed carbamate characteristic carbonyl stretching band at 1761 cm^{-1} apart from retention of other stretching frequencies from the control fabric such as 1632 cm^{-1} corresponding to the carbonyl amide stretching. Furthermore, we observed around 6±1% weight gain on the functionalized Nyco fabric swatches compared to the weight of control fabric. In the second step, to introduce amine functional groups onto the surface of the CDI functionalized fabric, we used EDA as a nucleophilic reagent in excess. One of the primary amine groups of EDA has replaced the imidazole group on the fabric to afford EDA functionalized fabric. The other primary amine group in EDA is still available for further chemical reactions. The conversion was further confirmed using ATR-FTIR spectra (Figure 4) of the functionalized fabrics. The FTIR spectra of EDA treated Nyco exhibited the characteristic urethane peaks at 1702 cm^{-1} (carbonyl urethane stretching) and 1530 cm^{-1} (C-NH vibration). Moreover, the carbonyl stretching peak at 1761 cm^{-1}related to the starting CDI functionalized fabrics vanished completely which all together clearly indicated the successful completion of these reactions on the fabric surface.

In the subsequent step of functionalization with Phytic acid on fabric, significant weight gain of about 10±2% was observed. The FTIR spectra of the FR treated fabric and control Nyco fabrics are shown below in Figure 4 and Figure 5 shows the FTIR spectra for Nyco control fabric and the multifunctional fabrics.

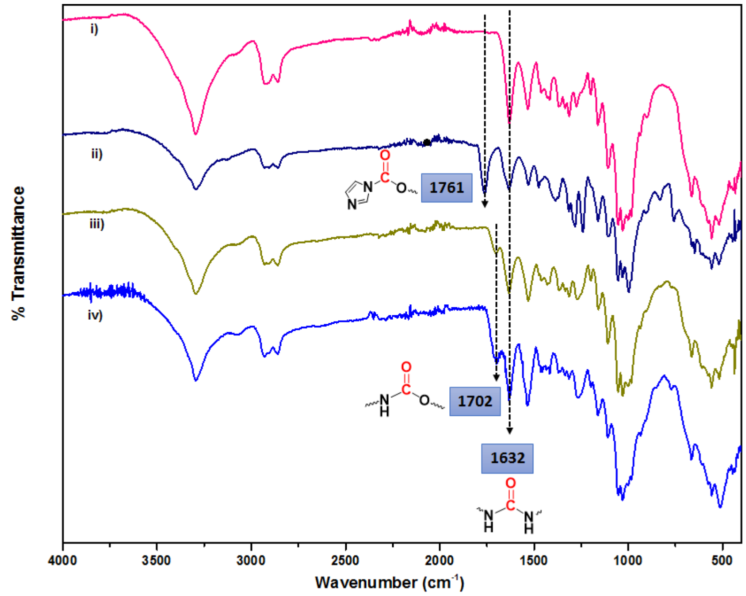


Figure 4: FTIR-ATR spectra of (i) Nyco control, (ii) CDI functionalized Nyco, (iii) EDA functionalized Nyco and (iv) PA attached FR Nyco

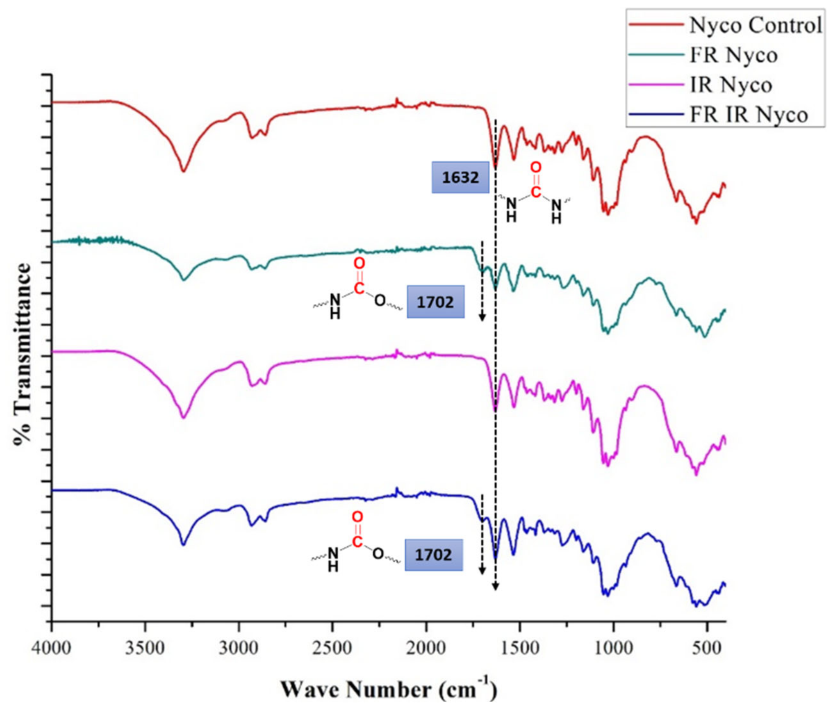


Figure 5: FTIR-ATR spectra of Nyco control, FR Nyco, IR Nyco and FR IR Nyco

4.3 Evaluation of Thermal Stability and Char Formation using TGA

Thermal degradation behavior and thermal stability of the functionalized Nyco fabrics were investigated using TGA 5500 (TA Instruments) under nitrogen atmosphere. The TGA decomposition graphs comprising the data of weight loss versus temperature for Nyco fabrics are shown in Figure 5. Nyco fabric has undergone a two-step degradation owing to its 50:50 nylon and cotton. The FR Nyco and the multifunctional Nyco fabric (FR IR Nyco) went through a three-step degradation process. The first degradation at around 300°C corresponded to the phosphate groups in the PA structure. Char residues at 700°C were also evaluated to assess the thermal stability of the treated fabric. It was observed that the char forming capacity of the functionalized nyco **increased from 10% for control nyco fabric to around 23% (2x increase)** for FR and multifunctional Nyco. This char forming phenomena is an essential part of flame retardant effect that is seen in the vertical flame test. The char formation in this case mainly occurs due the acid catalyzed (released during the pyrolysis) dehydration of cellulose in nyco. The char thus formed helps in reduction of the release of flammable volatiles and also serves as a thermal barrier protecting the underlying material from combustion.

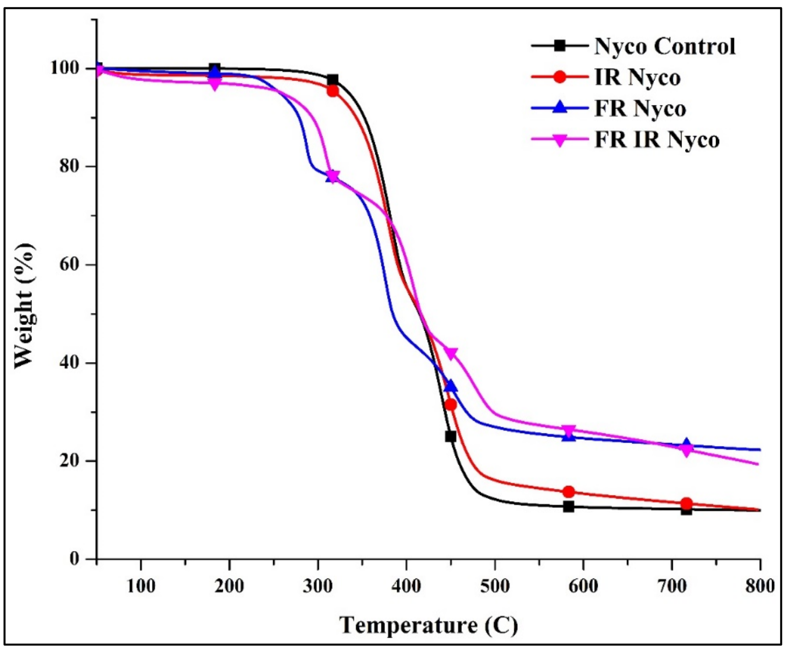


Figure 6: Thermograms of Nyco control, FR Nyco, IR Nyco and FR IR Nyco

4.4 Evaluation of Heat Release Properties using MCC

The flammability characteristics of functionalized and control fabrics were studied in accordance with ASTM D7309 using a small-scale flammability technique called microscale combustion calorimetry (MCC) or Pyrolysis combustion flow calorimetry (PCFC). This technique is used to evaluate the combustion parameters based on the consumption of oxygen during the process[19]. The essential parameters obtained from this technique are furnished in Table 2 along with the char residues that were measured using the TGA. Figure 7 shows the heat release curves for the same. The heat release capacity (HRC) and total heat release (THR) values give valuable information about the heat release characteristics of the material. The Nyco fabric functionalized with PA showed lowest heat release capacity of 229 J/gK and lowest total HR value of 15.1 kJ/g which are remarkably lower than 19.6 kJ/g of control fabric. These results suggest that the functionalization of PA to cotton in Nyco fabric led to a significant ***reduction of about 35% for HRC and 23% for THR***. In case of multifunctional Nyco fabric, HRC was seen to reduce by around 23% and the THR by 15.8% which indicate that the multifunctional Nyco fabric has better heat release properties compared to control Nyco fabrics.

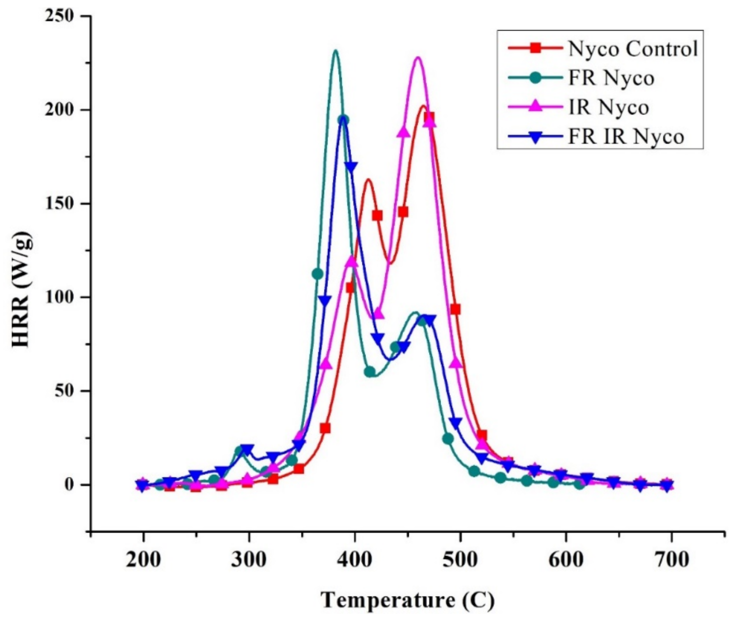


Figure 7: Heat Release Curves of Nyco control, FR Nyco, IR Nyco and FR IR Nyco

Table 2: Summary of Test results from MCC and TGA for Nyco, FR Nyco and Multifunctional Nyco

Property	Nyco Control	FR Nyco	FR IR Nyco
Heat Release Capacity (J/g-K)	325.5	229	252.4
Total Heat Release (KJ/g)	19.6	15.1	16.5
Residue at 700°C	3.5%	23.6%	22.4%

4.5 Evaluation of Fabric Flammability Properties using VFT

In order to evaluate the flame retardancy behavior of the multifunctional Nyco fabric, vertical flame test (VFT) was performed in accordance with ASTM D6413 [20] on control samples as well as functionalized Nyco fabrics. In a typical test, the sample size within the frame was 3”x12”. A Bunsen burner equipped with an automatic gas controller was used for sample ignition. The flame height was 1.5”, and the distance between the lower edge of the sample and the burner was 0.75”.

The ignition time was 12 seconds. The images taken after the VFT of control and the multifunctional (FR IR Nyco) fabrics are shown in figure 8 below.

As expected Nyco control burnt away completely whereas the FR Nyco and the FR IR nyco were self-extinguishing within 2 seconds after the ignition source was removed with a char length of about 5±1”. This suggests that the insect repellent, permethrin, being in very low concentrations (<0.5% by weight on the fabric) barely interacts with the burning behavior of the fabric after treatment and the FR action on the multifunctional Nyco is still intact.

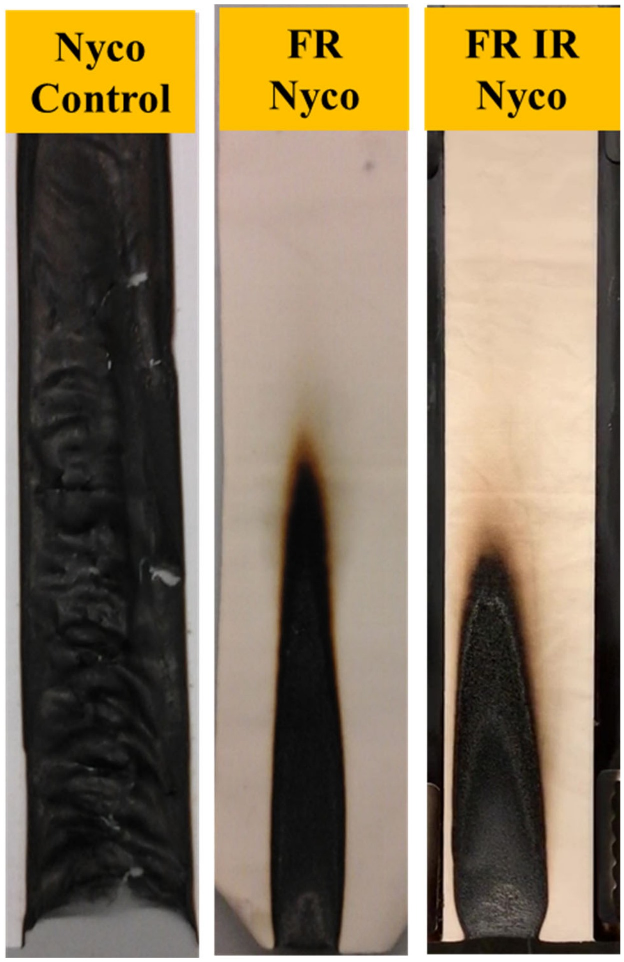


Figure 8: Post VFT images of Nyco control FR Nyco and FR IR Nyco

4.6 Evaluation of Insect Repellency using the WHO Susceptibility Test for Adult Mosquitoes

To evaluate the efficacy of the IR treated nyco fabric and the multifunctional nyco fabric to develop a basic understanding of the interaction of presence of FR on IR treated fabrics, the treated fabrics were tested according to a method that is prescribed by the World Health Organization called the WHO Tube Test for mosquito susceptibility[21]. The typical test setup consists of two tubes that are attached to each other. One of the tubes is covered by a fabric that has been treated and the other side of the tube is a clean tube (as shown in fig. 9 below) used as a holding cage for the mosquitoes being tested.

In a typical test, approximately 15-20 female Aedes aegypti mosquitoes are placed in the clean tube and are forced to enter the other tube to be exposed to the IR treated fabric for 2 minutes. After the exposure, the mosquitoes are forced back to move into the clean tube and their behavior is observed and the mortality is noted after 90 mins. Average of 3 test results are tabulated in Table 3 below for each type of treated fabric sample. The average mortality for IR and FR-IR treated fabrics was found to be >98% compared to 0% for untreated nyco fabrics.

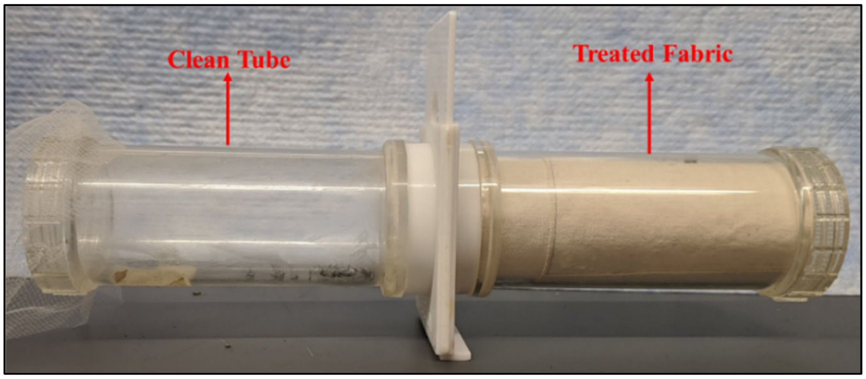


Figure 9: Test Setup for WHO's Mosquito Susceptibility Test

Table 3: Summary of test results from the WHO Tube Test

Sample	Total Number of Mosquitoes Tested	Mortality
Nyco Control	50	0%
IR Nyco	50	98±2%
FR-IR Nyco	50	98±2%

Current State of Research:

Currently, the launder durability of the multi-functional Nyco fabric is being tested in accordance with AATCC 135 test method. The laundered fabric will then be evaluated for its flammability properties and insect repellency effects in accordance with ASTM D6413 and WHO tube test. Alongside these tests, the breathability of the fabric before and after functionalization will be evaluated in accordance with ASTM D737, the standard test method for evaluation of air permeability of textile fabrics.

Initial studies on grafting a bio inspire material, Ethyl Chrysanthamate (figure 10) on Nyco fabric through plasma-assisted deposition is being carried out. The fabrics coated with ethyl chrysanthemate are currently being tested for their insect repellency properties according to the WHO tube test.

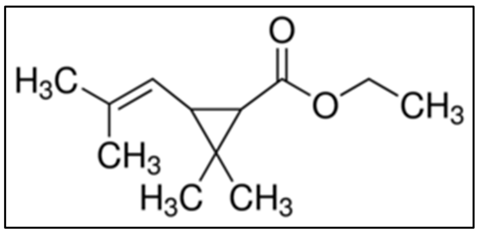


Figure 10: Chemical Structure of Ethyl Chrysanthamate

5.0 Conclusions

An approach to creating multifunctional Nyco fabric with both flame retardancy and insect repellency has been successfully demonstrated. This proof-of-concept functionalization process includes covalent attachment of bio-based material, phytic acid as a flame retardant and plasma deposition of permethrin as an insect repellent. The functionalized fabric was characterized using a variety of techniques. Infrared spectroscopy was used to confirm the grafting of FR moieties through the formation of carbamate bonds. The fire-retardant behavior of the multifunctional Nyco evaluated using a standard vertical flame test indicated that the treated fabric exhibits self-extinguishing characteristics within 2 seconds after the removal of the ignition source with less than 5±1" of char length. There was no dripping, after flame or afterglow in the functionalized fabrics. Advanced thermal characterization techniques TGA, MCC were used to study the thermal stability, char formation and heat release properties respectively of the multifunctional fabrics. TGA results indicate improved thermal stability and an increased char formation by > 2x (from 10% for untreated nyco to about 23%) for the multifunctional fabric. The heat release capacity for the treated fabrics reduced by 23% and the total heat release was reduced by 15.8% for the multifunctional Nyco compared to nyco control fabric.

The efficacy of the insect repellent treated fabric and the multifunctional fabric were evaluated according to a test method specified by the World Health Organization called the 'Tube Test'. It was found that the insect repellant (IR) treated fabric and the multifunctional (FR and IR treated) fabric exhibited good efficacy against female Aedes aegypti mosquitoes. The mortality rate of mosquitoes was greater than 98%.

This new fabric functionalization CDI chemistry successfully incorporated phytic acid, which acted as a flame retardant molecule to the fabric. Phytic acid and permethrin functionalized fabrics showed better thermal and flame-retardant properties than the control samples along with excellent insect repellent properties.

6.0 Implications for Future Research, Benefits and Transition Plan

This "limited scope" SERDP project has successfully demonstrated and proved the concept of surface functionalization of Nyco using Phytic acid (an abundant bio-based material) to impart fire resistance as well as plasma-assisted deposition of permethrin to impart insect repellant characteristics. The use of this bio-derived and safer material namely phytic acid will help reduce the risk of environmental toxicity and bioaccumulation which is a major concern with current flame retardant solutions. The covalent attachment of Phytic Acid to cellulosic hydroxyl groups on the cotton part of Nyco improves the launder durability of the FR.

Although permethrin is not an entirely safe insect repellant it is quite effective and is used widely by the department of defense to impart insect repellent characteristics. The durability of the permethrin coated on Nyco has always been a limitation. In this SERDP project, we have also proved that the Nyco fabric functionalized with Phytic acid can be treated with permethrin using atmospheric pressure plasma-assisted deposition and crosslinked on the surface of the fabric using acrylic monomers to improve the wash durability and reduce the risk of leaching out during laundering process. The current and future efforts in this project are focused on replacing permethrin with safer, bio-based/ bio-inspired insect repellants such as Chrysanthamates.

The current research being a limited scope project was a proof-of-concept demonstration of the feasibility of an innovative approach to producing a multifunctional Nyco fabric with both flame and vector protection. The covalent attachment of a bio-based material phytic acid (PA) as a flame retardant to the Nyco fabric followed by plasma-assisted deposition of permethrin as an insect repellent/ insecticide open new possibilities for Nyco fabric to exhibit both flame and vector protection.

In the next phase, optimization studies to reduce the reaction times will be carried out. Reduction of reaction time will make the process more feasible for scaling to an industrially relevant process. The use of microwave reactors where energy is supplied directly to the substrate will facilitate the reduction of treatment time and the volume of solvents required for the process. This will drive down the manufacturing costs associated with the treatments. Preliminary studies suggest that the reaction times can significantly be reduced by more than 80%.

Key technical objectives for future research include:

1. Improving the launder durability to survive at least 50 wash cycles when tested in accordance with AATCC 135 test method.
2. Process Optimization for the chemical functionalization of Nyco fabric with FR using Microwave-Assisted grafting
3. Optimizing plasma-assisted deposition of safer insect repellents such as Chrysanthamates after the deposition of FR
4. Scale-up efforts in collaboration with industrial partners such as Milliken will be explored
5. Arm-in-Cage tests will be performed to evaluate the efficacy of the repellent coated fabrics before and after laundering.

Benefits

This research will result in novel low cost and durable multifunctional fabrics that will empower and protect the Warfighter in harsh environments. The functionalization techniques described are simple, scalable and sustainable approaches to achieve multi-functionality on nylon/cotton (Nyco) blend fabric. Using plasma treatment and surface chemical functionalization involving bio-derived or synthetic flame retardants/insect repellents allows for retaining the mechanical properties of the textiles while substantially lowering the environmental or health risks associated with FR and the insect repellant. Furthermore, sustainable and effective flame retardants and insect repellants will not only protect from fires but also reduce the potential for vector-borne illness and improve readiness for the Warfighter.

Transition Plan

The FR through chemical functionalization can be scaled up using a microwave-induced grafting process and multiple dips and dryers for each reaction step (CDI and FR molecules attachment). For the plasma-induced deposition of insect repellants onto fabric, the industrial plasma machine (example shown in Fig. 11) can be used for scale-up. The process has already been scaled-up for high volume production using permethrin as the insect repellant. Optimization will be carried out with Chrysanthamates as the insect repellant.

Figure 10: Roll to Roll fabric treatment equipment (LaunchBay LLC)[22]

The plan is to transition this promising multifunctional coating technology with the help of SERDP and DEVCOM SC(6.2/6.3) programs, and eventually transition to higher TRL levels through an ESTCP program.

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