# Development of Inherently Super-Nonwetting Fibers and Fabrics

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## ABSTRACT

Work presented in this paper will introduce a revolutionary process which modifies fiber geometry and its surface structure, as well as the resulting fabric's weave structure with 3rd level reentrant features to achieve super liquid repellency. Weave structure modification is based on MIT's findings that omniphobic coated stainless steel meshes constructed with smaller sizes were shown to yield higher resistance to surface wetting and wetting-through (or "liquid robustness") by the impinging liquids than larger meshes.[1] Also, the introduction of 3rd level reentrant features on the fibers' surface is based on the fact that the addition of a dual hierarchical micro/nano-scale surface feature to an omniphobic fabric had resulted in an increase in liquid repellency.[2] Clemson University (Clemson), using a mono/bi-component extruder, spun bi-component fibers (Figure 1). Work to extract the water soluble portion of the fiber or fabric was conducted by the University of Massachusetts Lowell (UML) using a continuous extraction process (Figure 2). The application of dual hierarchical micro/nano-scale surface features (Figure 3) on the extracted fibers' surface were performed by Luna Innovations, Inc. (Luna). Inherently super nonwetting fibers and fabrics will be introduced, their inherently super nonwetting fiber concept explained, and their surface and physical properties will be discussed.

## 1 INTRODUCTION

Durable water repellent (DWR) finish has been in use for the past 40 years to treat fabrics used in rainwear and chemical protective clothing. However, DWR finish had been banned by the EPA in 2015 because it is a harmful chemical,[3] and is not durable after repeated washings.[4] Furthermore, low surface tension liquids including toxic industrial chemicals (TICs) can easily wet DWR treated clothing which is a grave concern to the users. Recently commercialized EverShield® Durable Omni Repellent (DOR) finish[5] was shown to be more durable than DWR finish and provides enhanced chemical protection as compared to DWR finished fabric[6] and DOR treated clothing repels oils and certain organic solvents, but is not as effective against very low surface tension polar and non-polar toxic chemicals.

Figure 1. LBS Extruder – Main Control Panel (Left); Mono/Bi-Component Fiber Unit (Right). Clemson.

Based on MIT's discovery in 2007[7,8] a team from government, academia, and industry areas was formed in 2013 under the technical guidance and direction of NSRDEC to design and develop inherently superomniphobic (SO) fibers. These SO fibers have engineered reentrant nano-features that negate the need for using C8 (perfluorooctanoic acid) or C6 (perfluorohexanoic acid) chemistry. The resulting inherently super nonwetting fibers would effectively repel a wide range of low surface tension liquids for a wide range of textile products, including self-cleaning and enhanced chemical/ biological (CB) protective clothing, shelters, as well as other commercial textiles and upholstery products.


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Figure 2. Continuous Extraction Process for Single Fiber Strand. UML.

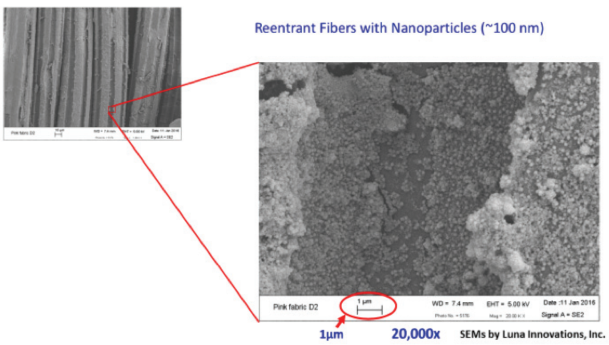



Figure 3. Application of a nano-scale surface features on reentrant fibers. Luna.

## 2 OBJECTIVE

The purpose of this presentation is to introduce a revolutionary novel fiber concept to achieving inherently super-nonwetting fibers and fabrics based on the creation of a new, novel fiber with reentrant dual micro-/nano-architecture. Once fabricated into protective clothing, their micro-trapezoidal channels around the fiber, and nano-features on its fibers will repel chemical warfare agents [e.g., HD, GD, GB, and VX (surface tensions: 43.2 mN/m @20°C, 24.5 mN/m @26.5°C, 26.5 mN/m @20°C, and 32.0 mN/m @20°C respectively)], as well as polar and nonpolar toxic industrial chemicals with extremely low surface tensions [e.g., Tetrachloroethylene, Methanol, and N-Hexane (surface tensions: 28.7, 22.1, and 18.4 mN/m respectively)].

The use of super liquid repellent fibers can offer added tradespace (i.e., with adding noticeably enhanced chemical protection while having virtually no interference to air and moisture vapor) when they are fabricated into thin, lightweight, and tightly woven textiles. Material concept, material selection, fiber designs, bi-component fiber processing and extraction, test methods used, results such as Scanning Electron Microscopy (SEMs), selected surface and physical properties of inherently SO fabrics will be discussed and compared to conventional fabrics that were untreated, and treated with fluorinated chemistries (i.e., C8 and C6) to provide technical guidance to interested researchers and material developers, and to welcome industry participation.

## 3 APPROACH

A theoretically effective reentrant fiber design was modeled and identified. Polymer distribution plates (Hills, Inc.) were then designed for bi-component melt-spinning to produce a reentrant fiber design (Figure 4).

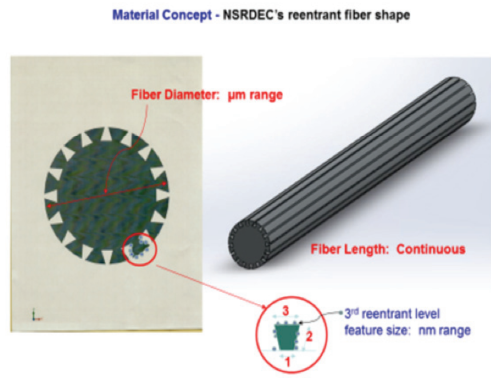



Figure 4. Cross-section and 3D views of reentrant fiber. NSRDEC.

Various melt spinning processing conditions were examined, and desirable bi-component fiber in the correct geometries were spun. Bi-component fibers were then subjected to various lab-scale as well as continuous fiber extraction experiments to arrive at the optimal fiber extraction conditions. Fibers were woven into fabric, and were further modified with nano-scale features in order to achieve 3rd level reentrant structure (Figure 5).[9] The resulting super nonwetting fibers were then tested for their surface and physical properties and compared to conventional fibers and fabrics.

### 4 RESULTS AND DISCUSSION

Recent work has resulted in favorable reentrant fiber structures. Examples of selected experimental polypropylene fiber structures and knitted fabrics are included in Figures 6 and 7 respectively.

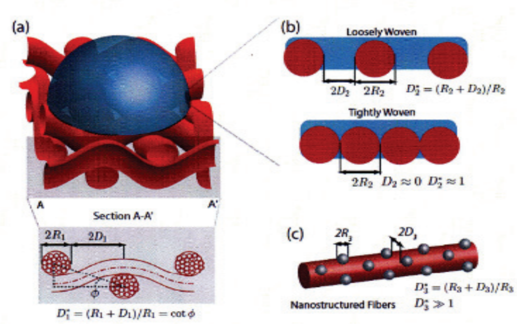


Figure 5. Introducing 3rd level reentrant structure to extracted reentrant fibers. MIT.

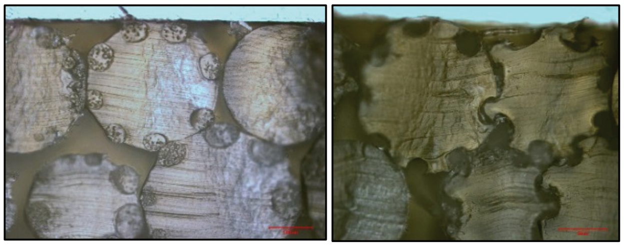


Figure 6. SEM showing unextracted and extracted polypropylene fibers' cross-section showing 8 reentrant features around the fibers. Clemson.

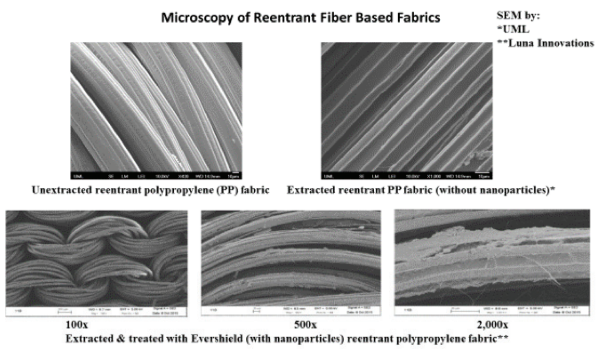
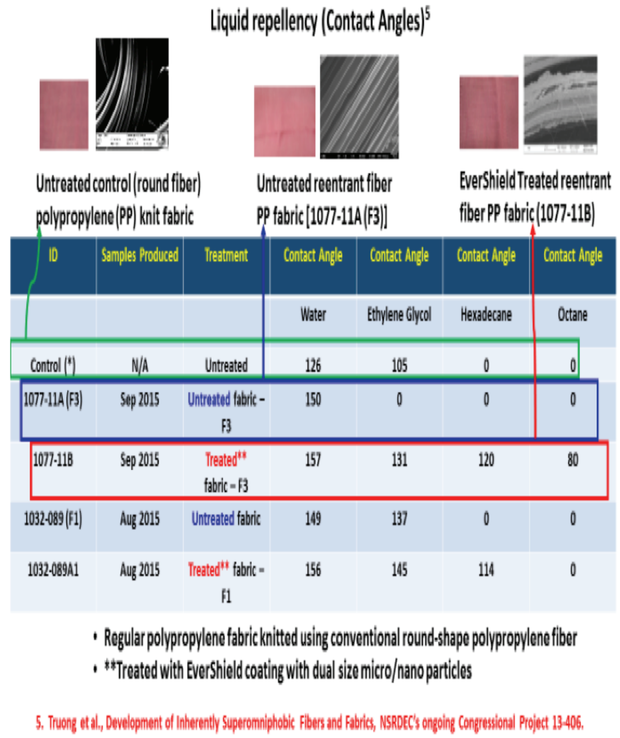



Figure 7. Unextracted and extracted 8-feature reentrant polypropylene fiber based fabrics

Below are contact angle data comparing control samples (cylindrical fibers) of knitted polypropylene (PP) fabric, reentrant (i.e., extracted PP knit fabric without 3rd level reentrant structure (i.e., nanoparticles), and Evershield® treated reentrant PP knit fabric (Figure 8). This data shows the added liquid repellency of the reentrant fiber structure as compared to the control PP knitted fabric (Water contact angle: 126° vs. 150°), and the increase in liquid repellency when the 3rd reentrant structure (nanoparticles) was added to the reentrant fiber structure. This is evident in the increased repellency to lower surface tension liquids [ethylene glycol, hexadecane (Contact angle: 0° vs. 120°), and octane (Contact angle: 0° vs. 80°)]. When comparisons were made between based knitted fabrics made with conventional fiber (control/cylindrical) and 3rd level reentrant fiber based knit fabrics, results showed that the contact angle of water had increased from 126° to 157°, while ethylene glycol increased from 105° to 131°.

Fiber's modulus was found to be statistically the same for non-extracted (i.e., bicomponent fiber) and extracted, with extracted (reentrant) fiber having higher tenacity because reentrant features cause entanglements between the extracted filaments (Table 1). Various additional surface and physical properties data such as water and oil ratings, electron microscopy, fiber tenacity, modulus, reentrant size, etc. will be reported at a later time.




| ID | Samples Produced | Treatment | Contact Angle | Contact Angle | Contact Angle | Contact Angle |
|---|---|---|---|---|---|---|
| | | | Water | Ethylene Glycol | Hexadecane | Octane |
| Control (*) | N/A | Untreated | 126 | 105 | 0 | 0 |
| 1077-11A (F3) | Sep 2015 | Untreated fabric – F3 | 150 | 0 | 0 | 0 |
| 1077-11B | Sep 2015 | Treated** fabric – F3 | 157 | 131 | 120 | 80 |
| 1032-089 (F1) | Aug 2015 | Untreated fabric | 149 | 137 | 0 | 0 |
| 1032-089A1 | Aug 2015 | Treated** fabric – F1 | 156 | 145 | 114 | 0 |

Figure 8. Liquid Repellency of untreated control (cylindrical fiber), untreated reentrant, and treated reentrant knit fabrics

Table 1. Reentrant Nylon Fiber Properties. Clemson.

| Sample | Nylon 6 Fiber | Nylon 6/ G Polymer Fiber | Nylon 6 Extracted Fiber |
|---|---|---|---|
| Fiber | Single Component | Bicomponent | Extracted |
| Polymers | Nylon 6 | Nylon 6 and G Polymer | Nylon 6 |
| Polymer Ratio | - | 1:1 (N6:GPOLYMER) | - |
| Fiber Shape | Round | New Gear Shape | New Gear Shape |
| Filaments | 19 | 19 | 19 |
| Denier | 495.9 | 603 | 279 |
| Denier/ Filament | 26.1 | 31.74 | 14.68 |
| Fiber Diameter | ~60um | ~60um | ~60um |
| Elongation | 520.04% | 70.01% | 236.99% |
| Tenacity | 1.63 gpd | 1.07 gpd | 2.63 gpd |
| Modulus | 5.75 gpd (SD: 0.41gpd) | 10.12 gpd (SD: 0.65gpd) | 9.26 gpd (SD: 0.56gpd) |

## 5 FUTURE WORK

Current efforts have yielded 16-reentrant fiber structures that are approximately 30-µm in diameter, where the reentrant angles of the features around the fibers are not yet optimized (Figure 9). Future work will focus on leveraging and optimizing woven fabric parameters beneficial to liquid repellency and liquid robustness using inherently SO fibers, more uniform nanoparticle dispersion/distribution on the reentrant fiber surface, extending the polymer range to include more difficult to extrude lower surface tension polymers, exploring repellency to wider range of liquids to include polar liquids that are being used as chemical agent simulants (Figure 10), chemical agents, and toxic industrial chemicals (ASTM F1001-12)[6] to further the development of NSRDEC's enhanced chemical/biological protective clothing to protect the individual Soldier as well as industrial chemical handlers and domestic preparedness personnel.

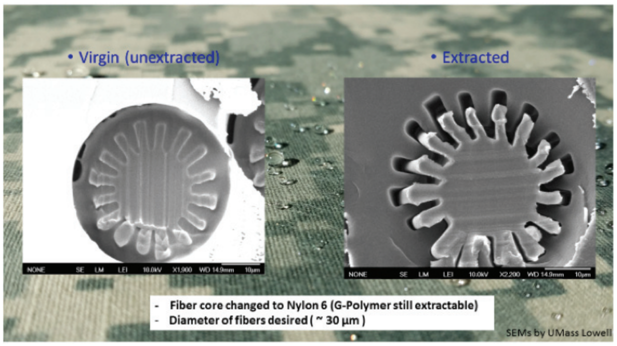



Figure 9. Unextracted and Extracted 16-Feature Reentrant Fiber

**Polar Liquids, CWAs, and their surface tensions**

UNCLASSIFIED

| Polar Liquid | Surface Tension (mN/m) | NOTES |
|---|---|---|
| Water | 72.8 | Protic solvent, @25°C |
| Dimethyl Sulfoxide (DMSO) | 43.54 | Lewisite (L) simulant. Aprotic solvent |
| Methyl Salicylate (MeS) | 41.84 | Sulfur mustard simulant |
| Dimethyl Methyl Phosphonate (DMMP) | 36.7 | Nerve simulant |
| 2-Chloroethyl Ethyl Sulfide (2-CEES) | 32.2 | Nerve simulant |
| Triethyl Phosphate (TEP) | 30.61 | Nerve simulant |
| Tributyl Phosphate (TBP) | 27.79 | Nerve simulant |
| Methanol | 22.1 | Protic solvent |

| Nonpolar CWA* | Surface Tension (mN/m) | NOTES |
|---|---|---|
| VX | 31.3[10] | Nerve chemical warfare agent (@25°C). Persistent (Volatility[10]: 10 mg/m$^3$ @20°C). |
| GA | 32.5[10] | Tabun nerve chemical warfare agent (@25°C). . Persistent (Volatility[10]: 610 mg/m$^3$ @25°C). |
| GB | 25.9[10] | Sarin nerve chemical warfare agent (@25°C). Non-persistent (Volatility[10]: 1.8x10$^4$ mg/m$^3$ @20°C). |
| GD | 24.5[10] | Soman nerve chemical warfare agent (@25°C). Non-persistent (Volatility[10]: 4x10$^3$ mg/m$^3$). |
| HD | 42.5[10] | Blister chemical warfare agent (@25°C). Persistent (Volatility[10]: 906 mg/m$^3$) |

*CWAs are nonpolar compounds, but they are soluble in water.

10. Agnieszka Anna Gorzkowska-Sobas, Chemical warfare agents and their interactions with solid surfaces." Norwegian Defense Research Establishment (FFI), FFI-rapport 2013/00574, 1 March 2013, Page 30. 22

Figure 10. Polar Liquids, CWAs, and their Surface Tensions[10]

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