# Greener Solutions for Durable Water Repellency

Partnered with W.L. Gore & Associates

Marianna Augustine, Emily Cook, Erin Creel, Sumana Raj, John Wright

**Greener Solutions** 

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# 1. Executive Summary

In the Fall 2017 semester at University California, Berkeley, this group of five graduate students worked with W.L. Gore & Associates ("Gore") to identify greener solutions to durable water repellency (DWR) coatings on textiles. Our goals included that the final product is highly hydrophobic for dynamic water repellency (rainfall), oleophobic for self-cleaning (which also contributes to hydrophobicity, insulation, and durability), durable, washable, and aesthetically pleasing to consumers.

This process first involved learning about the state of the sector: learning about the current standard DWR chemicals (per- and polyfluoroalkyl substances (PFASs)) and how they achieve high performing durable water repellency and oleophobicity. Looking toward non-fluorinated solutions, we were inspired by the natural hydrophobic mechanism of micro- and nano-hierarchical structuring found in the lotus leaf and other organisms. We explored literature to find possibilities to achieve this type of structuring with low hazard fibers and solvents. We maintained a long list of possibilities for Gore (explored in Section 3 of this report) and shortened the list to the two most promising solutions: silica nanosols and blow spinning (both described in Section 4), which reported the best hydrophobicity, potential for oleophobicity, and application to textiles.

A silica nanosol coating provides hierarchical structuring through silica nanoparticles that bond with the surface of a synthetic fabric (e.g. polyester). Silica nanosols are highly hydrophobic but not as oleophobic as desired. In this report, we suggest adding a liquid-like coating such as dimethyldimethoxysilane to the silica solution to improve oleophobicity.

Blow spinning is a process to create textured, microfiber mats which are hydro- and oleophobic, similar to the silver ragwort leaf. Blow spinning seems less hazardous than other processes (such as electrospinning) since the process uses a non-toxic compressed gas (i.e. air or argon) and can utilize ethanol or propanol as a solvent for a variety of synthetic polymers that then form the fibers. Due to the flexibility to choose materials used for blow spinning, there are several low hazard options we recommend.

Based on performance and hazard comparison, we recommend that Gore uses blow spinning to create microfiber mats to coat their clothing textiles. Poly(vinyl alcohol), ethanol, and air are low hazard materials that could achieve Gore's performance standards. Note that this literature-based study is limited to data that is publicly available. Thus, there are data gaps in both our hazard and performance analysis. The literature available for these proposed technologies did not necessarily pertain to the application of fabrics; therefore, textile

performance metrics such as durability and aesthetics is a major gap in this report. Further laboratory-based studies are needed to make an informed decision. Additionally, assessing hazards for the chemicals and processes discussed in this report is a challenging and complicated process. Sometimes there are data gaps, and sometimes sources contradict each other. Considering these facts, we make a clear distinction that a lack of literature does not mean a lack of hazard. We acknowledge that the literature can be limited and we attempted to take a conservative approach.

# 2. Introduction

#### 2.1. Need for durable water-repellent textiles

In an increasingly active world, textiles that are water- and oil-repellent as well as breathable, durable, soft, and attractive are demanded by a diverse set of consumers. From protective gear for firefighters and military members to warm, rain resistant gear for bikers or hikers, present-day consumer fabrics must be impervious to everyday dirt, wear, and tear. Water repellency keeps the wearer dry and warm when exposed to rain or snow. Oil repellency increases the durability of the waterproof coating by preventing sunscreen, soil, and skin oils from damaging the water repellent coating. The combination of hydrophobic and oleophobic properties, therefore, are essential to achieve durable water repellency (DWR). DWR textiles are a staple in the outerwear industry. A typical DWR treatment is the top coating of a multilayer "sandwich" of fabrics and membranes. Gore's membrane and fabric assembly is called GORE-TEX® laminate (Fig. 2.1).

Gore is a major contributor to the DWR market landscape, as their DWR coatings achieve some of the best omniphobic (both hydrophobic and oleophobic) properties in the textile industry. The product line GORE-TEX® is widely respected by consumers.



**Fig. 2.1.** The GORE-TEX® laminate consists of an inner lining, the GORE-TEX® membrane made of poly(tetrafluoroethylene) (PTFE), and an outer layer composed of the outer fabric coated with the DWR. The inset illustrates water beading up rather than wetting the surface (adapted from 34).

#### 2.2. State of the industry

The most effective way to achieve simultaneous water- and oil-repellency is by using fluorinated compounds to coat textiles. Fluorinated alkyl chains are unique due to the stable, hydrophobic, oleophobic, and non-reactive nature of the multiple carbon-fluorine (C-F) bonds, shown in Figure 2.2 (1). These characteristics together make fluorinated chemicals ideal components for achieving durable water repellency; indeed, no other chemicals are known to impart both hydro-and oleophobicity to textiles.



**Fig. 2.2.** Examples of common fluorochemicals. **a)** Generic fluoroacrylate polymer. **b)** Generic polyfluorinated (partially fluorinated) alkyl chain with amine functional groups. **c)** Perfluorooctanesulfonic acid (PFOS), a perfluorinated (fully fluorinated with no hydrogen atoms) alkyl chain with a sulfonic acid head group.

PFASs have long been used to create DWR materials; they are currently the best for achieving both water- and oil- repellency while maintaining the durability and feel of the fabric. Although fluorinated polymers and alkyl chains are useful, certain fluorinated compounds have been shown to be persistent, bioaccumulative, and toxic (PBT) to humans and other species (1,2). As a result, the Stockholm Convention now restricts two types of PFASs and the U.S. EPA has set drinking water health advisory limits for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) of 70 ppt (3,4).

Companies have been researching alternative methods to achieve water and oil repellency without fluorinated chemicals. For the past 15 years, there has been a industrial transition from using long-chain PFASs (perfluorinated alkyl chains containing eight or more carbons) to short-chain PFASs (fewer than eight carbons) in an effort to decrease the environmental persistence and toxicity of these chemicals (35,36). Although these short-chain compounds could potentially have a shorter half-life in human bodies, there are also concerns that short chain

replacements could be more toxic (5). Thus, there is a growing effort to replace all PFASs and their precursors outright in DWR applications.

Greenpeace launched an international Detox campaign in 2011, urging companies in the clothing industry to eliminate all hazardous chemicals from production, focusing specifically on PFASs (6). Together, Gore and Greenpeace defined per- and polyfluorinated chemical of environmental concern (PFCs-EC) as chemicals that are highly fluorinated (per- or poly-fluorinated organic substances), environmentally persistent (half-life greater than two months or greater than 60 days in water or soil), and small enough to be bioavailable (capable of crossing a cell membrane or molecular weight less than 3 kDaltons). Fluorinated polymers such as polytetrafluoroethylene (PTFE) are not included in this definition. Figure 2.3 illustrates the timelines for a range of companies (both in the U.S. and abroad) to eliminate PFASs from their products. The GORE-TEX® laminate is used by several of the manufacturers listed in Figure 2.3 including The North Face, Marmot, and Arcteryx, so Gore has partnered with Greenpeace to eliminate PFCs-EC from their products. Figure 2.4 illustrates the timeline for Gore's goals.



**Fig. 2.3.** Timeline of PFC reduction and elimination for companies partnered with Greenpeace's Detox Campaign (6).



**Fig. 2.4.** Gore aims to eliminate PFCs-EC from consumer laminate shipments corresponding to units of finished products. General outdoor products (e.g. jackets, shoes, gloves, and accessories) that provide durable protection for general outdoor activities will be free of PFCs-EC by 2020. Specialized outdoor products (e.g. firefighting gear) will be PFCs-EC-free by 2023.

#### 2.3. Fluorinated hazards

PFASs are known to be persistent and bioaccumulative, which compounds the toxicity effects over time. The mechanism of PFASs toxicity arises from their tendency to partition to the protein due to their hydrophobic and lipophobic nature. Unlike highly lipophilic compounds that tend to bioaccumulate in fatty tissue, PFASs sorb to liver proteins and blood serum (7,8). Affinity of PFASs for protein-complexes and lipids have been linked to endocrine disruption (9,10), cancer (11, 12) and elevated serum concentrations of PFASs in children (13). Through the life cycle of PFASs, transport occurs through air, soil, dust, and water (14,15).



**Fig. 2.5.** Structures of A) perfluorooctanoic acid (PFOA) and B) perfluorohexanoic acid (PFHxA), an eight-carbon and six-carbon fully-fluorinated alkyl chain with a carboxylic acid head group.

Uncertain Future of Fluorinated Compounds: Does Size Matter?

There are 42 families and subfamilies of PFASs (18), all with varying properties. Due to this variability, some have explored the possibility that short-chain compounds may differ from long-chain PFASs in persistence and toxicity (19). Research continues to explore the effects of chain length on toxicity (20,21), and debate still continues regarding their use (19,22). We selected two highly cited compounds, PFOA and PFHxA (Fig. 2.5), for hazard assessment and comparison to our potential alternatives (Table 2.1). PFHxA and PFOA both have half lives above the EPA criteria for persistence (greater than 60 days in water, soil, and air). Additionally,

PFOA or PFHxA may be formed in the environment due to the metabolism or breakdown of polymer side chain precursors or other PFAS precursors. PFOA is a central drinking water contaminant under litigation due to probable links to kidney cancer, thyroid disease, heart disease, and high cholesterol (16,17).





PFOA and PFHxA are both persistent, but not lipophilic (23). Bioaccumulation occurs through increased binding affinities to fatty acid proteins in the liver and blood (24,25,26), as well as enterohepatic recirculation (26). Due to the unusual chemical properties of PFASs (neither hydrophilic nor lipophilic),  $K_{ow}$  models for predicting bioconcentration factor (BCF) may under-predict accumulation in living systems (25,31). These features make them difficult to incorporate into environmental risk models using the BCF criterion to predict persistent, bioaccumulative, and toxic (PBT) compounds. PFOA and PFHxA may also exhibit non-estrogen mediated endocrine disruption, which makes them ineligible for endocrine disruptor screening program (EDSP) assays targeting estrogen and androgen receptors. The anticipated substitution of an 8-carbon PFAS with a 6-carbon PFAS may be based on the assumption that shorter chained PFASs are less bioaccumulative and, therefore, less hazardous. There are other metrics to measure hazard, however, and we have seen that PFHxA still poses human toxicity hazards as well as persistence in the environment. (19,22).

Our group decided—in addition to eliminating PFCs-EC—to eliminate all fluorinated compounds from our research. This decision came from our preliminary hazard assessment of PFOA and PFHxA, the scope and goals of this Greener Solutions class, and uncertainty of the PFAS life cycle (production, precursor compounds, and degradation) in the products. Although fluorinated polymers are not PFCs-EC (since they are not bioavailable), the production of polymers such as PTFE sometimes involves the use of other PFASs, such as PFOA, which are bioavailable. We do not investigate potential uses of fluorinated polymers in this project in order to ensure that bioavailable PFASs are completely eliminated from the life cycle of our suggested alternatives.

# 2.4. W. L. Gore's challenge

The goals, outcomes, and technical requirements for this project are outlined in Proposed W. L. Gore & Associates, Inc. Project for UC Berkeley Greener Solutions Course.

# Gore Technical Requirements for DWR Performance

Gore's specified performance metrics for our alternative are the following:

- Water resistance resulting in water contact angles equal to or greater than:
  - 115° (advancing angle)
  - 95° (receding angle)
- Oil repellency score of a minimum of two but preferably greater than or equal to five, as outlined in AATCC118-2007
- Ability to maintain performance standards after 20 home laundry wash cycles with detergent
- Lack of negative odor
- Color, texture, and feel of final product undiminished
- Materials exhibit low inherent toxicity and are not bioaccumulative
- Be capable of high volume manufacturing

# Gore Technical Requirements for Human and Environmental Health

Gore specified that the alternative must have low inherent toxicity, be non-bioaccumulative, and not comprised of components that are persistent. We assessed bioaccumulation using criteria described by the Environmental Protection Agency (EPA) and the European Union's Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). REACH and the European Chemicals Agency (ECHA) prioritize substances considered persistent, bioaccumulative, and toxic (PBT) on a "substances of high concern list" as described in Section 3.2 of ANNEX XIII (27).

The main characteristics of PBT are 1) high potential to accumulate (high BCF), 2) high octanol-water partitioning coefficient ( $K_{ow}$ ), 3) reproductive toxicity, and 4) slow degradation. Compounds that are lipophilic (high  $K_{ow}$ ) often interfere with endocrine (reproductive and developmental) nuclear receptors (28,29). Persistent organic pollutants (POPs) can bioaccumulate within organisms, reaching high concentrations over several trophic levels (26). Compounds with a high BCF can resist degradation and persist in soil and sediment due to low water solubility.

# 2.5. Approach

### Understanding PFASs

Our approach began with a literature review and study of PFASs and their current use in the textile industry. Understanding the chemical structure of fluorinated alkyl chains—how the structure controls durability, oleophobicity, and hydrophobicity of PFASs—was a useful first step in exploring what other less hazardous chemical compounds may or may not be available for a DWR coating. We found that perfluoroalkyl chains are unique; fluorine is the most electronegative element and, as a result, the carbon-fluorine bond is the strongest and shortest found in nature. Thus, PFASs have low polarizability and low surface tension, allowing them to resist wetting of nearly all fluids. These traits make it nearly impossible to replicate with other types of alkyl chains or polymers.

#### Bio-inspired design

Nature has found ways to repel fluids without the use of fluorine in its years of iterative design through evolution. We researched plants, animals, insects, and arthropods that have evolved to have water- and/or oil-repellent properties. Each of the team members focused on different species—lotus leaves, fish scales, snake skin, springtail exoskeletons, and rice leaves. Unexpectedly, we found that all these organisms, while spread across zoological and botanical families, displayed similar features. All had a nano- and micro- hierarchical structuring to create an omniphobic surface through texturing (Fig. 2.6) rather than through chemical means of altering surface tension thermodynamics. Additionally, many species had a type of wax coating coupled with the structuring to further improve performance.



**Fig. 2.6.** a) Photograph of the superhydrophobic leaf of the *Salvinia molesta*, b) SEM image of the micro- and nanostructuring, and c) a schematic of how air gets trapped in this structure and repels water (32).

Hierarchical structuring allows species to decrease the contact area between the surface and the fluid by trapping air pockets between the tiny structures. The condition where a fluid is suspended above a trapped gas on a rough surface is called the Cassie-Baxter state. The low surface contact results in minimal adhesion between the surface and fluid. In contrast, when a

droplet floods the pores in a structured surface, it is in a Wenzel state. The Wenzel state maximizes the contact area between the droplet and the surface thus increasing adhesion (Fig. 2.7).



**Fig. 2.7.** Moving from a flat to a hierarchically-structured surface decreases contact area between the fluid and the surface, increasing the effective repellency and contact angle.

# Possibilities ruled out

We ruled out strategies that were impractical or had high hazard or poor performance. For example, strictly looking at structuring to achieve an omniphobic textile surface, electron-beam (e-beam) lithography and 3D printing were first considered then quickly eliminated due to their lack of durability and feasibility. Electron beams can be used to carve shapes onto the surface of a material similar to what is found in nature. These synthetic structures are effective but are easily damaged (33). Additionally, these processes are expensive and slow to produce, making them not feasible for mass production of textiles. As technology advances and becomes less expensive, this technique may become more viable in the future.

# Narrowing our focus: performance and oleophobicity

As we examined literature, we maintained a long list of possible solutions (Section 3 of this report) that have some shortfalls, mostly in oleophobic performance. Simultaneously, we identified possibilities that seemed most promising, which we put on a short list. For this report, we chose two particular solutions that we thought were the most promising, which are described in Section 4 of this report. Narrowing our focus included major requirements; the solution had to be tested on fabrics, have high hydrophobicity, and have a promising solution for oleophobicity.

## Analyzing potential alternatives: metrics

While Gore provided specific performance standards to evaluate our alternatives, most of the accessible research reports used different, often easier to measure, metrics. In the cases where the metric Gore requested was not available, we used standards. The easiest way to determine a

surface's repellency toward a given fluid is to measure the static contact angle, the angle at which a carefully placed liquid droplet contacts a given solid surface (Fig 2.8a). Fluids that readily wet the surface (-philic) have static contact angles less than 90° while fluids that are repelled (-phobic) have a static contact angle greater than 90°. A surface is super hydro- or oleophobic when the static contact angle is greater than 150°. In the case of water, the measured contact angle is the "water contact angle" (WCA). The WCA was the most commonly used metric in literature due to ease of testing in laboratory environments.

More realistic measures of the liquid repellency of a textile in a use scenario are the dynamic contact angles. Simply stated, the dynamic contact angles are the contact angles between the surface of a droplet on the downhill (advancing) side of a tilted surface as well as the contact angle of the droplet on the uphill (receding) side of the surface (Fig 2.8b). A highly repellent surface will have approximately equal advancing and receding angles, indicating little tailing of the fluid droplet as it is distorted by gravity. A simple metric that encompases these two angles is contact angle hysteresis (CAH). CAH is the mathematical difference between the advancing and receding angles, so a -phobic surface has a 0° CAH ideally.

Finally, the roll-off angle (Fig. 2.8c) is the degree to which a surface must be tilted before the liquid droplet slides off. Roll-off angle is important in textile self-cleaning applications because the droplet aids in removing dirt and oils from the surface as it is shedded.



Fig. 2.8. Metrics for liquid repellency are a) static contact angle, b) dynamic contact angles, and c) roll off angle.

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# 3. Long List of Possible Alternatives

## 3.1. Background

There are myriad ways to achieve hydrophobicity and/or oleophobicity. These strategies use structure and/or surface chemistry to achieve the repellency. The following "long list" of possible solutions includes strategies that need significant improvement to achieve Gore's DWR goals. Some are strategies that can be used to enhance the liquid phobicity of another strategy but cannot stand on their own. Many alternatives on this list manage to achieve high hydrophobicity but minimal or no oleophobicity. All of these strategies fail to meet at least one of Gore's performance or hazard criteria for their DWR alternative and cannot be easily modified to achieve these goals. For this reason, they were not on our "short list," but still remain promising routes to pursue.

# 3.2. Octadecylamine-grafted nylon

A simple method for improving the hydrophobicity of nylon 6,6—one of the most common types of nylon used in textiles—is to graft aliphatic chains to the surface. One study used poly(acrylic acid) to functionalize the nylon and octadecylamine as the aliphatic chain source (Fig. 3.1) (1). Because nylon 6,6 has chains of six unfunctionalized carbons between its nitrogen-containing functional groups, it is relatively unreactive. Poly(acrylic acid) is highly functionalized with carboxylic acid groups, so grafting this polymer to the nylon increases the binding sites for the aliphatic chains. Octadecylamine binds to the poly(acrylic acid) in an acid-base reaction between the amine and carboxylic acid groups. This process imparts hydrophobicity to the fabric through the 18-carbon chains of octadecylamine coating.

However, octadecylamine's aliphatic carbon chain is highly oleophilic. Extensive modifications to improve the oleophobicity of this strategy are required to make it viable for DWR. The poly(acrylic acid) functionalization of nylon 6,6 may be useful to in other strategies to increase the binding sites on nylon for other chemicals.



**Fig. 3.1.** Chemical structures for the molecules used in grafting hydrophobic functional groups on nylon and water repellency performance for the resulting assembly as compared to Gore's current DWR (adapted from 1).

#### 3.3. Paraffin-wrapping

Inspired by the company Schoeller and their technology ecorepel® (Fig. 3.2), we investigated the water-repellent properties of paraffins. On their ecorepel® website, Schoeller only describes the technology as "based on long paraffin chains that wrap themselves in a spiral around the individual fibers". The website further states that the solution is abrasion resistant, breathable, dirt-repellent, and that the feel is not negatively affected.



**Fig. 3.2.** Schoeller ecorepel® graphic, illustrating paraffins wrapped around individual fibers to create a hydrophobic layer on fabrics (10).

Looking to literature to elucidate the mechanisms of this technique, a paper out of Korea describes using various chain-length paraffins on textiles to some success (2). Paraffins were synthesized using the monomers dodecyl acrylate, tetradecyl acrylate, hexadecyl acrylate, octadecyl acrylate, and docosyl acrylate and various emulsifiers and co-emulsifiers. This solution, autoclaved and diluted, was used to treat various fabrics with the dip and nip method (2).



Fig. 3.3. Static water contact angles with various lengths of paraffins on PET, nylon, and cotton textiles (2).

The resulting paraffinic coating method lowered the surface tension on the fabrics and achieved highly hydrophobic properties (Fig. 3.3) (2). The study only investigates water contact angles and surface tension; there were no results stated regarding durability, abrasion resistance, washability, or oleophobicity.

# 3.4. Multifilament fibers

The yarn that is woven in fabric manufacturing can have a variety of structures, such as monofilament, multifilament, and calendered. In a monofilament textile, the yarn is made of a single thread in contrast to a multifilament textile where the yarn is composed of a bundle of threads woven together as if they were one (Fig. 3.4a). The structure of the yarn can also be modified after the fabric is woven. For example, calendered fabric has been passed through a series of rollers to squeeze and flatten the fabric to make it more lustrous (Fig. 3.4b).

One study compared the hydrophobicity of octadecylamine- or PFOA-modified nylon with various fabric weave structures. The multifilament textile has much higher hydrophobicity than the monofilament or calendered monofilament textiles (Fig. 3.4c) due to the microstructuring of the fabric surface (1).

The weave of the fabric can confer microstructuring that only improves existing hydro- or oleophobicity to an extent. The textile must have some degree of -phobicity in order to reap the benefits. This is one way to improve hydrophobic fabrics such as polyester, polyolefin, and vinyl.



**Fig. 3.4.** Multifilament fiber structures and water contact angles. a) Scanning electron micrograph (SEM) of multifilament nylon, b) scanning electron micrograph of calendered monofilament nylon, and c) comparison in water repellency between octadecylamine- and PFOA-grafted nylon of different fiber structures (adapted from 1).

#### 3.5. Microfibers

The multifilament yarn strategy described above can be improved by using smaller fibers and a smaller, tighter weave. Traditional polyester (fiber diameter greater than 15  $\mu$ m) is less hydrophobic than microfiber polyester (fiber diameter less than 5  $\mu$ m) (Fig. 3.5) with the same surface treatment (3). The smaller structures on the microfiber textiles mean that there are more air gaps and less contact area between a liquid and the fabric for a given drop size. Again, this improvement in fluid-phobicity is minimal and only of use when the base structure already has some fluid-phobicity. See the Hazard portion of Section 4.2 for concerns over using microfibers.



Fig. 3.5. SEM of a) traditional and b) microfiber polyester with insets showing static water contact angle (3).

#### 3.6. Silicone nanofilaments

One of the most hydrophobic alternatives that we discovered was growing silicone nanofilaments on textiles. Tiny polymethylsilsesquioxane (PMSQ) hairs are grown on the surface of poly(ethylene terephthalate) (PET) fabric (Fig. 3.6) in a room temperature hydrolysis reaction, providing both physical and chemical hydrophobicity. The roll off angle of a drop of water released from a height onto the PMSQ-treated fabric was only  $2^{\circ}$  (4). The high static contact angle and a stream of water bouncing off the surface are shown in Figure 3.6.



Fig. 3.6. Silicone nanofilaments on PET. a) and b) SEMs of silicone nanofilaments grown on PET with inset showing a drop of water deposited on the fabric. c) A 5  $\mu$ L water droplet beads up on the surface, creating a static contact angle above the superhydrophobic threshold. d) A jet of water bounces off the treated fabric, showing no wetting behavior (4).

Spectroscopy has revealed that color change to the fabric after PMSQ treatment is very small and probably imperceptible to the human eye (4). Additionally, the PMSQ nanofilaments do not affect the tensile strength or feel of the fabric. The nanofilament PET maintained high hydrophobicity after 1450 abrasion cycles despite the destruction of the nanofilaments on the surface of the fabric. The three dimensional arrangement of the fibers means that only the outermost fibers get destroyed while the hydrophobicity is maintained by the deeper nanofilaments that remain intact. Unfortunately, washing the PMSQ-treated PET with detergent

at 30 °C resulted in water droplets wetting the fabric rather than remaining beaded on the surface. The silicone was likely damaged by the basic detergent but is likely resistant to acidic detergents. Thus, if this strategy were employed, customers would be instructed to use a particular type of detergent for washing.

Like many other strategies that offer high hydrophobicity without modification, the silicone nanofilaments could not be used in DWR due to the high oleophilicity of the silicone. The oleophobicity could be improved by using the dimethyldimethoxysilane coating modification that we suggest for the silica nanosols strategy, described in Section 4.1.

# 3.7. Slippery Liquid Infused Porous Structures (SLIPS)

Hierarchical structures inspired by the lotus leaf can exhibit omniphobicity under well-controlled conditions. However, they tend to fail at high or low temperatures or in a humid environment. Another strategy for achieving omniphobicity is SLIPS, inspired by the *Nepenthes* pitcher plant. In this alternative, instead of trapped air providing the omniphobicity, an ultrasmooth, slippery liquid lubricant provides a surface that is nonwetting to a variety of liquids and solids. The liquid-like nature of the SLIPS surface provides excellent dynamic dewetting behavior similar to the behavior of colloids. SLIPS also exhibit self-healing behaviors because the lubricant is redistributed to damaged areas (5).

The lubricant in SLIPS is held in place by a porous solid, usually a polymer-based network for textile applications. Though the lubricant for SLIPS is often fluorinated (5, 6), some studies have demonstrated fluorine-free omniphobic SLIPS using silanes. One study on a silicon wafer demonstrated CAH of  $<5^{\circ}$  and TAs of  $<20^{\circ}$  for water and three organic liquids (7). Another study created a non-fluorinated SLIPS on PET using poly(dimethylsiloxane) (PDMS) as the porous substrate and silicone oil as the lubricant (Fig. 3.7). The lubricated fabric was omniphobic, even after blotting the surface up to ten times with polymer wipes even though oil was absorbed by the wipes during these durability tests (8).



**Fig. 3.7.** Non-fluorinated SLIPS on PET. a) The SLIPS is created by curing a sandwich of PDMS and the fabric between two glass slides. The lubricant is added by soaking the PDMS-sandwiched fabric in silicone oil. b) The lubricated fabric maintains low CAH for both water (blue) and ethanol (green) after up to ten durability tests (adapted from 5).

While the omniphobicity of the fluorine-free SLIPS on PET is impressive, this strategy will need significant development to ensure that the lubricant stays intact during wear, abrasion, and washing. Blotting is not a rigorous enough durability test to emulate conditions of use.

#### 3.8. Titania nanosols

Treating a textile with titania  $(TiO_2)$  nanoparticles imparts UV-resistance, crease-resistance, self-cleaning, and antibacterial properties. Of particular interest to DWR is the self-cleaning resulting from the UV-activated photocatalytic behavior of semiconductor titania. A report of titania nanoparticles prepared by the sol-gel method and applied to cotton fabric using various crosslinkers will be used as a case study here (9). The nanosol-treated sample achieved the top score on the American Association of Textile Chemists and Colorists (AATCC) Soil Release Test after it was irradiated with UV light. The authors suggest that this self-cleaning effect results from the creation of reactive oxygen. Unlike the silica nanosol strategy presented in

section 4, the effect of the titania is photochemical rather than structural. In fact, the application of the titania nanosol smooths the fiber surface (Fig. 3.8) (9).



Fig. 3.8. SEMs showing the cotton fibers a) before and b) after treatment with titania nanosol (9).

Stain release technologies do not necessarily meet the performance metrics for DWR as outlined by Gore. Gore wants to avoid penetration of oily stains altogether, while stain release technologies instead ensure that the oils are removed in washing. Perhaps titania nanosols could be combined with another strategy to enhance oleophobicity.

# 3.9. Bioplastic fibers

Biodegradable, recyclable fibers are a greener alternative to petroleum-based, non-biodegradable textiles such as nylon.. Blends of these fibers can have a range of hydrophobicities, elasticities, and other properties(11). Poly(3-hydroxybutyrate) (P(3HB)) is a water-insoluble polymer produced from bacteria that is used for nano-indentations in fibers (12). Bacteria biosynthesize P(3HB) using the Entner-Doudoroff pathway from waste, sugars, or fatty acids (13). P(3HB) can be made with varying tensile strength, brittleness, and degrees of melt stretching, and can be used to produce nano structures (14). While these fibers are not necessarily higher performing than conventional fibers, they do generally pose less hazard due to their low environmental persistence.

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#### 4.1. Silica nanosol coatings

#### Background

Silica (SiO<sub>2</sub>) nanoparticles (NPs) can be applied to textiles to impart liquid repellency by adding nanostructuring to the microstructures formed by the threads in fabrics. The particles are typically applied through a solution-based method. The silica sol (solution) is composed of three parts: 1) silica NPs or their precursor, 2) organosilanes, and 3) water or low molecular weight alcohols, each serving a specific function. Silica NPs are chemically inert and provide the structure that enhances the fluid-repellency of the fabric. The silica sol can contain either commercially available NPs or chemical precursors to silica NPs such as tetraethoxysilane (TEOS). The organosilane component of the sol serves as the water/oil repellent coating on the nanoparticles and the binder that attaches the particles to the fabric. The organosilanes consist of three short chain alkoxy groups and a non-hydrolyzable functional group bound to a central silicon atom (Fig. 4.1).



**Fig. 4.1.** Organosilanes used in silica sols with short chain alkoxy groups indicated in red. a) hexadecyltrimethoxysilane (HDTMS), b) 3-aminopropyltriethoxysilane (APTES), c) 3-glycidoxypropyltrimethoxysilane (GPTMS), and d) phenyltriethoxysilane (PhTES) (1, 2, 3).



Fig. 4.2. SEM images showing a polyester fiber a) before and b) after coating with a silica nanosol (1).
Water or low molecular weight alcohols cleave the alkoxy chains from the silicon atom through hydrolysis. The consequently available bond sites allow the silane to bind to the NPs or the fabric. The remaining functional group on the surface-bound silane decreases the surface energy of the resulting structure. This change in surface energy gives the surface its fluid-phobic properties—hydrophobicity and/or oleophobicity. The NPs only enhance the liquid repellency, so the proper selection of the functional group on the organosilane is critical to the performance of the nanosols.

The silica sol can be applied to fabrics through spraying (1) or padding (dip and nip) (2, 4). We will focus on the padding method because it is commonly used in the textile industry (including in Gore's DWR application), provides a more even application of the coating to the fabric, and reduces the potential to volatilize the components of the sol. In padding, fabric on rollers is first immersed in the "dip" solution—here the nanosol—then the excess solution is squeezed out in the "nip" (Fig. 4.3). An optional curing step such as a drying oven completes the coating process.



**Fig. 4.3.** Schematic illustrating the application of coatings such as silica nanosols to fabrics through padding. The fabric is passed through the coating solution then squeezing rolls remove excess liquid. Finally, an optional curing oven dries the coating and binds it to the fabric (adapted from 5).

### Performance

#### Hydrophobicity

Several studies have reported high hydrophobicity using silica NPs. One such study looking at the incorporation of silica nanosols onto polyester reported highly hydrophobic water contact

angles (WCAs) for static, advancing, and receding angles (Fig. 4.4). These silica NPs were modified with surface alkyl groups from the presence of APTES and HDTMS (1). From the reaction of hydrolyzed APTES and Si-OH groups, the silica NPs aggregated to form clusters, creating a hierarchical surface structure (Fig. 4.2b) (1). Additionally, amine and Si-OH groups on these cluster surfaces bonded to the fabric fibers to enhance adhesion and increase the structural roughness of the fabric (1).



**Fig. 4.4.** Hydrophobicity of silica nanosol coated polyester. a) SEM image showing high static contact angle of a water droplet indicating high hydrophobicity. b) The silica nanosol coating imparts high static and dynamic contact angles (adapted from 1). The yellow lines represent Gore's goals for advancing and receding angles.

The resulting WCAs from the combined method of silica NPs with the APTES and HDTMS hydrolyzing coating exceeding Gore's goals of having advancing and receding contact angles greater than 115 and 95°, respectively (Fig. 4.4) (1). The static WCA is not quite superhydrophobic (greater than or equal to 150°) but is considered highly hydrophobic.

#### Oleophobicity

Unfortunately, current nanosol fabric coatings are not very oleophobic. One study (16) looked at a number of different organosilane additives to the nanosols but found minimal improvement in the oleophobicity of the fabric (Fig. 4.5) (16). It was only with the addition of fluorinated compounds that the oleophobicity improved significantly.



**Fig. 4.5.** The water and organic contact angles for various organosilane additives to nanosols. Data is shown for the silica sol alone and with 1, 8, and 16 carbon chain additives. The contact angles for a nanosol-free fluorinated coating are presented for comparison. Here, a glass slide is coated with the nanosol layer, but texturing is not expected to significantly increase the oleophobicity of the coating (16).

Recently, another study has shown that polymerization of a dimethyldimethoxysilane (DMDMS) on a surface can result in an omniphobic surface (17). This layer acts like a fluid, and so the interactions determining contact angles are more similar to liquid/liquid interactions than liquid/solid interactions (Fig. 4.6). While the static contact angle of oils on this surface is not very high, there is very little variation between the advancing and receding contact angles, which means that the dynamic wicking of the material is very good (Fig. 4.7). This coating uses the same hydrolysis chemistry as the organosilanes, so it can be incorporated into our nanosols. DMDMS nanosols have not , however, been tested on fabrics.



Fig. 4.6. Synthesis of DMDMS omniphobic coating (17).



**Fig. 4.7.** The DMDMS coating has very low contact angle hysteresis for a variety of solvents, which makes it a promising omniphobic coating (17).

Durability, Abrasion Resistance, Washability

To test washability, polyester fabric coated with silica nanosol was hand washed in a 1% detergent solution, rinsed with water, and air-dried at ambient temperature (1). This wash-dry cycle was repeated five times and the WCAs were measured again. After washing, the contact angles only decreased by a couple degrees, resulting in static and dynamic contact angles that are still well above Gore's goals (Fig. 4.8). However, Gore has a more rigorous wash-dry standard (20 wash/dry cycles), so further tests and studies would be needed to fully explore the washability of this method.



**Fig. 4.8.** WCAs for polyester coated with silica nanosol. Light blue shows the initial WCA values; dark blue bars show the WCAs after five hand wash/dry cycles with detergent. Yellow lines represent Gore's goals for advancing and receding angle (1).

The coated fabric was tested for abrasion resistance by being soaked first in a 1% detergent solution for 10 minutes then brushed with an Elcometer Abrasion Tester at a rate of 30 cycles/min for 600 cycles (1). After the brushing process, the fabric was rinsed with water and air-dried at ambient temperature. Only static contact angles were measured following a certain number of brushes; after starting at 145°, the static angle decreased to about 135° after 600 brushing cycles (Fig. 4.9) (1). Despite these decreases in WCAs, the final values are still greater than Gore's goals.



**Fig. 4.9.** WCAs measured for polyester coated with silica nanosol during abrasion testing. The WCA decreases by only a few degrees after a defined number of brushing cycles (1).

Feel and Appearance

Most silica nanosol films are essentially colorless and do not have strong odors. In fact, metal nanoparticles and other chemicals can also be added into the nanosol coating to provide specific colors. Increasing the weight percent (wt.%) solid in the nanosol coating can make synthetic fabrics stiff but has minimal effect on the breathability of the material (Fig. 4.10) (6). In literature, the percent solid in the nanosol coatings is not always listed and is likely to vary depending on the exact preparation method used. While some methods use up to 30 wt.% solid in their coatings, it may not be necessary to use such a dense coating for the desired properties.



**Fig. 4.10.** Aesthetics of silica nanosol coatings. a) Stiffness and b) breathability of fabric as a function of solid content of nanosol coating. a) The stiffness of rayon (viscose) fabric increases with the solid content of the sol. b) Considering the error bars, the breathability of polyester does not change significantly as the solid content of the coating increases (6).

#### **Modifications**

One (3) experimented with adding another study silane component, 3-glycidoxypropyltrimethoxysilane (GPTMS), to improve the washability of the silica sol-gel coating. The improved washing durability for polyester was attributed to the additional epoxide group that GPTMS provided. Fabrics without GPTMS lost hydrophobicity after 50 laundering cycles; polyester with GPTMS, however, retained superhydrophobicity after 50 washing cycles (3). Additionally, using GPTMS increased the silica particle size from about 250 nm to about 550 nm and caused the particles to be more regularly shaped, possibly decreasing the bioavailability of the nanoparticles (3). This experiment proves that, even with drawbacks to silica NPs, there could be chemical (silane) additives to improve performance in hydrophobicity and, potentially, oleophobicity. Modifications such as this one can be further researched in order to specifically improve oleophobicity of this alternative.

# Hazards

### Nanoparticle Revolution: Applications and Uncertainty

Nanoscale materials (1-100 nm) are the driving force behind the nanotechnology revolution of a new generation of materials, valued at over a trillion dollars in the U.S. market (23). A nanoscale substance is 100,000 times smaller than a single sheet of paper and the size of only a few blood cells (Fig. 4.11). In the past decade, innovations have been made using nanotechnology in medicine, computers, water remediation, and almost all industrial sectors, resulting in a wide range of nanoparticles entering the environment. Silicate, titanate, and zirconate nanoparticles (13-15 nm) have unique properties such as wettability and hardness. Titanates (TiO<sub>2</sub>) are used in sunscreens and toothpaste (40-100 nm) (24). Gold NPs have been used in cancer treatment (7); however, certain sizes have been shown to adversely affect the permeability of veins and arteries (25). Zero valent iron NPs have been used as a reducing agent for groundwater remediation (8).



Fig. 4.11. Comparative size scale of nanomaterials to familiar objects (adapted from 20).

The surface to volume ratio of an object is inversely proportional to the size of the object. Therefore, nanoparticles have a very high surface to volume ratio, which increases reactivity and certain toxicological effects (21). Many agencies such as the U.S. National Institute for Occupational Safety and Health, (NIOSH), U.S. Occupational Health and Safety Administration (OSHA), International Organization for Standardization (ISO), United Nations (UN), European Chemicals Agency (ECHA), and U.S. Environmental Protection Agency (USEPA) are involved in classification, regulation, and safety of nanomaterials through regulations and acts such as ECHA Registration; Evaluation, Authorization, and Restriction of Chemicals (REACH); UN Global Harmonized System (GHS); USEPA Toxic substances Control Act (TSCA); and USEPA Resource Conservation and Recovery Act (RCRA)s (24). To protect ecological resources, efforts are being made to adopt a new legacy of cautious implementation (similar to European chemical regulation) when there is a lack of understanding of long term environmental and health consequences. Both the size and reactivity of NPs are potentially causes for concern. Nanoscale particles have the ability to pass through many of the body's and access vulnerable systems.

### Human Health Effects: Silica Particles

Potential exposure windows of silica include the mining and transportation of the bulk silica constituents, preparation of the nanosol, and application of the nanosol onto the textile. Once applied and cured on the textile, respirable exposures should be minimal unless end-of-life disposal involves bulk mechanical shredding of the textile. The population of concern for high-level exposure to silica consists of occupational workers in the manufacturing process of the textile. Ideally, the manufacturing process will comply with U.S. occupational safety standards and employ adequate controls and exposure assessment. The highest potential for exposure occurs during mixing of constituents before polymer synthesis. Because the silica constituents may arrive in bulk and must be poured from the packaging, free silica may be generated and present high concentrations of respirable particles. Adequate respiratory protection, ventilation, or "dust control" methods should be used during this step to reduce or eliminate potential exposures. Special consideration was taken for specifying the use of amorphous rather than crystalline silica due to the nature of worldwide manufacturing; some countries may not have regulations mandating a hierarchy of exposure controls. While our proposed solution may use both polymorphs of silica, the amorphous form was selected for its low toxicity relative to the crystalline form to account for working environments with lower safety standards. Increased controls for quality must be pursued, particularly as contamination with crystalline silica may occur (26). To reduce the risk of respirable silica particles, we recommend that Gore synthesize the silica nanoparticles from an organosilane in solution, directly on the fabric.

Penetration of NPs through different cell barriers has large dependence on size. At 100 nm, particles permeate cell membranes; particles less than 35 nm in diameter can penetrate the barrier of the brain. The shape of NPs may also affect toxicity; spherical particles may be more toxic than rods (24), but both are highly diffusible into cells. The most toxic form of silica is the free

crystalline form (quartz, cristobalite, tridymite), which causes short, accelerated, and long-term progressive lung injury (silicosis) and carcinogenesis in miners and industrial workers as well as being linked to increased risk of rheumatoid arthritis, kidney disease, and tuberculosis (27). Crystalline silica induces silicosis and pulmonary disease (26, 27), but effects of amorphous silica were not persistent nor fibrogenic. However animal studies show partially reversible inflammation, granuloma formation, and emphysema but no fibrosis. Care must be taken when sourcing amorphous silicas as some epidemiological studies have shown amorphous silica may often be contaminated with the more harmful crystalline form (11, 27). This lower level of toxicity from amorphous silica NPs is regarded as an effect of more rapid clearance due to lack of surface silanols present in crystalline forms which damage particle clearing macrophages (11).



**Fig. 4.12.** Routes of toxicity of nanoparticles with segmented bar showing risk of translocation, repair, and toxicity (top to bottom) in literature (28).

Modeling the fate and transport of NPs to organs suggests that nanoparticle translocation to liver, bone, digestive, respiratory systems may occur (Fig 4.12); primarily, the NPs enter the lungs and

respiratory tract and are then transported into blood and organs (27). Silica has been shown to exhibit immunosuppressant, hypocholesterolemic, anti-allergenic, anti-apoptotic and anti-histamine functions (11).

Due to many differences between manufacturing practices, size, exposure duration, surface properties, and dose, the human health effects of nanosilica are still uncertain.

### Environmental Toxicity: Silica Nanoparticles

Silica is most commonly found in nature as sand or quartz, a ubiquitous material with diverse uses (consumer products, biomedical, drug delivery, surfacing). Silica NPs may arise in urban areas from road dust and transported into the air and contribute to particulates on surfaces (roads, sidewalks) (14). Different NPs from various sources are flushed into stormwater in sewers or streams and may pose a risk to aquatic organisms (14). However, environmental exposure models for inorganic nanoparticles suggests that interactions between organic matter and NP mixtures are not well understood (33). Observed toxicity in fish, daphnia, and algae may result from particles that block gills (15). The presence of different types of NPs has an adverse effect on the microbial diversity and activity in wastewater treatment, and treatment membranes may ultimately be a sink for certain sizes of silica NPs (10-100 nm) (22). Depending on particle type, environmental translocation of NPs can have multiple outcomes (24), and it is difficult to make comparisons regarding NP life cycle in the environment. A hazard summary of silica nanoparticles is presented in Table 4.1.

# **Hazards of Silanes**

There is some disagreement regarding the safety of silanes, which are often confused with cyclosiloxanes. Due to potential for persistence, some cyclosiloxanes (e.g. decamethylcyclopentasiloxane (D5)) have been restricted by REACH. Discrepancies can be found among reports; D5 is not listed on California Prop 65 list for reproductive or developmental toxicity, but it is listed as a chemical of high concern in Maine, Minnesota, and Oregon (32). Estrogenic activity at certain estrogen receptor types, and other adverse reproductive effects have been shown for D5 (30), but inconsistencies are found (31).

Our strategy uses 3-aminopropyltriethoxysilane (APTES) and hexadecyltrimethoxysilane (HDTMS) as silanols that can be produced as functional coatings on silica nanomaterials. Both are considered respiratory toxicants. APTES and HDTMS can hydrolyze in water, biodegrade, and are not persistent (15). In the manufacturing of respiratory toxicants, safe conditions for industrial workers is a primary concern (29). Caution should be used in manufacturing but may not extend to manufacturing environments without engineering controls that reside outside of U.S. jurisdiction (29). APTES requires closed systems with engineering controls (proper ventilation, containment, safety equipment). A hazard summary for APTES and HDTMS is

presented in Table 4.1. Since APTES is sensitive to hydrolysis, which may occur during testing, we should note that some hydrolysis products, such as ethanol and trisilanol, may produce adverse health effects.

	Human Toxicity				Environmental Toxicity			
	Mutagenicity	Organ	Respiratory	Reproductive	Persistence	Aquatic	Fate	
<b>Silica nanoparticles</b> Amorphous Silica	Negative cytotoxic, structure- dependent effects (2,3,4,5,13,14)		Structure- dependent (6,7) DG (3)	MAK Group C (no risk) (13,14) DG (12)	Not persistent (13,14)	Low risk (13,14) DG (10,12) Microbial effects (19)	Not persistent or bioaccumulative (13,14)	
<b>(3-aminopropyl)</b> triethoxysilane (APTES)	Low risk not mutagenic or carcinogenic (15,16) potential metabolites (DG)	Skin, eye irritant (13, 17) DG (potential metabolites)	Low potential (13, 17)	Low potential (13,17)	Not bioaccumulative (13,15,17,18)	Aquatic risk (18,15,13,)	Persistent in sediment, not bioaccumulative (13,15,17)	
<b>Hexadecyltrimethoxysilane</b> (HDTMS)	Pre-registration (20,21)	Skin, eye irritant (13)	Respiratory irritant (13)	DG (20,21)	Not bioaccumulative (13)	Aquatic risk (13,18)	Persistent in sediment, not bioaccumulative (13)	

 Table 4.1. Summary of human and environmental hazards of silica nanosols.

For silica nanoparticle methods, particle size and structure may increase human toxicity. Monitoring of silica nanoparticles in occupational exposures would be recommended, as well as considerations of long term effects on human health and the environment. Chronic exposures to nanoparticles may have more unknown health and environmental effects. The functional coatings of silanes (APTES/HDTMS), may need further testing for effects of silanols, a potential degradation product. We did not assess implications of large chemical spills, which may require additional assessments. In both cases considerations for skin irritation, and respiratory harm would be important for manufacturing. Environmental persistence of silica nanosols was assessed to be less significant than the current fluorinated-DWR technology, but data gaps in scientific studies preclude a true comparison of health effects.

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# 4.2. Spinning of nanofiber mats

# Background

The *Jacobaea maritima* (silver ragwort) leaf has an almost superhydrophobic WCA of 147° (Fig. 4.13a). It achieves this impressive water repellency because of its hierarchical micro- and nanostructuring. The leaf is composed of a tangled net of fibers that are 6  $\mu$ m in diameter (Fig. 4.13b); this provides the microstructure. Additionally, each fiber is not smooth but is roughened on the nanoscale (Fig. 4.13c) (1). As discussed in Section 2.5, a hierarchical structure greatly improves existing hydro- and oleophobicity.



**Fig. 4.13.** Silver ragwort leaf. a) Digital photograph of a leaf with a beaded water droplet. b) and c) SEM images showing the tangle of fibers and the structuring on the fibers.

One way to replicate the hierarchical structuring of the silver ragwort leaf synthetically is by creating a nanofiber mat through a spinning process. Electrospinning can emulate the woven fiber microstructure and even the nanostructured fiber surface (Fig. 4.14) (1, 2). Electrospinning uses a high voltage to force a charged solution out of a small nozzle. As the solution exits the tip,

the solvent evaporates and a polymer fiber remains, producing fibers with diameters down to tens of nanometers. Varying the voltage, solvent, charge, and collection method can result in a variety of fiber diameters, textures, and fiber assemblies (Fig. 4.14) (2, 3). Additionally, these fibers can be made from polymers commonly used in garments such as polyamide, PET, and poly(vinyl acetate) (PVA) (3, 4).



**Fig. 4.14.** SEM examples of fiber mats and fiber morphologies from electrospinning. a) and b) show different fiber diameters and densities from different electrospinning conditions. c) Fibers with beads and d) textured fibers are also possible (1, 2).

Instead of using an electric field, solution blow spinning uses an annulus of high pressure gas surrounding the nozzle to create thin polymer fibers (Fig. 4.15). This method is faster and often easier to scale up for industrial applications. Additionally, since the solvent behavior in an electric field is irrelevant, a wider range of solvents (including safer solvents) can be used in blow spinning than in electrospinning. Blow spinning, however, can only produce fibers that are about 100 nm in diameter and have less variability in diameter (5). With less flexibility in fiber size, the optimal structure for liquid repellency may not be achievable with blow spinning. More literature was available on the hydrophobicity and oleophobicity of electrospun mats, and so they will be the focus of this discussion, but these properties can be replicated using blow spinning.



**Fig. 4.15.** Diagram of solution blow spinning method. High pressure gas shapes a polymer solution into micro and nanofibers that are then collected (5).

### Performance

### Hydrophobicity

Highly hydrophobic and superhydrophobic fiber mats can be made using electrospinning. Figure 4.16 shows that while individual fibers have low contact angles, the overall wetting behavior indicates a large effective static contact angle with the fiber mat due to the hierarchical structure.



**Fig. 4.16.** SEMs of an oil droplet on an electrospun nanofiber mat. a), b) At low magnifications, the droplet appears to have a high effective contact angle with the fiber mat, but c), d), e) the higher magnifications show the wetting of the individual fibers (4).

The water repellency of the mat can be tuned by the choice of solvent(s) and the ratios of solvents and polymers. For, example the static WCA and the water roll-off angle vary dramatically with the ratio of two solvents, tetrahydrofuran (THF) and dimethylformamide (DMF) (Fig. 4.17). In this case, the weight ratio of 1:3 THF:DMF gave the maximum static WCA and minimum water roll-off angle, which is indicative of good dynamic water repellency (Fig 4.17).



**Fig. 4.17.** Hydrophobicity of electrospun mats. a) WCA and b) water roll-off angle for polystyrene fiber mats. By varying the ratio of the two solvents used, tetrahydrofuran (THF) and dimethylformamide (DMF), mats were made with different degrees of hydrophobicity(2).

These optimal polystyrene fibers had a number of small grooves on the surface, mimicking the silver-ragwort leaf structure (Fig. 4.18). Other studies have shown that fiber mats containing a high density of small polymer beads can also increase hydrophobicity through increased structuring (1). Sub-micron poly(styrene-*b*-dimethylsiloxane) fiber mats are superhydrophobic with a static WCA of 163° and contact angle hysteresis of 15° (6), indicating good static and dynamic water repellency.



**Figure 4.18.** Image of polystyrene fibers made with a 1:3 ratio of THF:DMF. The fiber surface is covered with small dense grooves. This texture improves the hydrophobicity of the material (1).

### Oleophobicity

Few studies have investigated the oleophobicity of non-fluorinated nanoscale fiber mats. Still, Figure 4.19 shows a marked increase in the oil contact angle of a fiber mat compared to a flat surface of the same fluorinated chemical. The synthetic fibers such as nylon and polyester are oleophilic; texturing them will not make them oleophobic, so a coating should be used. A featureless DMDMS coating has a diiodomethane contact angle of  $71^{\circ}$  (13). Therefore, we expect a textured nanofiber mat coated with DMDS to have a greater, oleophobic contact angle.



**Fig. 4.19.** Increase in silicone oil contact angle from a flat coating to a nanofiber mat. The contact angle of the oil on a flat polyamide-6 (nylon) (PA6) surface with a fluoropolymer coating is 72.8° but increases to 111° on a fluoropolymer-coated PA6 fiber mat (5).

### Durability, Washability, and Aesthetics

An advantage of nonwoven nanofiber mats is that since they are similar synthetic fibers to what is commonly used in activewear, they should have the same washability, feel, and appearance as other synthetic fibers currently used in making outerwear. Additionally, the fiber mat will not decrease the breathability of the garment as shown in Fig. 4.20. However, there are some unknowns about the durability. It is possible that the three dimensional web could collapse or be

damaged under abrasive forces. We recommend that Gore use the same adhesive for attaching the nanofiber mat as the company currently uses for attaching the PTFE membrane. That adhesive is robust for attachment of PTFE, but to our knowledge it has not been tested for attachment of a fiber mat.



**Fig. 4.20.** Breathability of electrospun polypropylene fiber mats as a function of mat thickness. Typical fabric fall in the range of 50-125 cm3/s/cm<sup>2</sup> (15).

#### Hazard

#### Nano and microfibers

Spun fibers are generally smaller than 100  $\mu$ m in diameter, making them microplastics. Microplastics and microfibers are an emerging global contaminant; they are degradation products from plastics and textiles in the size range of 0.1  $\mu$ m to 5 mm. Each home laundry cycle may produce more than 4,500 microfibers; these fibers escape wastewater treatment plants and contaminate the ecosystem (7). Polyethylene, polypropylene, polystyrene, and nylon are considered significant sources of environmental microfibers. The size of microfibers is similar to that of food for aquatic invertebrates and shellfish, so the fibers are easily ingested. Micro plastics and fibers can also absorb high concentrations of lipophilic chemicals (10). Ingestion of plastics by aquatic life threatens biodiversity, and may accumulate in the food chain (8,9).

During production of monomers of the polyester family of polymers, carcinogenic compounds are involved (e.g. styrene and benzene) and may pose occupational hazards. The actual nylon/polystyrene fibers used in this strategy, however, produce low occupational harm because

polymers are fairly inert. Polyester fibers cannot be biodegraded, but must be recycled. To reduce the environmentally persistent of fabrics later in their life cycle, many companies are pursuing biodegradable, recyclable fibers. These include the family of polyhydroxyalkanoate (PHA) polymers, i.e., poly-3-hydroxyvalerate (PHV), poly-3-hydroxybutyrate (P3HB), and poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV). PHAs can degrade to carbon dioxide ( $CO_2$ ), methane, and water. Chemical precursors of PHA may be corn, sugar, or waste. Biodegradation occurs through bacterial enzymes, achieving American Society for Testing and Materials (ASTM) biodegradation standards of complete removal of carbon in the plastic to  $CO_2$  within 180 days (12). In a life cycle assessment model, poly-3-hydroxybutyrate (bioplastic polymer) shows significant reduction in carbon dioxide emissions, greenhouse gases, and fossil fuels as compared to polyethylene production (11).

#### Spinning solvents

Fiber spinning involves the choice of common solvents: THF, DMF, acetone, and dimethyl sulfoxide (DMSO). Although these are frequently used, reports have shown human toxicity arising from exposures to all of these solvents (Fig. 4.21 and Table 4.2). However, volatile organic solvents are often more easily purified and isolated, reducing their threat to the environment. When seeking a greener solution for DWR, we recommend choosing a less hazardous solvent such as acetone, cyclopentylmethylether (CPME), ethanol, or water.



### EHS assessment of organic solvents

**Fig. 4.21.** EHS assessment of various organic solvents. While the barard level of different solvents varies, most are flammable, have negative health effects, and environmental hazar

#### Greener Solvent Solutions

Spinning solvents must be chosen with care; many volatile organic solvents are flammable, acute and chronic toxicants for humans, and environmental hazards. Figure 4.21 summarizes the hazards of various organic solvents. Selecting a safer solvent will be key to minimizing the hazard associated with these fiber mats. Greener alternatives (Fig. 4.22) produce fewer peroxides than THF and have less solvent loss during reactions. CPME can be produced in a nontoxic method, is more stable than THF, resists peroxide formation, and improves laboratory safety. Ethyl lactate is a commercially available (Sigma) safer alternative to acetone, causing no carcinogenicity, and is easily recyclable (14).



Figure 4.22. Safer solvents that could be used in the spinning process.

	Human Toxicity				Environmental Toxicity		
	Mutagenicity	Organ	Respiratory	Reproductive	Persistence	Aquatic	Fate
<b>Tetrahydrofuran</b> (THF)	Carcinogen, liver, kidney, (1,2,3,5,6,12)	CNS, liver, Skin, eye irritant (1,2,3,4,5,9, 10,12)	Respiratory (3,5,10)	Not significant (3,5,10)	Volatile, short half-life (days) in soil (3,5,10,13)	Low risk (3,5,12,13)	Volatile, mobile, not persistent (13)
<b>Dimethylformamide</b> (DMF)	Prop 65 carcinogen (1,14, 17,20,26)	Eye, skin Chronic exposure-Liver, digestive (1,14,17, 20)	Respiratory (15,16,17)	Embryotoxic, fertility and development (1, 14,15,17, 20)	Short half-life (days) (13)	Low risk (13)	Not persistent, potential air pollutant and hazard (1), volatile, mobile (13)
<b>Dimethyl sulfoxide</b> (DMSO)	Cell toxicity (21,22,23)	CNS(23,24)	Respiratory (27)	Potential transfer (18) to unborn child	Short half-life (hours)	Low potential risk (12,13,25)	Not persistent (13)
Acetone	Cell proliferation (28), negative mutagen	CNS Skin, eye irritant (1,29)	Respiratory (1,29)	DG (1)	Biodegradable (28)	Low risk 48 hLC50 Daphnia 8000 mg/L (28)	Low bioaccumulation potential (28)
Cyclopentyl methyl ether (CPME)	Negative mutation test, micronucleus test(31,32)	Eye (H319), H302 (harmful if swallowed) (31,32)	Inhalation toxicity at 4.0 mg/L (Repeated exposures) (32)	Not significant (32)	Biodegradable (32)	Low risk: NOEL fish 220 mg/L (32)	Not bioaccumulative or persistent (32)
	ſ	Hazard scale	DG: data gap	Low Mediu	ım High		

Table 4.2. Relative comparison of the human and environmental hazards of the solvents used in spinning.

Solvent exposure control and considerations

In consideration of the life cycle of this strategy, potential exposure windows occur during synthesis of the solvent and their constituents, preparation of the solution, formation of the fiber mat, application to the textile, and curing. Once applied and cured on the textile, respirable exposures should be non-existent to consumers as the volatile solvents evaporate during the curing process. The population of concern for exposure to high levels of volatile solvents consists of occupational workers in the manufacturing of the textile. Ideally, the manufacturing process will comply with U.S. occupational safety standards and employ adequate controls and exposure assessment. Solvent constituents arrive in bulk and must be poured from the containers in which they were shipped into a hopper for the mixture. As a result, the solvents may generate harmful vapors at high concentrations as well as pose a risk of dermal exposure. Adequate respiratory protection, dermal protection, eye protection, ventilation, or engineering controls should be used during these steps to reduce or eliminate potential exposures.

Spinning fiber mats to produce DWR materials affords the possibility of producing greener textiles and using greener solvents. Nylon (which is recyclable) could be replaced by the newly developed bioplastics composed of biodegradable PHA (see Section 3.9). These new polymers would need to be investigated as a method to completely eliminate toxic chemicals in this process, as well as for their performance. The traditional use of solvents such as THF/DMF,

acetone, and butanol may not be as environmentally problematic as fluorinated - DWR textile production. However, these solvents could be replaced by ethyl lactate or CPME.

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# 5. Conclusions

### 5.1. Hazard comparison

Assessing the hazards of an entire DWR design and process is a complicated task, with many moving parts and sources of uncertainty. Despite this fact, our goal was to compare our most promising solutions with a traditional fluorinated DWR in Table 5.1 in order to determine which alternative was safer. Taking into account the wide range of sometimes contradictory literature and data gaps, we made a combined hazard table based on color as a simplified guide to choose the safer alternative. This table (Table 5.1) is based on relative hazard; low hazard (green) does not necessarily mean "safe". We also wanted to propose solvents that would be as effective as those we saw in literature, but safer. We recommend a precautionary approach in hazard evaluation. All compounds can be poisonous (1,2); therefore potency, exposure, dose, and population sensitivity must be considered for each endpoint, even when a chemical is 'greener'.

Table 5.1 first lists the "bad actors" of this report, the PFASs. PFOA, the more studied compound, is shown frequently with high hazard (red) and serves as the baseline for comparing the other chemicals used in our potential solutions. PFHxA has less hazard but includes more data gaps than PFOA. Both rank poorly in environmental toxicity because of their persistence and ability to bioaccumulate, as previously discussed.

The second section (amorphous silica, APTES, and HDTMS) corresponds to our silica nanosol alternative. This solution has an even mix of low and medium hazard compounds; silica poses some of the highest hazards in this section due to the facts that we propose to use nanoparticles and that silica is inorganic and thus will persist in the environment.

The last section includes solvents used in the available electrospinning literature (THF and DMF) and proposed solvents that we think would be safer and still effective for the process. As we described in Section 4.2, we believe that blow spinning could offer more flexibility in choosing solvents and, therefore, safer solvents (acetone or cyclopentylmethylether) could be chosen over THF and DMF. Indeed, water is also a potential solvent that could be used in the blow spinning process, and its performance should be investigated by Gore. The polymers used to make the fibers were not included in the table since they are not the major source of hazard and many of them are already in use at Gore.

**Table 5.1.** Hazard table comparing currently-used DWR materials to our alternatives. The bold lines separate the different alternatives; the dashed line separates the more hazardous spinning solvents from the less hazardous.

		Human	Toxicity		Environmental Toxicity		
	Mutagenicity	Organ	Respiratory	Reproductive	Persistence	Aquatic	Fate
<b>PFOA</b> 8-carbon perfluorinated alkyl chain							
<b>PFHxA</b> 6-carbon perfluorinated alkyl chain							
<b>Silica nanoparticles</b> Amorphous silica							
(3-aminopropyl) triethoxysilane (APTES)							
<b>Hexadecyltrimethoxysilane</b> (HDTMS)							
<b>Tetrahydrofuran</b> (THF)							
Dimethylformamide (DMF)							
Dimethyl sulfoxide (DMSO)							
Acetone							
Cyclopentyl methyl ether (CPME)							
		Hazard scale	Low N	ledium High			

# 5.2. Performance comparison

To compare the performance of PFAS-based DWR with silica nanosols and spinning processes, we made a spider diagram with endpoints of human and environmental hazard and performance metrics (Fig. 5.1). PFAS performance served as the comparison, its hydrophobicity, oleophobicity, durability, and aesthetics (feel, color, breathability) being the score to beat. As shown in Fig. 5.1, if the line touches the outer ring, it signifies a high rating; the larger the area contained in the curve, the better it performs.

Both nanosols and spinning achieve hydrophobicity comparable to PFASs, but both fall short in oleophobicity and durability metrics. Additionally, spinning results in excellent breathability, feel, and color, but nanosols have shortcomings in aesthetics. When the performance metrics are combined with hazard assessment, spinning out-performs nanosols and PFASs in all aspects, except for durability and oleophobicity. Spinning achieves the highest marks for toxicity and fate. Based on these results and the hazard assessment, we have identified spinning as the most

promising solution for Gore to continue researching, with the recommendation of looking toward oleophobic modifications such as a dimethyldimethoxysilane coating.



**Fig. 5.1.** Relative hazard and performance comparison between PFAS and the two alternatives presented in this report. A strategy is better performing if its endpoints lie closer to the outer ring of the chart. More hazardous and poorer performing alternatives will score closer to the center.

### 5.3. Feasibility

In comparing feasibility, we considered whether our suggested solutions had been tested with success on fabrics, if they used similar processes to the ones Gore currently uses in fabric production, and how many materials the process require. Based on these criteria, we ranked silica nanosols and spinning on a scale of one to five, five being the most feasible (already used in industry with success).

Silica nanosols have been tested on fabrics and have been shown to produce highly hydrophobic surfaces on polyester. However, the studies we examined did not have rigourous wash-dry cycles and our method to improve oleophobicity using dimethyldimethoxysilane has not been tested on fabrics. Silica nanosols can be applied using the dip and nip application method, currently used by Gore, and only requires three to four compounds for the solution. All of the materials needed (amorphous silica and various silanes) are commercially available through vendors such as Sigma Aldrich. Since further testing is required for the washability, durability, and oleophobicity of nanosol coated fabrics, *we rank the feasibility of silica nanosols: 3.* 

The spinning process creates microfiber mats out of polymers to create textured, tangled fibers, which has direct applicability to fabrics. These mats have been shown to be superhydrophobic, breathable, and washable, but the washability has not been thoroughly investigated. Additionally, oleophobicity of these mats has not been tested. This process could potentially only use a gas, one or two solvents, the desired polymer (e.g. polystyrene), and a binding agent. However, binding this textured mat on top of the base Gore fabric has not been tested, and further testing of the oleophobicity is needed. Thus, *we rank the feasibility of spinning: 4.* 

### 5.4. Next steps

Blow spinning nonwoven nanofiber mats should be optimized with safer solvents (water, ethanol, acetone, etc.) and biodegradable polymers if the fate of microplastics is in the scope of Gore's long-term lifecycle goals. The solvent(s) used and experimental conditions (type of gas solvent, polymer, solution concentration, amount of pressure) should be modified to produce high performing materials. Particular attention should be paid to the oleophobicity of the material; experiments with dimethyldimethoxysilane coatings should be conducted to determine if it imparts the desired oleophobicity on the final fabric product. Finally, the best way to graft this fiber mat onto the outer layer of Gore outerwear, should be determined. We recommend that Gore first experiments with using the same adhesion technique to attach the nanofiber mat as the company currently uses for attaching the PTFE membrane.

If Gore wants to pursue a nanosol coating as the DWR layer on their fabrics, they should first test a silica nanosol solution (silanes, organosilanes,  $SiO_2$ , DMDMS, and water) on their fabrics to determine the baseline performance. If the nanosol performs well, Gore should experiment with varying the concentrations of the solution to determine which concentrations do not affect breathability, flexibility, or dying processes. (We suggest starting with 5% weight of the silica nanosol solution on the fabrics.) Once the hydrophobicity and oleophobicity are attained, Gore can test the fabric using their standard durability and washability tests. A combination of a nanosol coating on an nanofiber mat can also be explored.

### 5.5. Recommendations to Gore

Considering the proven performance, known hazards, data gaps, and feasibility of the two non-fluorinated DWR alternatives presented here, a *spun nanofiber mat with a dimethyldimethoxysilane (DMDMS) coating is the most promising alternative*. An illustration of this solution is depicted in Figure 5.2. Spinning makes a hierarchical micro- and nanostructure, which the silver ragwort leaf and other animal and plant species use to repel liquids. The addition of a DMDMS coating is necessary to impart oil repellency to the structure, and the texture of the fiber mat will improve the baseline oleophobicity of a smooth DMDMS coating.



**Fig. 5.2.** Graphical depiction of the most promising strategy. A spun fiber mat coated with DMDMS is used as the DWR coating on the garment textile.

Due to the covalent bonding of DMDMS to the fiber mat, we expect this coating to be durable. However, spun fiber mats have not been subjected to the rigorous abrasion and washing tests necessary to be confident that the nanofibers will withstand normal wear and use. The nanofibers are composed of polymers already used in wearable textiles and the open structure imparts more breathability than a traditional weave, so we expect that the fiber mat will not affect the look or feel of the finished product. Additionally, we expect that the DMDMS will not impact the aesthetics because of their chemical similarity to the silicone nanofibers, which do not detract from the appearance of the fabric.

### 5.6. References

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# Appendices

## **Appendix A: Project members**

*Marianna Augustine* is a PhD candidate in the Molecular Toxicology Program at UC Berkeley. As a student researcher in the lab of Professor Chris Vulpe she employs genomics approaches in nontraditional animal models (zebrafish, Daphnia magna) to elucidate molecular mechanisms of toxicity. She investigates comparative toxicity from endocrine disrupting compounds and green biofuels. For this project, her role was to summarize environmental and health impacts of current and proposed technologies.

*Emily Cook* is a PhD student in Environmental Engineering at UC Berkeley, studying under Lisa Alvarez-Cohen in her environmental microbiology laboratory. Currently, Emily researches how to transform (chemically break down) per- and polyfluoroalkyl substances (PFASs) in contaminated groundwater using a combination of chemical oxidation and aerobic microbial degradation. On this project, Emily helped with understanding the structure and chemistry of PFASs, finding alternative solutions in literature, and she used her experience in environmental engineering to address the feasibility, practicality, and potential environmental impacts of this group's proposed alternatives.

*Erin Creel* is a PhD candidate in Physical Chemistry at UC Berkeley. Her doctoral research in Professor Bryan McCloskey's lab focuses on converting carbon dioxide to chemical fuels and feedstocks on nanostructured metal surfaces using inputs of only water, light, and electricity. Erin used her expertise in nanotechnology and chemistry to look for structural modifications that conferred some of the desirable properties of PFASs without chemical additives.

*Sumana Raj* is a PhD candidate in Physical Chemistry at UC Berkeley. As part of the Saykally Group, she uses ultrafast nonlinear spectroscopy to study the liquid state of carbon, which is prepared through ultrafast melting of a carbon source. In this project, she used her chemistry expertise to determine and assess viable chemical replacements for PFASs with similar desirable properties.

*John Wright* is a MPH candidate in Environmental Health Science with a concentration in Industrial Hygiene at UC Berkeley. His research focuses on assessing technological feasibility of personal exposure limits set by regulatory agencies. His expertise in industry practices and regulations was used to assess the impacts on worker health as well as the technological feasibility of the proposed replacements for PFASs.
### **Appendix B: Annotated bibliographies**

#### Section 2: Introduction

Buck, Robert C., et al. "Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins." Integrated environmental assessment and management 7.4 (2011): 513-541.

In this critical review, Buck et al. explore the properties, classifications, and ubiquitous nature of different types of PFASs as well as the chemical methods of forming PFASs. The authors provide a clear understanding and uniform, descriptive terminology to assist scientists and the general public to fully understand these chemicals; their presence in the environment, humans, and industry; and relevant implications. Although this paper does not necessarily provide new, distinct conclusions, it has been a valuable resources for this team to fully grasp the breadth and depth of the PFAS classification. It succinctly illustrates where different PFASs are found in nature and how hazardous each are. Additionally, it has been a useful beginning resource to understand which types of PFASs are able to be metabolized by animals or humans. The first author of this paper has been working with Dupont and Dupont's spin-off company, Chemours, for many years in the area of PFASs. His fellow authors are associated with various universities in Europe in areas of chemistry, environmental health and safety, environmental science, and toxicology.

### Darmanin, Thierry, and Frédéric Guittard. "Superhydrophobic and superoleophobic properties in nature." Materials Today 18.5 (2015): 273-285.

This review paper was in informative and inspirational look into many of the diverse creatures that have evolved superhydrophobic and superoleophobic properties. They describe the mechanisms of these properties for the lotus leaf, leaf hoppers, springtails, *Salvinia molesta*, rose petals, rice leaves, insect wings (such as mayflies, cicadas, and butterflies), moth's eyes, gecko's feet, and different fish and shark species. This paper served as a point of reference and inspiration for closer research into some of the bio-inspired solutions to our water- and oil-repellent issues. We focused specifically on the lotus leaf and the micro- and nano-hierarchical structuring found in many of the arthropods discussed in this review. From this paper, we concluded that our final solution must incorporate this nano- and microstructuring and, potentially, a chemical coating to improve the oleophobicity. The review's authors are both from University of Nice Sophia Antipolis in France; the latter being a professor who has focused his research on looking both at bio-inspired hydro- and oleophobicity and also fluorinated solutions to these desired properties.

Honda, Koji, et al. "Molecular aggregation structure and surface properties of poly(fluoroalkyl acrylate) thin films." Macromolecules 38.13 (2005): 5699-5705.

This paper describes in detail the surface properties of poly(fluoroalkyl acrylate), which is an example of the fluoroacrylate polymers currently used in Gore's DWR textiles. In addition to giving the team more understanding of the currently used technology and direction for what surface properties we need, this paper continued to confirm how unique—and desirable—fluorinated chemicals are. Knowing how effective fluoroacrylate polymers are at oil-and water-repellency gave the team the drive to find possible alternative solutions and the understanding that these fluorinated chemicals are unique; there won't be a simple replacement solution to this problem. The main conclusion of this paper was that hydrophobicity was directly attributable to the fluorinated side chains being orientated next to each other at the outermost surface, at the interface with water droplets. Longer, highly order fluorinated chains resulted in high hydrophobicity. These conclusions allow the team to look into solutions that could be comparable to these fluorinated chains at the surface-water interface of our textiles.

#### Section 3: Silica nanosol

Daoud, Walid a, John H Xin, and Xiaoming Tao. "Superhydrophobic Silica Nanocomposite Coating by a Low-Temperature Process." J. Am. Ceram. Soc. 87.9 (2004): 1782–1784.

A Chinese textile study used multiple mixtures of hexadecyltrimethoxysilane (HDTMS), tetraethyl orthosilicate (TEOS), and 3-glycidyloxypropyltrimethoxysilane (GPTMS) to create a transparent superhydrophobic silica-coating film on cotton textiles. The coating was achieved using ambient curing temperatures. Cotton was used due to its high hydrophilic properties to study the extent of superhydrophobicity which can be achieved through modification of surface texture and the application of GPTMS to achieve durable adhesion during wash cycles. The best results were found when coupled with a 10% by weight mixture of TEOS. The results of the study found that knit cotton water uptake decreased from 170% to 3% and only rose to 17% after 20 wash cycles. The study concluded that GPTMS achieves surface adhesion to establish washable durability of the silica-coating and thus feasibility in textile application. This procedure would have to be tested on synthetic fibers for Gore's purposes.

## Yu, Minghua et al. "Superhydrophobic Cotton Fabric Coating Based on a Complex Layer of Silica Nanoparticles and Perfluorooctylated Quaternary Ammonium Silane Coupling Agent." Applied Surface Science 253.7 (2007): 3669–3673.

This was a joint study compiled by two Chinese universities in which both surface texture and fluorinated coupling agents were used to increase hydrophobicity and oleophobicity. In the study, cotton fibres were treated with a silica nanogel to improve surface roughness in conjunction with perfluorinated silanes to decrease energy. A series of nanogels were tested with different particle sizes varied through  $NH_3$  concentration. Oleophobicity and hydrophobicity were found to increase as a function of nanoparticle size. The paper hypothesizes that the

increase in both were due to increase in surface roughness. Because this procedure simply involves surface roughness and texturing, we are confident that it could be extended to synthetic fibers.

### Zhao, Qin et al. "Ambient-Curable Superhydrophobic Fabric Coating Prepared by Water-Based Non-Fluorinated Formulation." Materials and Design 92 (2016): 541–545. Web.

The study conducted in this paper aimed to determine the possibility of superhydrophobicity on cotton, polyester, cotton polyester blends using silica nanoparticles with 3-aminopropyl triethoxysilane (APTES) and hexadecyltrimethoxysilane (HDTMS). The results of the study found that APTES stabilizes silica nanoparticle dispersion in water as well as enhancing adhesion of the nanoparticles on the fabric surface. HDTMS is found to contribute to the superhydrophobic performance by further enhancing surface roughness and surface energy. It was applied using a spraying process, which cures at room temperature. Durability was tested using a simulated wash and abrasion test and was found to remain consistently stable after both tests. Water contact angle was found to be greater than 150 degrees with only 10 degree hysteresis, confirming superhydrophobicity.

## Wang, Hongxia et al. "Superhydrophobic Fabrics from Hybrid Silica Sol-Gel Coatings: Structural Effect of Precursors on Wettability and Washing Durability." Journal of Materials Research 25.7 (2010): 1336–1343.

This paper enhanced our understanding of what kinds of sols are available and possible to use in a silica nanosol coating. Additionally, non-fluorinated sols were directly compared to fluorinated sol for polyester, wool, and cotton. We focused on the polyester results since Gore is only looking to use synthetic fabrics. Polyester treated with tetraethylorthosilicate /hexadecyltrimethoxysilane (TEOS/HDTMS) (which have been used in other papers cited in this report) was superhydrophobic, as well as polyester treated with methyltriethoxysilane (MTES)/ TEOS. Additionally, glycidoxypropyltrimethoxysilane (GPTS) was added to the solution to improve adhesion and to increase washability, which proved to be successful. Significant conclusions included that superhydrophobicity could be achieved without the fluorinated alkyl chains; the driving force was instead the rough surface structure. Additionally, the longer the alkyl chains in the sol, the higher the water contact angles. Finally, the hydroxyl and/or carboxyl groups on the ends of polyester fibers facilitated the adhesion of the coating to the fabric fibers. This paper guided our deeper understanding of the mechanisms of silica NPs and sols and framed our alternative.

Murugadoss, Sivakumar, et al. "Toxicology of silica nanoparticles: an update." Archives of Toxicology (2017): 1-44.

This is a very recent review that provides a large collection of scientific citations for human health effects from silica nanoparticles. The summary chronicles past silica NP work and needed work (knowledge gaps) in the realm of in vivo and in vitro toxicity. An unbiased, mechanistic approach was used, beginning with the structural varieties, dose, exposure, and modulations for safety. In addition to lab studies, the author contributes statistics on production rates, diverse applications used, and practical considerations regarding the inevitable ubiquity of silica NPs. He outlines exposure rates that are size dependent. A range of studies that include size, DNA damage, organ toxicity, cell toxicity, and blood toxicity is described. Differences in surface chemistry between types of nanoparticles (amorphous and crystalline silica, surface group chemistry, and production type) influences toxicity. This summary was a collection of literature from diverse test methods and included many relevant 'considerations' and explanations for inconsistencies between data sets.

Wang, Shutao, et al. "Fate and transformation of nanoparticles (NPs) in municipal wastewater treatment systems and effects of NPs on the biological treatment of wastewater: a review." RSC Advances 7.59 (2017): 37065-37075.

This was a study from China, written by two engineers (municipal engineering) regarding the effects of NPs in wastewater treatment plants. The issues reported were the bacterial biomass reduction, community shifts, and differences between a short NP exposure and a longer one. It was useful that the study examined both "efficient removal" studies as well as poor removal cases. This perspective was useful in understanding the life cycle of silica NPs.

Yang, Yi, et al. "Nanoparticles in road dust from impervious urban surfaces: distribution, identification, and environmental implications." Environmental Science: Nano 3.3 (2016): 534-544.

This article presented the largest lens of NP transport—dusts. Although this article falls into the "naturally occurring so it must be safe" perspective, authors did explain how dust is everywhere on the globe and should not be understood to be "inert." Combining these findings of aerosolized samples with what others have shown of the toxicity in vitro, it is obvious there is a problem with these tiny particles moving into the environment. They did include that inhalable chemicals near e-waste recycling plants are found in blood samples, and lead in the atmosphere at certain sites was higher in the local population. This study suggests that urban environments or locales which are sites of automobile exhausts, transport systems, manufacturing will have an more impacted population. This information was useful in considering how our alternative is manufactured, the exposure to the worker, and the community at large. The publication appeared in the Royal Society of Chemistry, funded by a NSF Nanotechnology project between China and Virginia Tech University.

#### Section 4: Electrospinning

Stachewicz, Urszula, et al. "Wetting Hierarchy in Oleophobic 3D Electrospun Nanofiber Networks." ACS Applied Materials & Interfaces 7.30 (2015): 16645–16652.

This study is a detailed examination of the wetting behavior of nanofiber mats. It provides insight into how the hierarchical structure affects the apparent contact angle for oils on the fiber network by examining the wetting behavior of individual fibers and the network as a whole. Although the paper focuses on a Nylon 6 mat with a fluoropolymer coating, its results can be extended to other systems. The supporting information also includes some details on the performance of the uncoated fiber network. This paper will help us predict how the structuring of electrospun fiber networks will affect the properties of our DWR coating independent of what our starting chemicals are.

Ma, Minglin, et al. "Superhydrophobic Fabrics Produced by Electrospinning and Chemical Vapor Deposition." Macromolecules 38. 23 (2005): 9742–9748.

This paper examines the hydrophobicity and oleophobicity of various electrospun fiber networks. The fibers were made of poly(caprolactone) and coated with a fluoropolymer through chemical vapor deposition. The fluoropolymer coating was used to enhance the hydrophobicity and oleophobicity of the fabric, but the hierarchical structuring of the material was also examined. Specifically, the authors studied how both the fiber diameter and beading on the fibers affects hydrophobicity. Thinner fibers with a high density of small beads were the most hydrophobic as they have the most surface roughness. Again, while the fluorinated coating is not useful for us, the details into possible and desirable electrospun fiber textures are valuable.

# Miyauchi, Yasuhiro, et al. "Fabrication of a Silver-Ragwort-Leaf-like Super-Hydrophobic Micro/Nanoporous Fibrous Mat Surface by Electrospinning." Nanotechnology 17. 20 (2006): 5151-5156.

The silver ragwort leaf has dense covering of microfibers and the fibers themselves have nanometer scale grooves. This study sought to mimic the structure of silver ragwort leaves using electrospun polystyrene fibers. Different starting solutions of polystyrene yielded different fiber textures, and the fibers that had the most surface texturing and pores were the most hydrophobic. This is not surprising, but this paper is useful because it has specific formulations for making these textured surfaces and does not consider a fluorinated material. It also directly ties electrospun fiber networks to a biological system.

Section 5: Slippery Liquid-Infused Porous Surfaces

Damle, Viraj G. et al. "Insensitive' to Touch: Fabric-Supported Lubricant-Swollen Polymeric Films for Omniphobic Personal Protective Gear." ACS Applied Materials and Interfaces 7.7 (2015): 4224–4232.

In this study, polyester fabrics were treated with silica-encapsulated alumina nanoparticles or covered with Sylgard-cross-linked polydimethylsiloxane (PDMS) coating. The samples were lubricated with silicone oil and hung to dry. While the samples achieved low contact angle hysteresis, the performance degraded rapidly when the fabric was blotted with cellulose-fiber wipes. We have concerns about the feel of this fabric as well; does it feel wet like other fabric that has been soaked in oil? The described technology is an interesting alternative, but it is a long way from being commercially viable.

Kim, Philseok et al. "Hierarchical or Not? Effect of the Length Scale and Hierarchy of the Surface Roughness on Omniphobicity of Lubricant-Infused Substrates." Nano Letters 13.4 (2013): 1793–1799.

This study investigates the optimal length scale or length scale combination (in a hierarchical structure) for the texturing under various sheer conditions for SLIPS on an Al substrate. In contrast to the lotus-leaf inspired surfaces, the authors found that the structures with uniform nanofeatures provided more liquid repellency at high shear forces than flat, microstructured, or hierarchically-structured surfaces. This paper effectively explains the advantages of SLIPS, including their ability to self-heal by redistributing the lubricant throughout the porous surface coating. The concepts discussed in this paper are useful, but the technical information is not as useful because of the non-fabric substrate and the use of fluorinated compounds as the lubricant.

Liu, Qi et al. "Durability of a Lubricant-Infused Electrospray Silicon Rubber Surface as an Anti-Icing Coating." Applied Surface Science 346 (2015): 68–76.

While this study focuses on the anti-icing properties of SLIPS surfaces, uses fluorinated compounds as the lubricant, and uses Al as the substrate, it is a good fundamental study of the phenomenon and will be helpful in our understanding. It provides a good diagram and explanation of ideal lubricant characteristics and behavior. This is also one of the only studies to do a test with simulated rainfall rather than carefully placed droplets.

### Section 6: Adaptations to Synthetic Fibers

Gao, Lichao, and Thomas J. McCarthy. "Artificial Lotus Leaf" prepared Using a 1945 Patent and a Commercial Textile." Langmuir 22.14 (2006): 5998–6000.

This paper compares microfiber cloth versus more loosely woven alternatives and finds that the microfiber performs better because the pores in the microfiber are smaller than water droplets.

The authors also present a convincing argument about the importance of advancing and receding contact angle hysteresis being more indicative of water repellency on fabrics than static contact angles. The citations of foundational studies on water repellent fabrics are useful. The study focused on polyester dipped in methylsilicone, which we have eliminated as a strategy due to the lack of oleophobicity.

### Michielsen, Stephen, and Hoon J. Lee. "Design of a Superhydrophobic Surface Using Woven Structures." Langmuir 23.11 (2007): 6004–6010.

This paper presents a good review of Young's equation and the Wenzel and Cassie-Baxter nanostructure theory and modifications to the equation. Octadecylamine-modified nylon fabrics exhibit high hydrophobicity, but this strategy cannot be implemented without modification due to the lack of oleophobicity. However, this treatment is simple and provides a strategy for functionalizing nylon, so it could be helpful in enhancing other alternatives. The insightful comparison between calendered (flattened), monofilament, and multifilament fibers in this study shows that multifilament woven fabric enhances water repellency over the other two options. Microfibers were not studied in this paper.

## Kim, Taekyeong, Hyejin Kang, and Namsik Yoon. "Synthesis of non-fluorinated paraffinic water repellents and application properties on textile fabrics." Fibers and Polymers 18.2 (2017): 285-289.

Paraffinic polymers were used in this study to increase the hydrophobicity of textiles. The monomers used were dodecyl acrylate, tetradecyl acrylate, hexadecyl acrylate, octadecyl acrylate, and docosyl acrylate. With the polymerized solution (made with other co-reagents besides the monomers), polyester, nylon, and cotton were treated in a pad-dry-cure process. The resulting water contact angles for polyester and nylon were approximately 130-140° and 110-120°, respectively, depending on the alkyl chain length. The results and methods of this paper have been informative as to the possibility of treating fabrics with paraffins—a process we know is currently used in industry. Although there are few papers on this process, we know that companies such as Schoeller use similar methods in their ecorepel product line. This paper can lead us in the direction of what companies are currently doing with paraffins coating their textiles.