Greener Solutions to Fluorinated Durable Water Repellency

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

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Durable water repellency (DWR) is best achieved using perfluorinated chemicals.
Effective DWR textiles currently require hazardous PFASs

Fluoroacrylate Polymers

Perfluorinated Alkyl Chain

Polyfluorinated Alkyl Chain
Fluorinated definitions and current restrictions

Background

Nanosols

Spinning

Eliminations

Improvables

Nanosols

Spinning

Eliminations

Improvables

PFC

à Outdated, general term for fluorinated compounds

PFC-EC

à Defined as highly fluorinated, small enough to be bioavailable, and persistent

PFASs

à Currently used term in literature for fluorinated compounds

Restricted under Stockholm Convention:

- PFOS (an 8-carbon perfluorinated sulfonate)
- PFOS-F (an 8-carbon perfluorinated sulfonyl fluoride)

Restricted by Gore with Greenpeace:

- All compounds that fall under this designation

Restricted under Stockholm Convention:

- PFOS (an 8-carbon perfluorinated sulfonate)
- PFOS-F (an 8-carbon perfluorinated sulfonyl fluoride)

Restricted by EPA:

- PFOS – 70 ppt drinking water health advisory
- PFOA – 70 ppt drinking water health advisory

All PFASS

Background

Eliminations

Improvables

Nanosols

Spinning

Conclusion
Fluorinated compounds are persistent

Lipophilic chemical classes:
- PCBs, POPs, PAHs, flame retardants

PBT criteria: EPA, REACH
Hazard: High BCF
### PFASs hazards

<table>
<thead>
<tr>
<th>Mutagenicity</th>
<th>Organ</th>
<th>Respiratory</th>
<th>Reproductive</th>
<th>Persistence</th>
<th>Aquatic</th>
<th>Fate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kidney, breast, and testicular cancer</td>
<td>High cholesterol; liver, kidney, heart, blood toxicant</td>
<td>Some airway inflammation</td>
<td>Reproductive and developmental toxicity</td>
<td>Bio-accumulation; persistent organic pollutant</td>
<td>Fish and invertebrate toxicity</td>
<td>Not biodegradable</td>
</tr>
</tbody>
</table>

- **PFOA**: 8-carbon perfluorinated alkyl chain

*Italics: based on animal studies*
### Criteria for greener alternatives

<table>
<thead>
<tr>
<th>Hydrophobicity</th>
<th>Oleophobicity</th>
<th>Durability &amp; Washability</th>
<th>Appearance &amp; Feel</th>
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<tbody>
<tr>
<td><img src="image1.png" alt="Hydrophobicity" /></td>
<td><img src="image2.png" alt="Oleophobicity" /></td>
<td><img src="image3.png" alt="Durability" /></td>
<td><img src="image4.png" alt="Appearance" /></td>
</tr>
</tbody>
</table>

- **Hydrophobicity**: Water-repellent properties
- **Oleophobicity**: Oil-repellent properties
- **Durability & Washability**: Resistance to wear and ease of cleaning
- **Appearance & Feel**: Visual appeal and tactile comfort
Criteria for greener alternatives

Hydrophobicity

PFAS performance:
Static: 118°

Metrics:

Static contact angle (CA)

High CA (phobic)
Low CA (philic)
Criteria for greener alternatives

Hydrophobicity

Gore goals:
Advancing > 115°
Receding > 95°

PFAS performance:
Static: 118°

Metrics:
Dynamic contact angles

Contact angle hysteresis
Advancing angle – Receding angle
Ideal: 0
Criteria for greener alternatives

Hydrophobicity

Gore goals:
Advancing > 115°
Receding > 95°

PFAS performance:
Static: 118°

Metrics:
Roll-off angle

PFAS performance:
Static: 118°
Criteria for greener alternatives

Hydrophobicity

Gore goals:
- Advancing > 115°
- Receding > 95°

PFAS performance:
- Static: 118°

Oleophobicity

Gore goals:
- No penetration of high surface tension oils for 30 s
  - Proxy: oil contact angle

PFAS performance:
- Static: 118°
- n-heptane: 40°
- n-hexadecane: 70°
Criteria for greener alternatives

**Gore goals:**
**Advancing > 115°**
**Receding > 95°**

**PFAS performance:**
**Static: 118°**

**Oleophobicity**

**Gore goals:**
No penetration of high surface tension oils for 30 s
Proxy: oil contact angle

**PFAS performance:**
n-heptane: 40°
n-hexadecane: 70°

**Durability & Washability**

**Gore goals:**
Resist 20 laundry wash cycles with detergent

**PFAS performance:**
Meets requirements
## Criteria for greener alternatives

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<tr>
<td><strong>Gore goals:</strong></td>
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</tr>
<tr>
<td>Advancing &gt; 115°</td>
<td>No penetration of high surface tension oils for 30 s</td>
<td>Resist 20 laundry wash cycles with detergent</td>
<td>No negative odor</td>
</tr>
<tr>
<td>Receding &gt; 95°</td>
<td>Proxy: oil contact angle</td>
<td></td>
<td>Color not affected</td>
</tr>
<tr>
<td>PFAS performance: Static: 118°</td>
<td>PFAS performance: n-heptane: 40° n-hexadecane: 70°</td>
<td>PFAS performance: Meets requirements</td>
<td>Comparable texture and feel</td>
</tr>
<tr>
<td><strong>PFAS performance:</strong></td>
<td></td>
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<td><strong>PFAS performance:</strong></td>
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<tr>
<td>Static: 118°</td>
<td></td>
<td>Meets requirements</td>
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Environmental and Human Health

Gore goals:
- Low inherent toxicity
- Not bioaccumulative
- Not persistent
- Low environmental hazard
Looking to nature for inspiration

Hierarchical structures for improved phobicity

Contact area

Flat → Microstructure → Nanostructure → Hierarchical

Contact angle
Lithography and 3D printing are impractical

- Omniphobic
- No fluorinated compounds
- Expensive
- Easily damaged

Graft hydrophobic functional groups on nylon


Octadecylamine

poly(acrylic acid)

nylon 6,6

✗ Not oleophobic
## Choice of fabric substrate

<table>
<thead>
<tr>
<th>Textile</th>
<th>Hydrophobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulosic fibers (cotton, rayon)</td>
<td>✗</td>
</tr>
<tr>
<td>Protein fibers (wool, silk)</td>
<td>✗</td>
</tr>
<tr>
<td>Spandex</td>
<td>✗</td>
</tr>
<tr>
<td>Nylon</td>
<td>✗</td>
</tr>
<tr>
<td>Vinyl fibers (vinyon, saran)</td>
<td>✗ Not oleophobic</td>
</tr>
<tr>
<td>Polyolefin</td>
<td>✗</td>
</tr>
<tr>
<td>Polyester</td>
<td>✗</td>
</tr>
</tbody>
</table>

Multifilament yarns improve hydrophobicity through texturing

\[ \begin{align*}
\text{Octadecylamine} & \quad \text{PFOA} \\
\text{Water Contact Angle (°)} & \\
\text{Monofilament} & \quad \text{Multifilament} & \quad \text{Calendared} \\
0 & \quad 20 & \quad 40 & \quad 60 & \quad 80 & \quad 100 & \quad 120 & \quad 140 & \quad 160 & \quad 180
\end{align*} \]

✗ Not oleophobic

Microfiber improves hydrophobicity

Traditional polyester

Microfiber polyester

✗ Not oleophobic

Silicone nanofilaments

- ✓ Hydrophobicity
- ✓ Handle
- ✓ Color

✗ Washability
✗ Oleophobicity

Water contact angle after washing

Silica nanosols provide nanotexture

SiO$_2$ nanoparticles or precursor + organosilanes + water → Texturized fabric

Dip and nip application

Before treatment

After treatment

Silica nanoparticles or precursor

organosilanes

amino silicone

water

polyester

Zhao et al. Materials and Design (2016).
Silica nanosols are highly hydrophobic on polyester

![Graph showing water contact angle (°) for static, advancing, and receding conditions. The graph indicates superhydrophobic threshold at approximately 155°.](Zhao et al. Materials and Design (2016).)
Organosilanes have poor oleophobicity

Improved oleophobicity with dimethyldimethoxysilane


- Has not been tested on fabrics

Background
Eliminations
Improvables
Nanosols
Spinning
Conclusion
Silica-based nanosols are washable and durable

Zhao et al. Materials and Design (2016).
Silica-based nanosols are washable and durable

Zhao et al. Materials and Design (2016).
Thin coatings do not affect aesthetics

Stiffness

Breathability


solid content of SiO\textsubscript{2} nanosol on viscose fabric

<table>
<thead>
<tr>
<th>Weight % solid</th>
<th>0.3%</th>
<th>1%</th>
<th>2%</th>
<th>5%</th>
<th>10%</th>
<th>15%</th>
<th>20%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lm\textsuperscript{-2}s\textsuperscript{-1}</td>
<td>80</td>
<td>120</td>
<td>160</td>
<td>80</td>
<td>120</td>
<td>160</td>
<td>80</td>
</tr>
</tbody>
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The figure shows the stiffness and breathability of SiO\textsubscript{2} nanosol on viscose fabric at different weight percentages. The breathability increases with weight percentage, while the stiffness is affected minimally.
Nanoparticle background and applications

High surface to volume ratio

Nanoscale: 1-100 nm

Diverse sources

Diverse Functionality

Nanosol properties:
- Assembly
- Size Control
- Surface modification
- Composition
- Multi-functionality
- Shapes


Background  Eliminations  Improvables  Nanosols  Spinning  Conclusion
Nanomaterials target specific body systems

Silica
- Size dependent toxicity
- Penetrate cell barriers
- Respiratory toxicity
- Cellular toxicity
- Aquatic toxicity
- Environmental toxicity

Nanosols
- Respiratory irritant
- Kidney toxicity

# Nanosol hazard profile

<table>
<thead>
<tr>
<th>Compound</th>
<th>Human Toxicity</th>
<th>Environmental Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mutagenicity</td>
<td>Organ</td>
</tr>
<tr>
<td>Silica nanoparticles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous Silica</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3-aminopropyl) triethoxysilane</td>
<td>Skin, eye</td>
<td></td>
</tr>
<tr>
<td>(APTES)</td>
<td>irritant</td>
<td></td>
</tr>
<tr>
<td>Hexadecyltrimethoxysilane</td>
<td>Skin, eye</td>
<td></td>
</tr>
<tr>
<td>(HDTMS)</td>
<td>irritant</td>
<td></td>
</tr>
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- **Silica nanoparticles**:
  - Amorphous Silica: Not PBT

- **(3-aminopropyl) triethoxysilane (APTES)**:
  - Skin, eye irritant: Not bioaccumulative, Aquatic risk

- **Hexadecyltrimethoxysilane (HDTMS)**:
  - Skin, eye irritant: Not bioaccumulative, Aquatic risk

<table>
<thead>
<tr>
<th>Hazard scale</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
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- **Hazard scale**:
  - Low
  - Medium
  - High
## Persistence of nanosol coating

<table>
<thead>
<tr>
<th>Partition</th>
<th>EPA PBT Criteria</th>
<th>Silanes</th>
<th>PFOA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (days)</td>
<td>&gt;60</td>
<td>38</td>
<td>180</td>
</tr>
<tr>
<td>Soil (days)</td>
<td>&gt;60</td>
<td>75</td>
<td>360</td>
</tr>
<tr>
<td>Air (days)</td>
<td>&gt;2</td>
<td>0.3</td>
<td>31</td>
</tr>
<tr>
<td>Sediment (days)</td>
<td>&gt;60</td>
<td>340</td>
<td>1600</td>
</tr>
<tr>
<td>Bioconcentration factor</td>
<td>1000-5000</td>
<td>4.6</td>
<td>56</td>
</tr>
<tr>
<td>Fish chronic value (mg/L)</td>
<td>&lt;10</td>
<td>2.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Inspiration for spinning: the silver ragwort leaf

147° water contact angle

Electrospinning textured fiber mats

Solution blow spinning for manufacturing

- Safer solvents
- Faster
- Easier to scale up

Highly tunable polystyrene nanofiber mats

**Graph 1:**
- **Y-axis:** Water contact angle (°)
- **X-axis:** Weight ratio of THF/DMF
- Data points show a trend where the water contact angle increases with decreasing weight ratio of THF/DMF.

**Graph 2:**
- **Y-axis:** Water-roll angle (°)
- **X-axis:** Weight ratio of THF/DMF
- The water-roll angle decreases as the weight ratio of THF/DMF increases.

Oleophobicity from structuring

53° contact angle on siloxane-coated slide

>90° contact angle on siloxane nanofiber mat

PA6+fluoropolymer coated glass slide

Breathable thin fabric coatings

- Washable
- Flexible
- Transparent

Typical fabrics

>80% of plastic in water is <5 mm

- Marine invertebrates accumulate <1 mm
- Microplastic particles are 200 µm – 5 mm
- Plastics break down to 40 – 100 µm

Cole, 2016. Scientific Reports
Rochman, C. 2016. ET&C.
Short life cycle of bioplastics meets ASTM biodegradation standards

Possibilities:
- Poly(lactide) PLA, P(3HB)
- Microbial Polyesters & Blends

## Spinning solvent hazards

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</thead>
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<tr>
<td></td>
<td>Mutagenicity</td>
<td>Organ</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>Carcinogen: liver, kidney</td>
<td>Skin, eye irritant</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>Eye, skin irritant; chronic toxicity (liver, digestive)</td>
<td>Respiratory</td>
</tr>
<tr>
<td>Dimethyl sulfoxide (DMSO)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td></td>
<td>Skin, eye irritant</td>
</tr>
</tbody>
</table>

**Hazard scale**
- Low
- Medium
- High

**Environmental Toxicity**
- Persistance
- Aquatic
- Fate
Strategy summary

- Human Toxicity
- Environmental Toxicity
- Environmental Fate
- Aesthetics
- Oleophobicity
- Durability
- Hydrophobicity

Legend:
- Orange: PFASs
- Blue: Nanosols
- Green: Spinning

Background
Eliminations
Improvables
Nanosols
Spinning
Conclusion
Research needs for future development

1. Improve oleophobicity
   - Nanosols: test dimethyldimethoxysilane on fabrics
   - Spinning: incorporate a nanosol

2. Optimize spinning using the least hazardous solvents and additives

3. Fully test durability and aesthetic of alternatives
   - 20 home wash-dry cycles
   - Abrasion testing
We thank Barb Henry for being an excellent partner and mentor, and for setting up the wonderful tour at Gore Innovation Studio! Thank you also for connecting us with many Gore associates.

Thank you also to our instructors, Meg, Tom, and Billy for their guidance, inspiration, and support. It has been incredible to learn different perspectives from three such accomplished people.

Finally, thanks to our classmates Oana, Zach, Kathy, Katie, and Audrey! It has been so fun to go through this class with you and to see your group progress with amazing designs and ideas!