Water Repellency without Fluorine – Learning from Nature

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Switzerland

Performance Days 2016 / Munich / 20 April 2016

HEIQ
ECO DRY
Eco-Friendly Durable Water Repellency (DWR)
Staying clean & dry

Learning from Nature

[1]

[2]

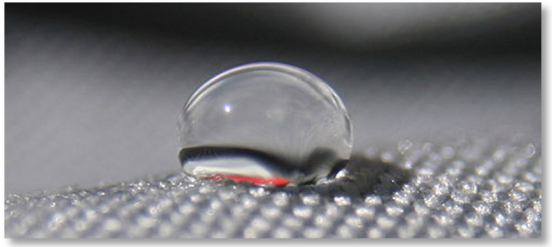
[3]

[4]

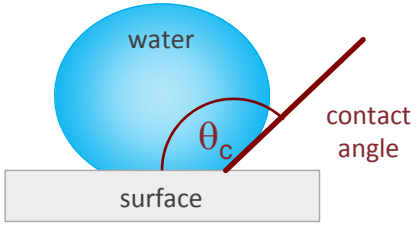
[1] https://commons.wikimedia.org/wiki/File%3AWater_drop_on_a_leaf.jpg (accessed October 2015), By photo taken by flickr user tanakawho (flickr) [CC BY 2.0 (http://creativecommons.org/licenses/by/2.0)], via Wikimedia Commons
[2] https://commons.wikimedia.org/wiki/File%3AFeather_and_water_droplet_(292952818).jpg (accessed October 2015), By aussiegall from sydney, Australia [CC BY 2.0 (http://creativecommons.org/licenses/by/2.0)], via Wikimedia Commons
[3] https://commons.wikimedia.org/wiki/File:ValleyOfFlowers_MorningDew.JPG#/media/File:ValleyOfFlowers_MorningDew.JPG (accessed October 2015), by User:Pankaj Says So - Own work. Licensed under Public Domain via Commons
[4] https://commons.wikimedia.org/wiki/File%3ADew_on_a_Equisetum_fluviatile_Luc_Viatour.jpg (accessed October 2015), I, Luc Viatour [CC BY-SA 2.5-2.0-1.0 (http://creativecommons.org/licenses/by-sa/2.5-2.0-1.0)], via Wikimedia Commons

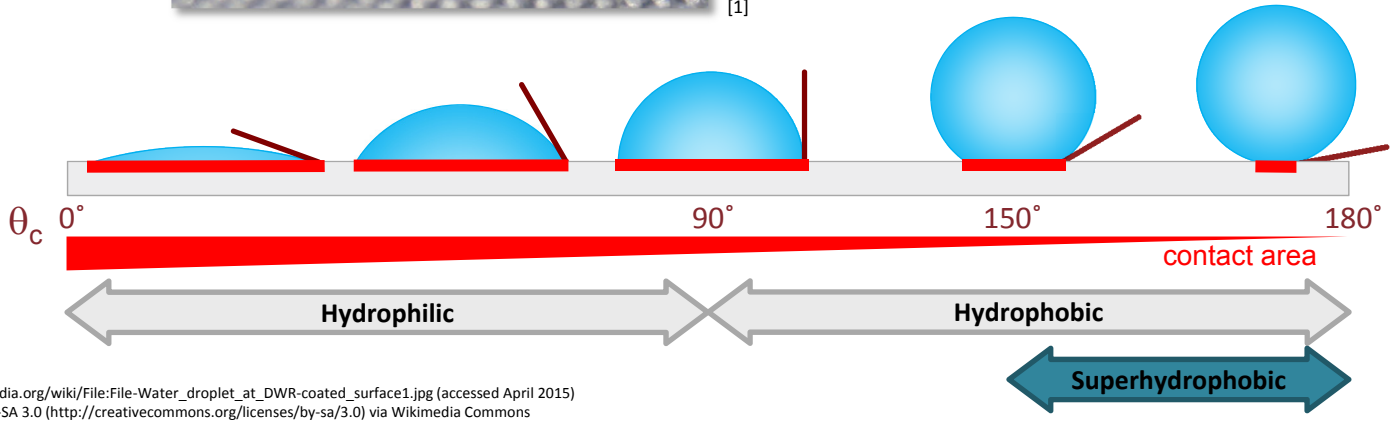
Repellency

- Clean & Dry → minimize contact between substance and textile
- Contact occurs at the interface
  - Closer look at interface between water and surface…



[1]

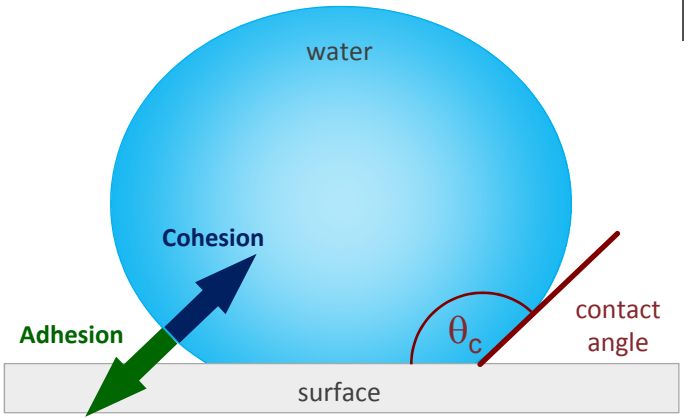




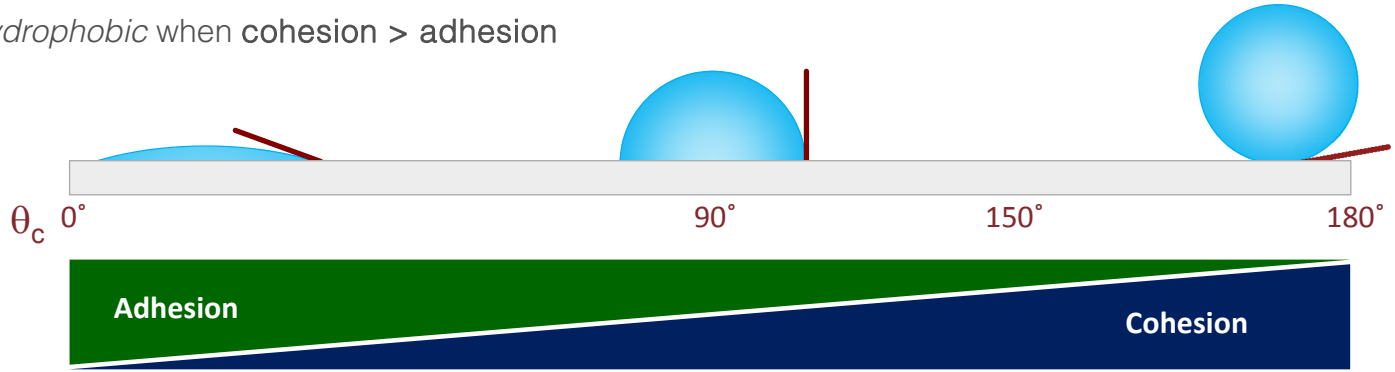
[1] http://commons.wikimedia.org/wiki/File:File-Water_droplet_at_DWR-coated_surface1.jpg (accessed April 2015)
Brocken Inaglory [CC BY-SA 3.0 (http://creativecommons.org/licenses/by-sa/3.0) via Wikimedia Commons

Repellency

- Droplet shape from a balance of forces [2]
  - **Cohesion** – molecular properties of liquid (L/L)
  - **Adhesion** – molecular properties of solid surface (S/L)



- *Hydrophobic* when **cohesion > adhesion**



[2] Yuan, Y., & Lee, T. R. (2013). Contact angle and wetting properties. In Surface science techniques (pp. 3-34). Springer Berlin Heidelberg.

Repellency

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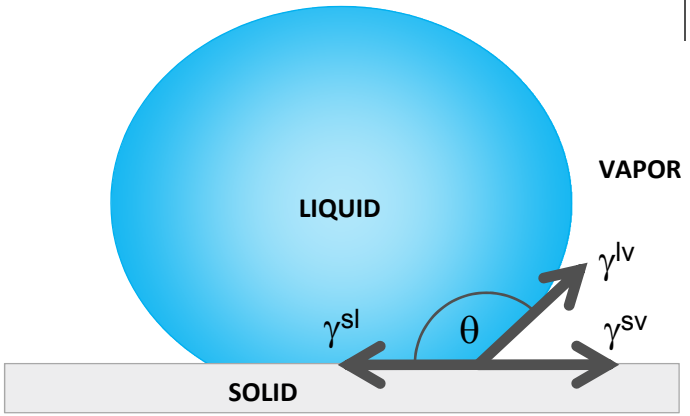


- Use chemical treatments to modify the molecular properties of the surface:
  - Lower the surface energy (surface tension) to give less adhesion

Young's equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos\theta$$

θ	contact angle
γ^{sl}	solid/liquid interfacial free energy
γ^{sv}	solid/vapor surface free energy
γ^{lv}	liquid/vapor surface free energy

[2] Yuan, Y., & Lee, T. R. (2013). Contact angle and wetting properties. In Surface science techniques (pp. 3-34). Springer Berlin Heidelberg.

Repellency

Liquids

Substance	Surface energy (mN/m)
Water	72
Paraffin oil	31
Octane	22

[3]

Solids

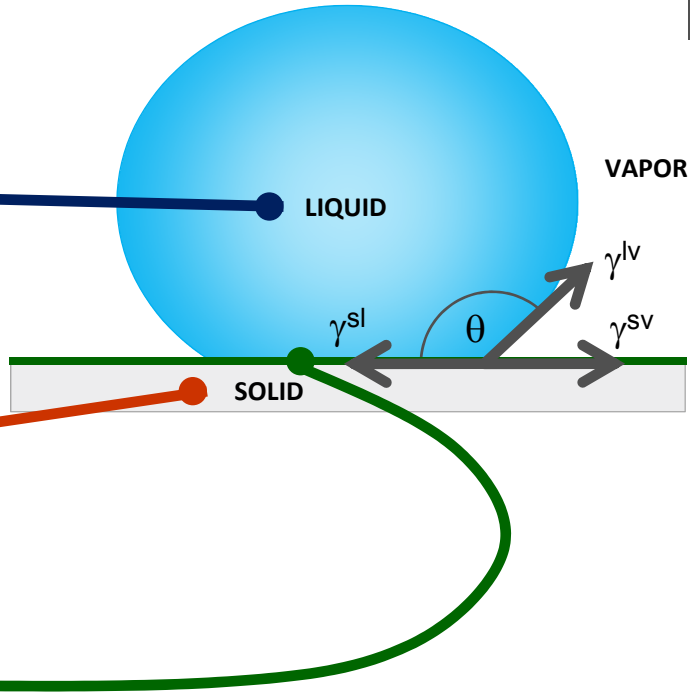
Substance	Surface energy (mN/m)
Polyamide (PA)	46
Polyester (PET)	43

[3]

Surface groups

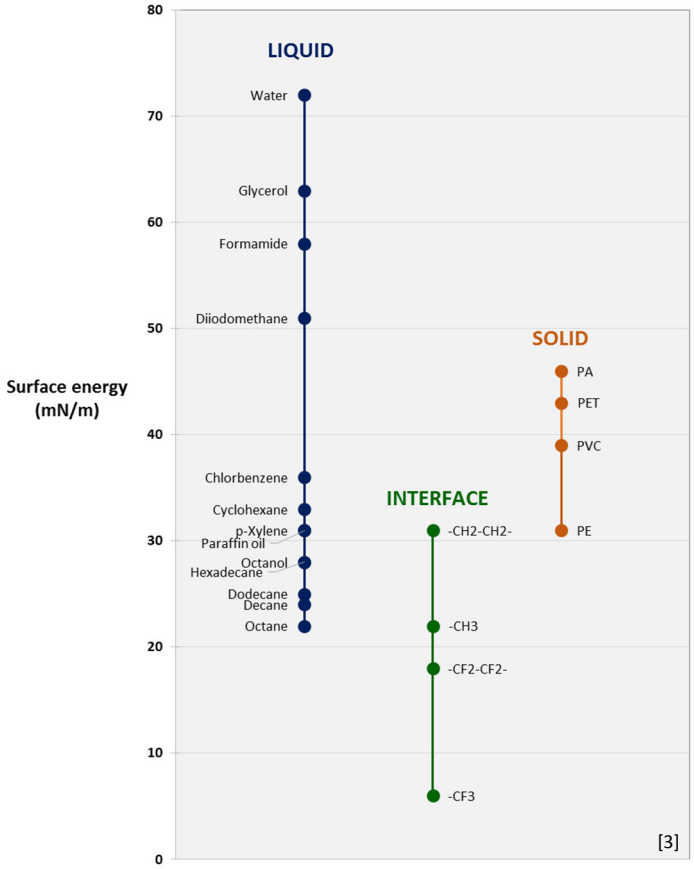
'Building block'	Surface energy (mN/m)
$-CH_2-CH_2-$	31
$-CH_3$	20 - 24
$-CF_2-CF_2-$	18
$-CF_3$	6

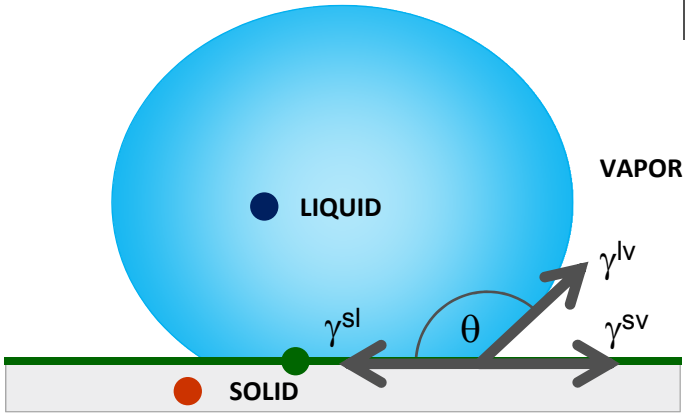
[3]



[3] B. Mahltig, "Hydrophobic and oleophobic finishes for textiles" in Functional Finishes for Textiles: Improving Comfort, Performance and Protection, Woodhead Publishing Series in Textiles (Editor: Roshan Paul) Elsevier, 2014

Repellency





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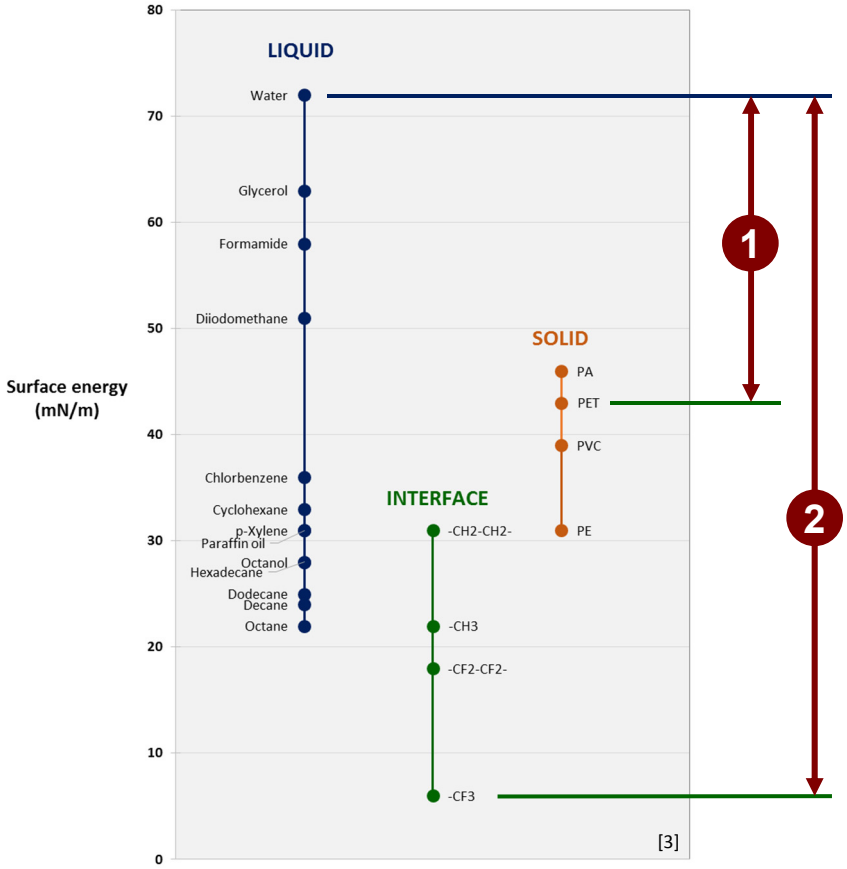
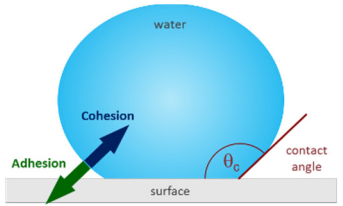
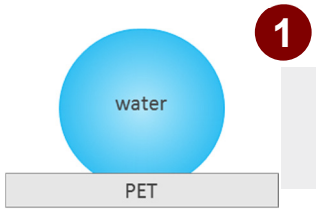
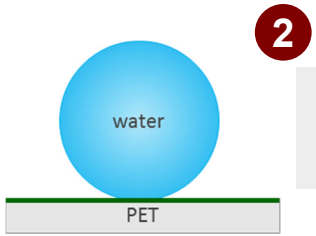
Repellency







High cohesion
Low adhesion
→ low wetting



High cohesion
Very low adhesion
→ very low wetting

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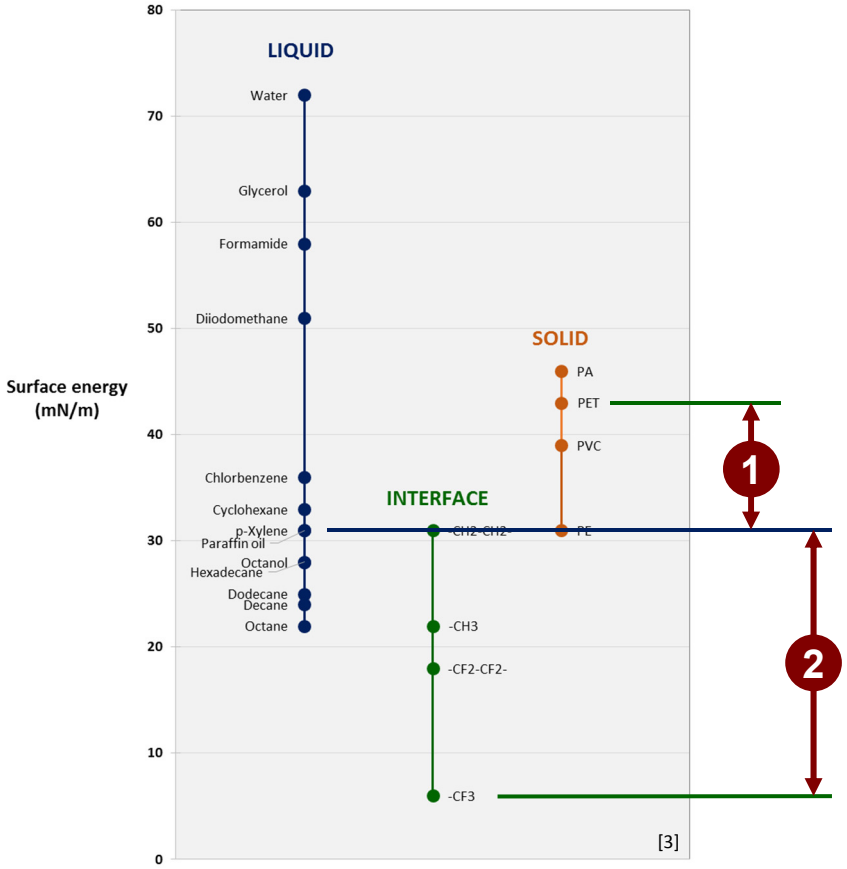
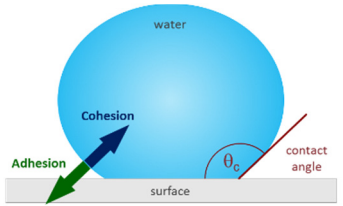
Repellency



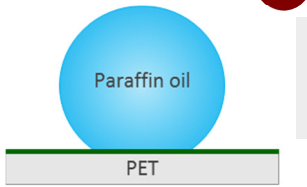


1

Low cohesion
High adhesion
→ Strong wetting

2

Low cohesion
Very low adhesion
→ Low wetting



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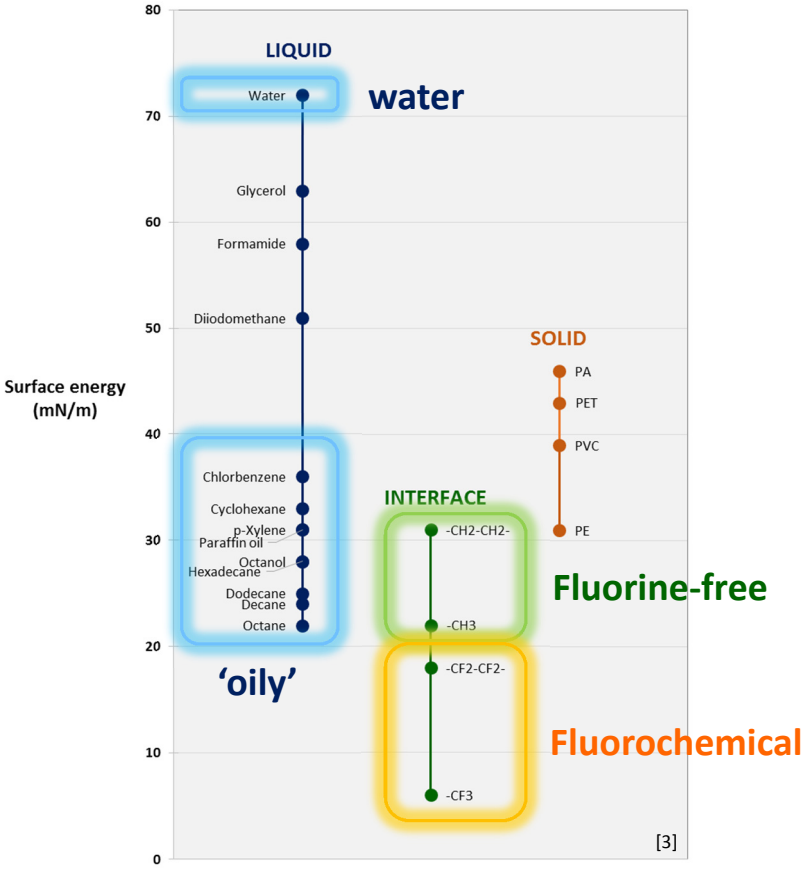
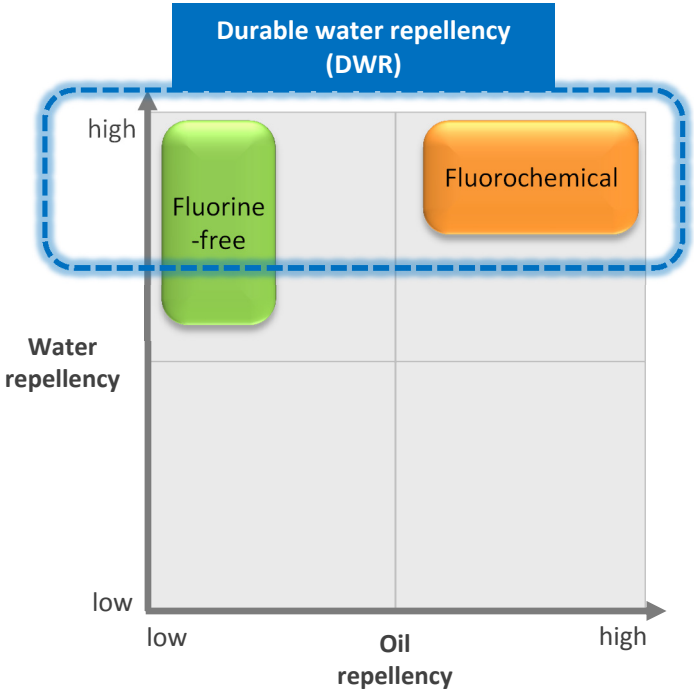
Repellency

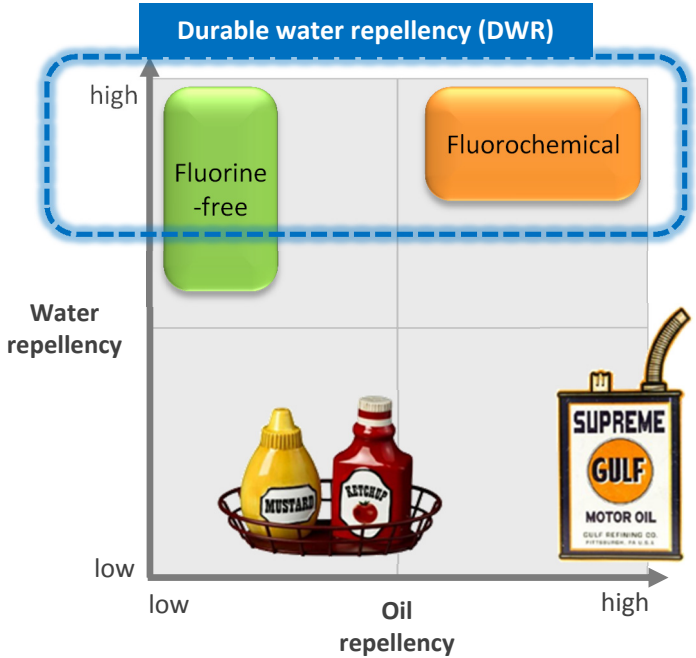




[3] B. Mahltig, "Hydrophobic and oleophobic finishes for textiles" in Functional Finishes for Textiles: Improving Comfort, Performance and Protection, Woodhead Publishing Series in Textiles (Editor: Roshan Paul) Elsevier, 2014

Oil Repellency?

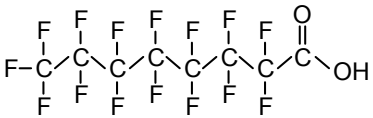
- Oil repellency has historically been a desirable property of fluorine-based treatments
- For most textile applications durable water repellency is clearly the primary target
  - Oil repellency is a bonus
- Why is oil repellency helpful?
  - Helps to keep textiles free of stains
- Legacy oil repellency targets need re-framing for fluorine-free treatments:
  - Treatment enables removal of stains after laundry with detergent?
  - Does the treatment enhance the quality of use and lifecycle durability of the textile?



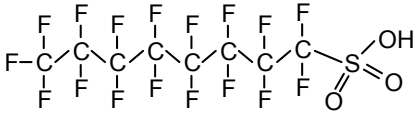
Why fluorine-free?

- Fluorine-based products: transition from C8 to C6

PFOA Perfluorooctanoic acid $C_7H_{15}COOH$



PFOS Perfluorooctane sulfonate $C_8H_{17}SO_3H$

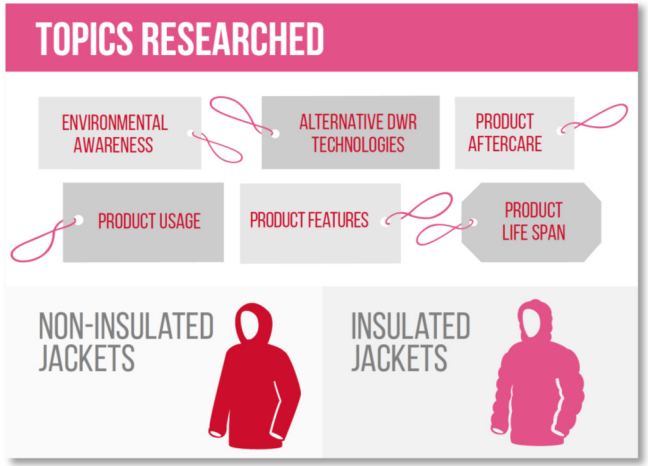


  - By-products: PFOA/PFOS traces are found in wastewater, water, human blood
  - C6 products minimise/avoid PFOA/PFOS residues associated with C8 products

- PFC-free: achieve DWR effects without fluoro-based concerns

Consumer Perception

- Study by de Montfort University, School of Fashion and Textiles
  - Published by the European Outdoor Group, October 2015
- Survey of consumers and outdoor brands
- Incl. environmental awareness of PFCs...

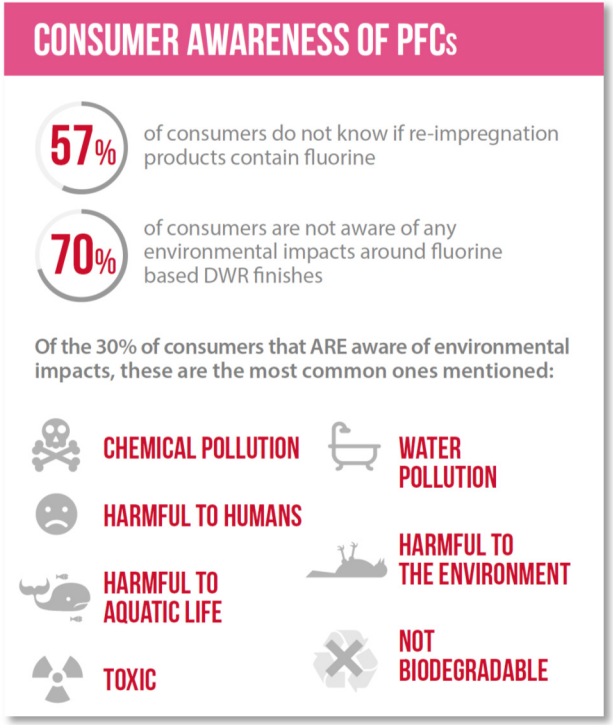


[4]

[4] European Outdoor Group, "Outdoor Jackets With Durable Water Repellent Finish: A Consumer & Brand Perspective On Product Features, Usability & Product Aftercare", 2015, http://www.europeanoutdoorgroup.com/files/EOG_Durable_Water_Rep_Fabric_Report.pdf

Consumer Perception

- Significant consumer awareness of PFCs and environmental impact of fluorine:
  - 30 to 45% depending on Region
- Consumer perception of fluorine:
  - *Chemical pollution*
  - *Water pollution*
  - *Harmful to humans*
  - *Harmful to the environment*
  - *Harmful to aquatic life*
  - *Toxic*
  - *Not biodegradable*
- Growing demand for PFC-free DWR...

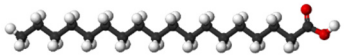
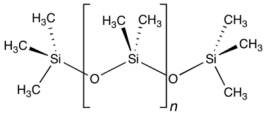
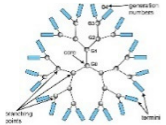


[4]

[4] European Outdoor Group, "Outdoor Jackets With Durable Water Repellent Finish: A Consumer & Brand Perspective On Product Features, Usability & Product Aftercare", 2015, http://www.europeanoutdoorgroup.com/files/EOG_Durable_Water_Rep_Fabric_Report.pdf

Fluorine-free treatments

- Various approaches to provide $–CH_3$ and $-CH_2-CH_2-$ ‘building block’ groups at the interface
- Aim to provide low surface energy without fluorine groups

Category	Illustrative structure	Chemical basis	Comment
Paraffins	 [5]	eg. fatty acids & waxes	*Hydrocarbon chain with various approaches for anchoring to substrates*
Silicones	 [6]	eg. polysiloxanes	*Hydrocarbons along silicon-based polymer chain*
Multi-branched	 [7]	eg. polyurethanes	*Maximize presentation of low energy $–CH_3$ groups* [8]

[5] http://commons.wikimedia.org/wiki/File%3AStearic-acid-3D-balls.png (accessed April 2015). By Jynto and Ben Mills (Derived from File:Caproic-acid-3D-balls.png.) [Public domain], via Wikimedia Commons
[6] http://commons.wikimedia.org/wiki/File%3APmdsStructure.png (accessed April 2015). By Smokefoot (Own work) [CC BY-SA 3.0 (http://creativecommons.org/licenses/by-sa/3.0)], via Wikimedia Commons
[7] http://commons.wikimedia.org/wiki/File%3AGraphs.jpg (accessed April 2015). By Olukin at en.wikipedia (Transferred from en.wikipedia) [Public domain], from Wikimedia Commons
[8] ZDHC, “Durable Water and Soil Repellent Chemistry in the Textile Industry – A Research Report”, www.roadmaptozero.com/df.php?file=pdf/DWR_Report.pdf (accessed April 2015)

Fluorine-free treatments

- DWR desirable properties:
  - General comparison. Wide spectrum of properties and characteristics available.

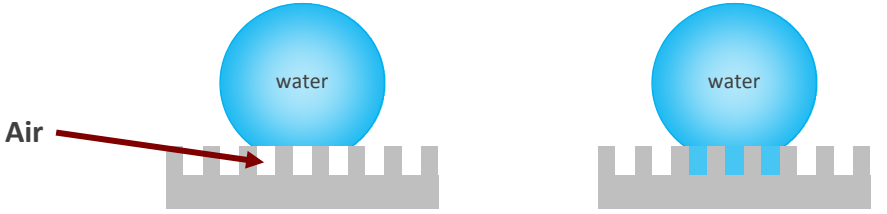
Category	Water repellency	Oil repellency	Wash durability	Abrasion resistance	Breathability	Mechanical handle
Paraffins	✓	✗	v	v	v	v
Silicones	✓	✗	v	v	✓	✓
Multi-branched	✓	✗	✓	✓	✓	✓
Fluorine (C6)	✓	✓	✓	✓	✓	✓
Fluorine (C8)	✓	✓✓	✓✓	✓	✓	v

v = performance may vary significantly between different products in the category

Repellency – Structure

- Repellency achieved through ‘film layer’ approach
  - Focus on chemical properties of the interface

- Repellency is also influenced by **structure**



Cassie & Baxter [9] Wenzel [10]

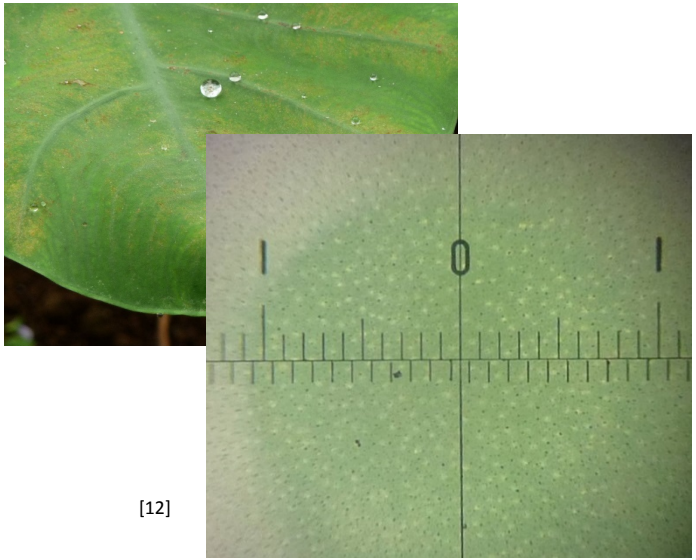
- Structure can further reduce contact between substance and the surface → higher repellency

[9] Cassie, A. B. D., and S. Baxter. "Wettability of porous surfaces." Transactions of the Faraday Society 40 (1944): 546-551.
[10] Wenzel, Robert N. "Resistance of solid surfaces to wetting by water." Industrial & Engineering Chemistry 28, no. 8 (1936): 988-994.

Repellency – Structure

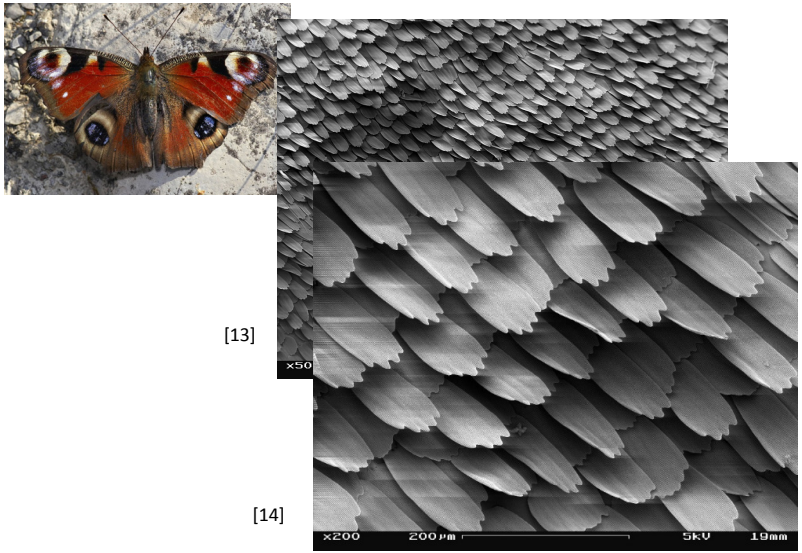
- Natural inspiration: numerous fluorine-free structures evident in nature to learn from… [11]

Leaf



[12]

Butterfly wing

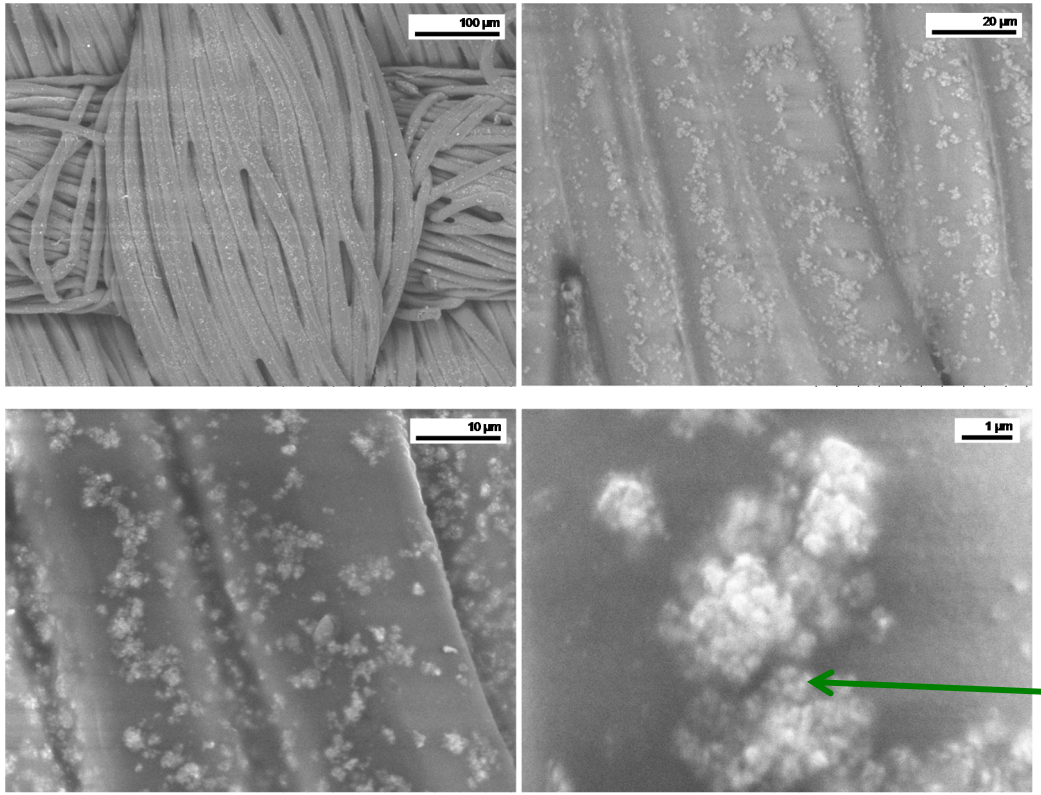


[13]

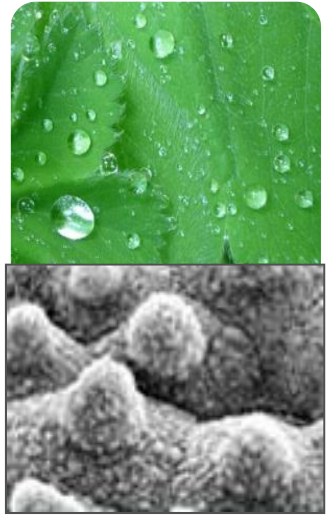
[14]

[11] Liu, Kesong, Xi Yao, and Lei Jiang. "Recent developments in bio-inspired special wettability." Chemical Society Reviews 39, no. 8 (2010): 3240-3255.
[12] http://commons.wikimedia.org/wiki/File%3ALotus_effect_on_leaf_of_taro_and_leaf_magnify.jpg (accessed April 2015). By Namazu-tron (Self Shot) [CC BY-SA 3.0 (http://creativecommons.org/licenses/by-sa/3.0)], via Wikimedia Commons
[13] http://commons.wikimedia.org/wiki/File%3AInachis_io_top_MichaD.jpg (accessed April 2015). By I, MichaD [CC BY-SA 2.5 (http://creativecommons.org/licenses/by-sa/2.5)], via Wikimedia Commons
[14] http://commons.wikimedia.org/wiki/File%3ASEM_image_of_a_Peacock_wing%2C_slant_view_2.JPG (accessed April 2015). By SecretDisc 11:38, 16 January 2007 (UTC) (Own work) [CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0/)], via Wikimedia Commons

Structure example: Barrier RCF by HeiQ®



Leaf – natural repellency



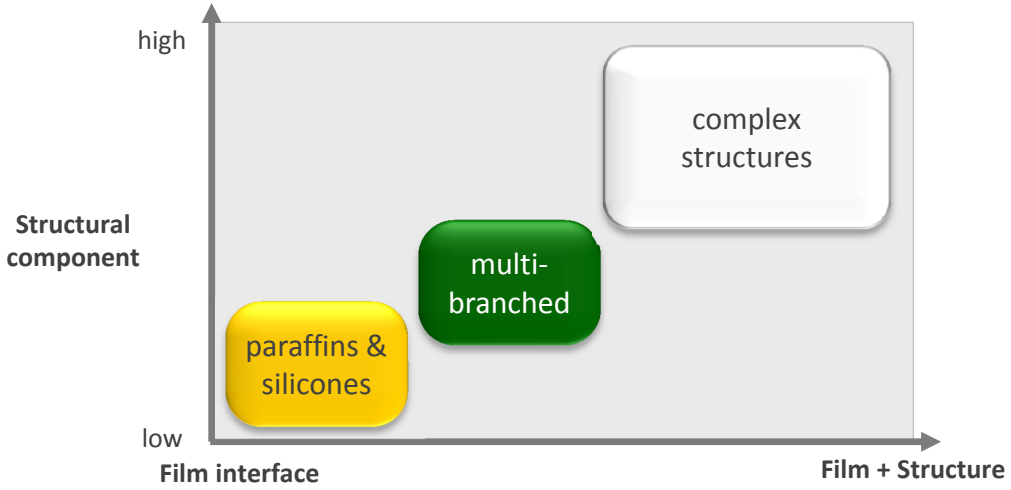
Micron-sized particles replicate leaf surface structure

Scanning Electron Microscope (SEM) images of PES woven fabric treated with *Barrier RCF by HeiQ®*

Repellency – Structure

- Repellency is influenced by:
  - Interface chemistry
  - Surface structure

- Structure + Chemistry gives increased scope to influence repellency
  - Structure is extremely relevant to achieve DWR performance with fluorine-free treatments



Summary

- Durable Water Repellency (DWR) is a key functionality for numerous technical textiles
- Demand for fluorine-free DWR treatments is increasing
- Fluorine-free repellency is an opportunity to learn from nature:
  - Interface chemistry
  - Surface structure
- Nature-inspired structures are a powerful basis for effective fluorine-free DWR treatments

Inside HeiQ – SWISS TECH INSIDE

10 Years of Innovation

HeiQ is a Swiss specialty textile effects company with 30 employees, 15 nationalities, in 7 countries on 4 continents

HeiQ was founded in 2005 as Spin-off of the Swiss Federal Institute of Technology (ETH) Zürich

bluesign® approved

HeiQ offers textile brands innovation R&D, customized chemical manufacturing and ingredient branding in one

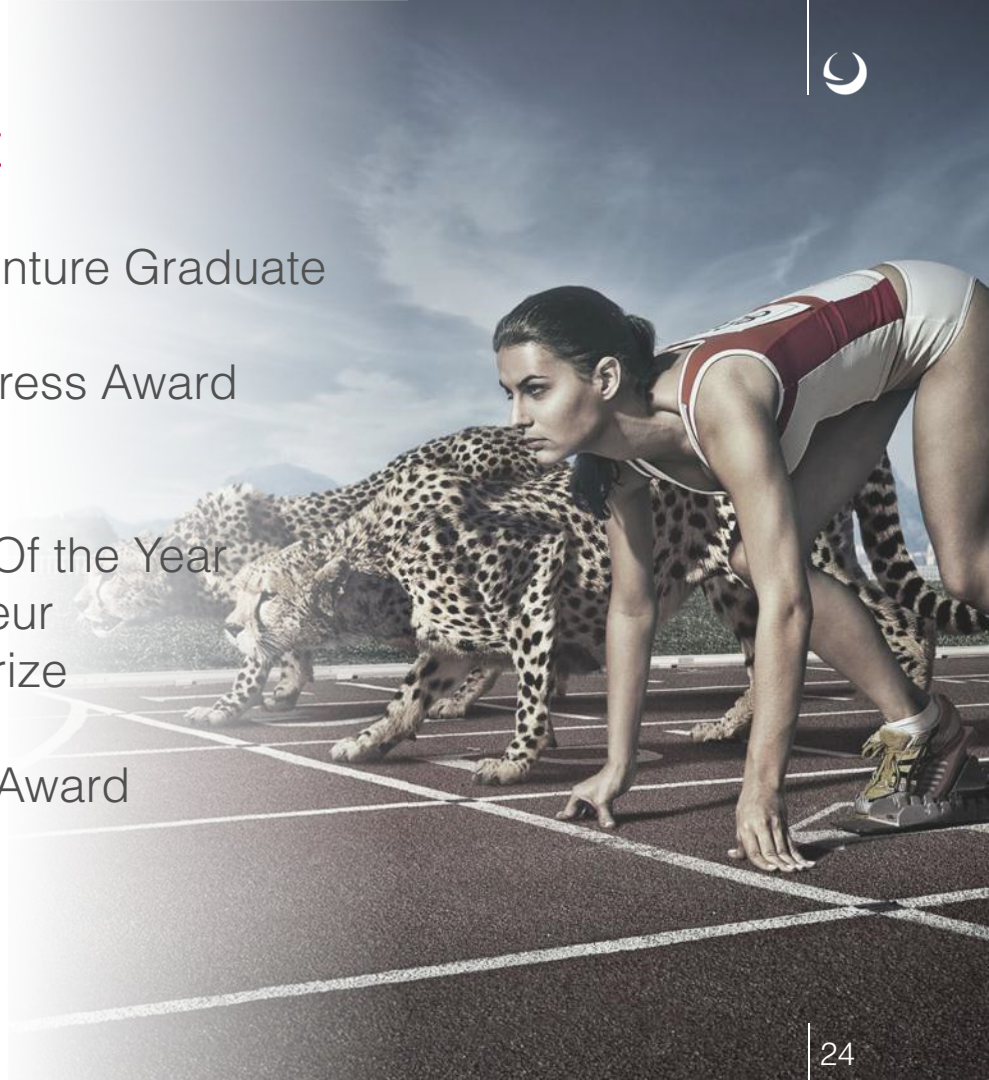
CONFIDENCE IN TEXTILES
Tested for harmful substances
according to Oeko-Tex® Standard 100
00000000 Institute

HeiQ's key product innovation families are:

HEIQ SMART TEMP | HEIQ FRESH TECH | HEIQ ECO DRY | HEIQ GLIDE | HEIQ SUN BLOCK | HEIQ CLEAN TECH

HeiQ Entrepreneurial Spirit

2015	Swiss Top 10 McKinsey Venture Graduate
2013	Finalist Swiss of the Year
2011	European Environmental Press Award
2010	Swiss Technology Award
2010	Swiss Equity Fair Winner
2009	Finalist E&Y Entrepreneur Of the Year
2008	KTI Technology Entrepreneur
2007	McKinsey / ETH Venture Prize
2007	Venture Leaders Award
2006	W.A. DeVigier Foundation Award
2006	IMD Startup Award
2005	Siska-Heuberger Prize



HeiQ Global Presence

Innovation & HeiQ

"Scientific research is one of the most exciting and rewarding of occupations. It is like a voyage of discovery into unknown lands, seeking not for new territory but for new knowledge. It should appeal to those with a good sense of adventure."

Frederick Sanger
1980 Nobel Prize winner for Chemistry

SWISS TECHNOLOGY® AWARD

HeiQ's Scientific Board Network

- Connection to forefront of research & innovation
- Access expertise through broad academic networks

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Wey Yang Teoh Prof. Dr.	City University Hong Kong	Nanotechnology & Photocatalysis

Thank You For Your Interest

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HeiQ provides textile innovation, customized manufacturing and consumer branding.
The company was founded in 2005 as a spin-off company of the Swiss Federal Institute of Technology. HeiQ was bestowed with the prestigious Swiss Technology Award.