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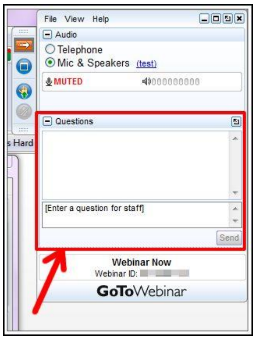

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FELLOW

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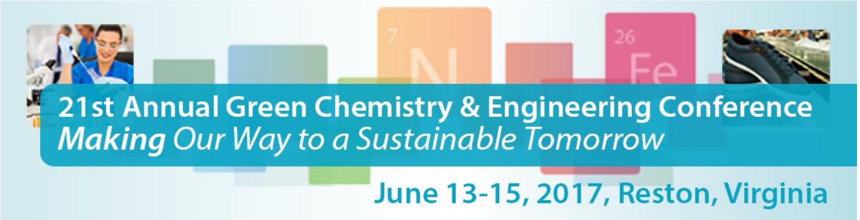

- Sustainable Chemicals
- Flexible Chemical Manufacturing
- More Efficient Processes
- Green Chemistry Curricula
- Circular Economy Considerations
- Sustainable Materials
- Academic-Industry Collaborations
- Chemicals Policy
- Cosmetics
- And More!

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Upcoming ACS GCI Webinar!

Nanomaterial Design Guided by the Principles of Green Chemistry

Thursday, May 18 @ 2-3pm ET

How can green chemistry be applied to nanotechnology to achieve the high performance needed for advanced applications while preventing or reducing health and environmental impacts? Join James Hutchison from the University of Oregon as he discusses the foundations for greener nanotechnology and presents a case study that uses nanomaterial product innovation guided by green chemistry.

Register Now!

What You Will Learn

- The opportunity to achieve a net environmental benefit by bringing together green chemistry with nanoscience
- The role that green chemistry plays in designing high performance nanomaterials and efficient nanomaterial production
- How green chemistry and nanoscience can be used together to develop innovative new products with environmental benefits

ACS Webinars

Experts

James Hutchison
University of Oregon

Joe Fortunak
Howard University

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Upcoming ACS Webinars
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Thursday, April 13, 2017

The Good, The Bad and the Uncertain: *Public Perception of the Chemical Enterprise*

Session 3 of the Industry Science Series

Mark Jones, Executive External Strategy and Communications Fellow, Dow Chemical
William Carroll, Founder, Carroll Applied Science and Adjunct Professor of Chemistry, Indiana University

Thursday, April 20, 2017

Cystic Fibrosis: *Discovery of CFTR Modulators*

Session 4 of the 2017 Drug Design and Delivery Symposium

Peter Grootenhuis, Senior Director Chemistry, Vertex
Nick Meanwell, Executive Director, Bristol-Myers Squibb

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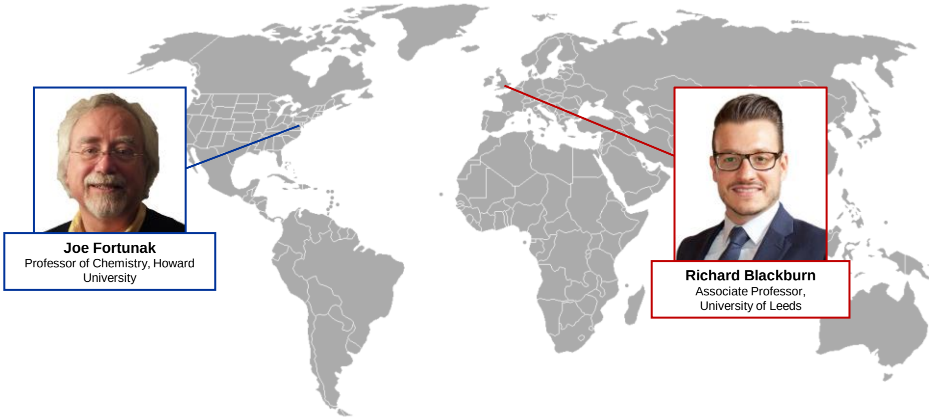
"Sustainability Challenges of the Textiles, Dyeing and Finishing Industries: *Opportunities for Innovation"*



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Sustainability Challenges of the Textiles, Dyeing and Finishing Industries:
Opportunities for Innovation

Dr. Richard Blackburn

Sustainable Materials Research Group

University of Leeds

@RichardBlackb18

Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Which is the most sustainable textile fibre?

Cotton

Polyester

Wool

Nylon

Necessity for Sustainable Products

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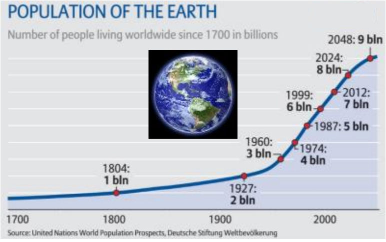
- 2012 - world population 7 billion
- 2050 - expected to rise to over 9 billion
- Increases demand
  - food, energy, water, resources, chemicals
- Increases environmental burden
  - pollution
  - depletion of finite non-renewable resources (*e.g.* fossil fuels)

- **Synthetic chemical products and processes afford a significant improvement in quality of life**
- **Growing middle class want these consumer products too**



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Synthetic Fibre Revolution

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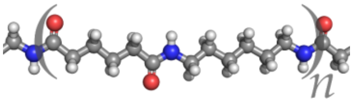
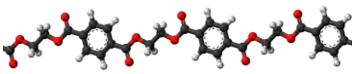
20th Century polymers

- nylon, 1935
- polyurethane, 1937
- polyester: Terylene, 1941; Dacron, 1946
- acrylic, 1944
- polypropylene and HDPE,1951





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Synthetic Fibre Sustainability Challenges

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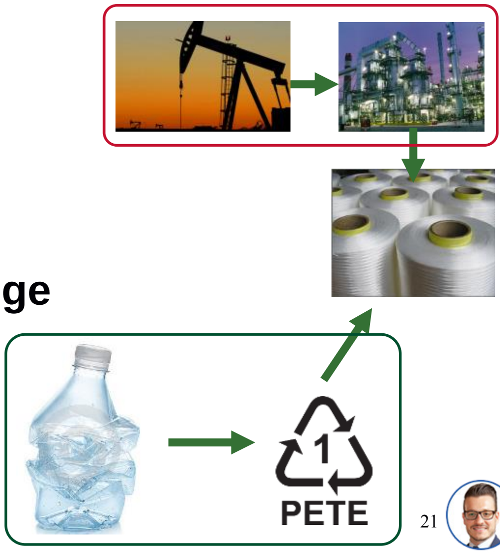
- Non-degradable, non-renewable
- <u>But</u>, polyester highest share of textile market
  - >50m tpa
- **Raw materials for fibres must change**
- Recyclable – mechanical or chemical?



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Sustainability Considerations

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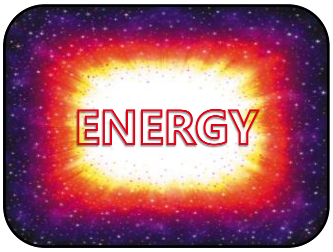

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Public Perception

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- Demand (and rejection) for consumer products can be driven by the public and the media
- “*Biodegradable*”, “*Natural*”, “*Organic*”
  - perceived by the public to be good for the environment
- “*Synthetic*”, “*Non-organic*”, “*GM*”
  - perceived by the public to be bad for the environment
- “*Chemistry*”
  - Public perception of science…
- Do the public understand what “*Sustainable*” means?

Physics

Chemistry

Ideal Sustainable Product

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- Provide an **equivalent function** to the product it replaces
- **Performs as well as or better** than the existing product
- Is designed to be **desirable**
- Be available at a **competitive or lower price**
- Have a minimum environmental footprint for **all the processes involved**
- Be manufactured from **renewable resources**
- Use only **ingredients that are safe** to both humans and the environment
- **No negative impact** on food supply or water

Textile Dyeing Processes

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- Traditional dyeing processes use 5.8 trillion litres water p.a.
  - ~3.7 billion Olympic swimming pools
- 10-20% dye remains after dyeing (plus other chemicals), leaving potential for wastewater pollution
  - One fifth of the world's industrial water pollution (World Bank)
- 391 billion kWh energy for dyeing processes
- **Innovative technologies needed to reduce, or eliminate, water, energy and auxiliary chemicals in dyeing**

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Treatment of Textile Dyeing Effluent

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- Wastewater from dyeing processes one of biggest contributors to textile effluent
- Mainly residual dyes and auxiliary chemicals
- >50,000 tpa dye discharged into effluent

Dye Class	Fibre	Loss to Effluent (% applied)
acid	polyamide (nylon)	5-20
basic	acrylic	0-5
direct	cotton	5-30
disperse	polyester	0-10
metal-complex	wool/polyamide	2-10
reactive	cotton	10-50
sulphur	cotton	10-40
vat	cotton	5-20

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Treatment of Textile Dyeing Effluent

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- Dyeing effluent in a watercourse aesthetically undesirable, but has a more serious environmental impact
- High BOD combined with spectral absorption of dye
  - Can affect photosynthetic processes
  - Reduction in O_2 levels in water → suffocation of aquatic flora and fauna
- Dyestuffs may be also have aquatic toxicity (metals, AOX)
- Several methods developed to remove colour from effluent
- Varying in effectiveness, economic cost, and environmental impact (of the treatment process itself)

Blackburn RS, *Environ. Sci. Technol.* **2004**, *38*, 4905.

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Polyester Dyeing Process

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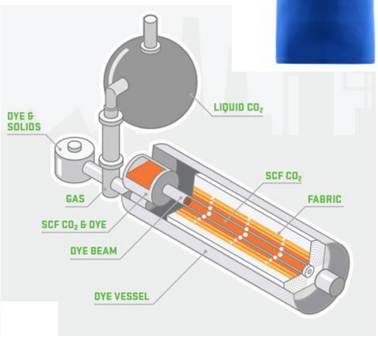
- Hydrophobic fibre dyed with hydrophobic disperse dye
- Traditional aqueous process requires dispersing agents/surfactants and high temperatures (typically 130 °C) under pressure
- Other dyeing auxiliaries often required
- Large amount of waste dye left over in effluent
- Surface dye removed with surfactants and/or reducing agents
- **Innovation in $scCO_2$ dyeing to completely change polyester dyeing process**



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$scCO_2$ dyeing

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System comparison with traditional polyester dyeing

WATER
Zero water used

PROCESS CHEMICALS
No auxiliary chemicals

WASTEWATER
Nearly 100% dye used in process. **Zero** waste

FOOTPRINT
¼ of physical footprint to dye same mass of fabric

ENERGY
Reduces energy consumption by 63%

EFFICIENCY
40% faster than traditional dyeing processes

drydye

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$scCO_2$ dyeing - limitations

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- Machines are more expensive than traditional water-dyeing machines
  - “costs will come down through scale and lower water and energy expenses“
- Only works on polyester fabrics and can't be used to dye cotton
  - Cotton makes up about 35% global fibre market
  - Some relatively unsuccessful work on modifying cotton
- **Significant opportunity to develop low or zero water dyeing systems for coloration of cellulosics**

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Coloration of Cotton

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- Dyeing of cotton primarily conducted using **reactive dyes**
- Despite development of dyes with high fixation, dyeing still uses high quantities of **salt**, **water** (and energy), and creates **colour pollution**

- **Soil too alkaline to support crops**
- **Kills aquatic life**
- **Fresh watercourses turned saline downstream from dyehouses**
- **Difficult to remove from effluent**

- **10-40% dyestuff hydrolysed**
  - Goes down drain
  - Aesthetically unpleasant
  - Blocks sunlight and kills aquatic life
- **Clean effluent**
  - High cost

- **High level in dyeing**
- **Incredible volume in wash-off**
  - Up to 10 separate rinsings
  - High energy consumption
  - 50% total cost dyeing procedure

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Wash-off of Reactive Dyeings on Cotton

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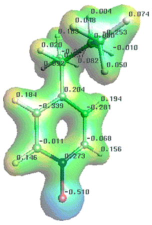
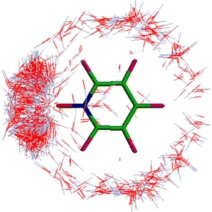
- Dye transfer inhibiting (DTI) polymers (used in laundry detergents) were employed to remove unfixed dyes
- Much more efficient, economical and sustainable process developed
- Significantly reduces operation time, water consumption and energy consumption
  - poly(vinylpyridine-*N*-oxide) polymers were the most effective
  - poly(vinylpyridine betaine) polymers also highly efficient





Procedure	Time (min)	Water (L/kg fabric)	Energy (MJ/kg fabric)
recommended wash-off	250	60	9.21
DTI wash-off	50	30	0.84

Amin MN, Blackburn RS, *ACS Sus. Chem. Eng.* **2015**, *3*, 725.

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Bigger Problems with Cotton

- **NATURAL doesn't necessarily mean sustainable**
- Cotton production >25 million tpa
- High levels of pesticides (25% world total)
- High levels of insecticides (11% world total)
- Very high irrigation levels
  - 1 kg of cotton fibre requires 20,000-40,000 L
  - Water average person consumes in a lifetime
- Only grows in certain climates
  - Deforestation to grow cotton
- High area of land for mass of useable fibre

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Sustainable Cotton?

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Organic cotton

- Widely promoted as the answer to cotton's problems
- Global production (in over 20 countries, mainly India) only 1.1% of world cotton production
- No genetically modified seed permitted
- No herbicides or pesticides
- Ethical labour employment standards
- Requires approximately 1.4x area of land to produce same mass of fibre
- Still has very high water consumption
- Not a viable alternative on a global scale to completely replace non-organic cotton

USDA ORGANIC

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Sustainable Cotton?

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Better cotton

- GM pest-resistant strain referred to as 'Bt cotton'
  - Naturally occurring protein (used by organic gardeners) – kills bollworm pests (moth larva)
  - Reduces pesticide sprays from 5 sprays to 0
  - Poisoning of workers virtually eliminated
  - More productive, particularly in India
  - Bt cotton is regarded as less 'natural'
  - Cannot be classed as 'organic'
- Better Cotton Initiative (BCI) set up to foster improvements in the sustainability of cotton production methods

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Alternative Sustainable Cellulosic Fibres

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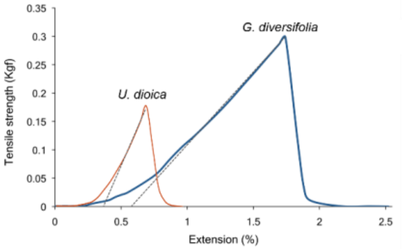
Bast Fibres

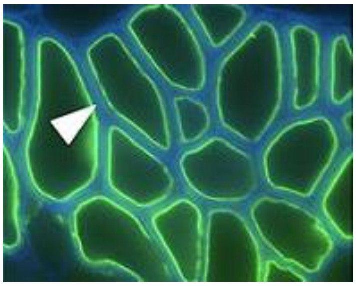
- From stem of plants (flax, hemp, jute, ramie, nettle, kenaf, abaca)
- **Plants with opportunities for performance fibres (*e.g.* Himalayan nettle)**

Lanzilao G, Goswami P, Blackburn RS, *Mater. Letts.*, **2016**, 181, 200.



- Processing to separate ultimate fibres is of concern
- **Opportunities for innovation into alternative separation techniques (*e.g.* enzyme-assisted technologies)**

Blake AW, Marcus SE, Copeland JE, Blackburn RS, Knox JP, *Planta*, **2008**, *228*, 1.



TENCEL® (lyocell) – Most Sustainable Fibre Production Process

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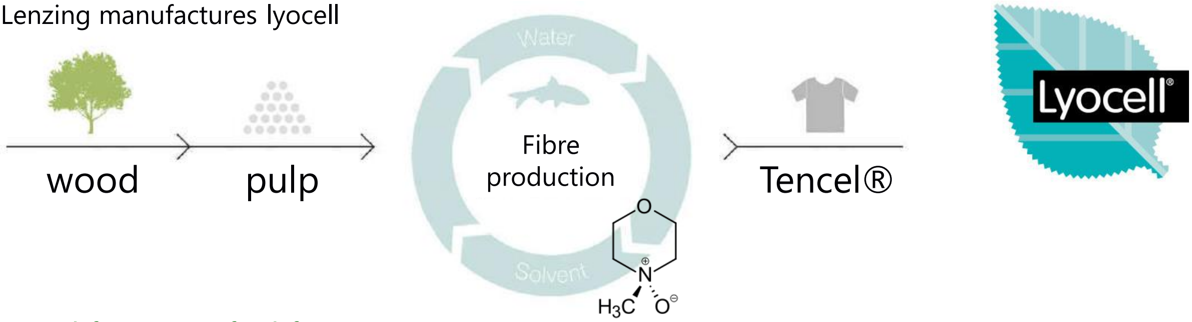
- Regenerated cellulosics made from trees
- Lenzing manufactures lyocell



- Wood from certified forests
- Direct closed-loop dissolution process
- *N*-methylmorpholine-*N*-oxide (NMMO)
- >99% recovery of solvent

Goswami P, Blackburn RS, Taylor J, White P. *Cellulose*, **2011**, 18, 1063.
Široký J, Blackburn RS, Bechtold T, Taylor J, White P. *Carb. Polym.*, **2011**, *84*, 299.

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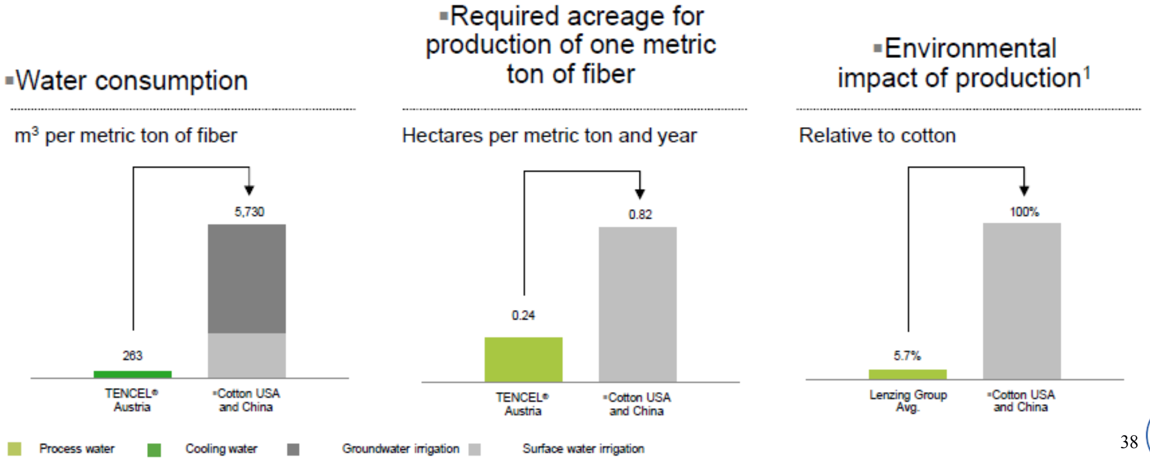
Green Footprint vs. Cotton

UNIVERSITY OF LEEDS

- More than 50% of Lenzing's fuel consumption sourced from renewable resource



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Refibra™

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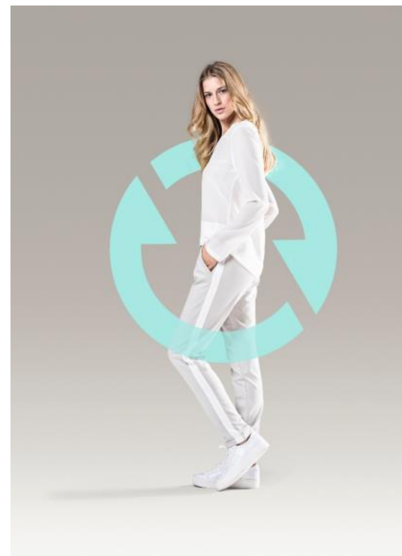
- New Lenzing fibre manufactured from industry waste, both cotton and lyocell
- Made from pulp that contains cotton scraps left over from cutting operations



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Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Which textile fibre is lightweight and breathable, cool in the heat, warm in the cold, carries away moisture, has excellent odour management properties and a low carbon footprint?

Cotton

Polyester

Wool

Nylon

allbirds

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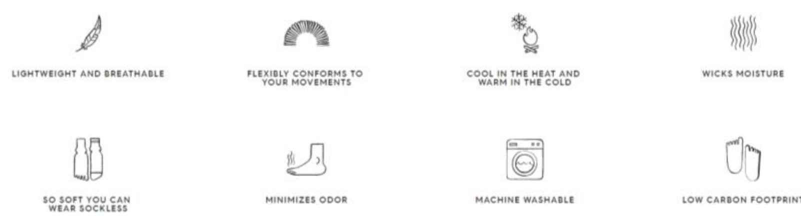
- Designing environmentally friendly and comfortable footwear

- Wool Runner – minimalist sneaker made of superfine New Zealand merino wool



Best Way to Mix Colours?

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Nano-level

- Mixture of different dye molecules in dyebath to create desired shade

Micro-level

- Mixture of different dyed fibres in yarn formation process to create desired shade

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Does Fibre Coloration Have to be Through Dyeing?

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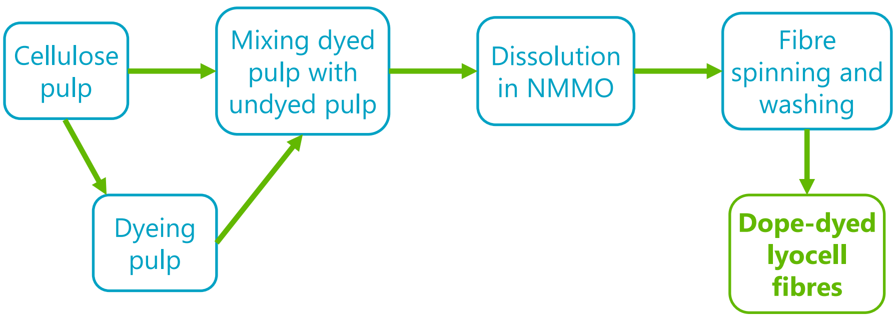
- **Dope-dyeing:** incorporation of colorant into spinning process
- Lyocell process makes this possible for cellulosics



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DyeCat Process

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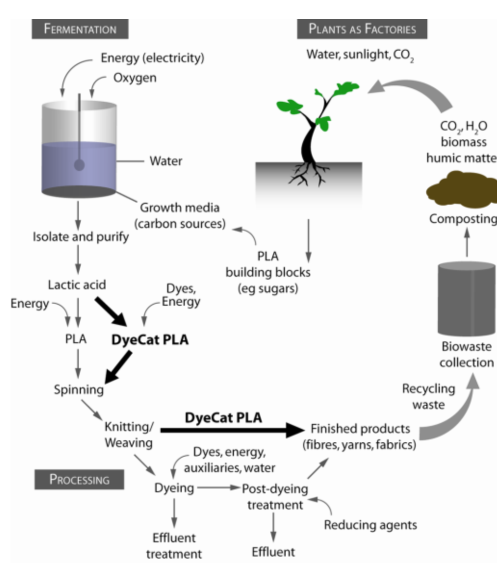
- Catalytic process that allows colour to be integrated directly into polyesters
- Eliminates need for conventional dyeing
- Colour in fibre is generated at the same time the polymer is made
- Colours 'locked into' fibre providing a technically superior product
- No need for wasteful dyeing processes
- **DyeCat poly(lactic acid) fibre**
  - **Renewable**
  - **Technically superior**
  - **Saves chemicals and energy**



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DyeCat Process

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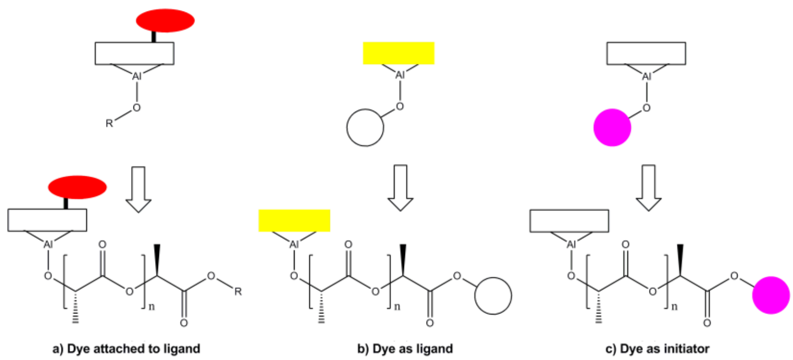
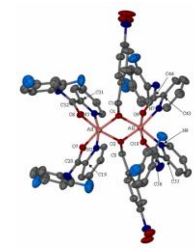
- Coloration of polymer during synthesis
- Demonstrated on PLA using coloured catalysts



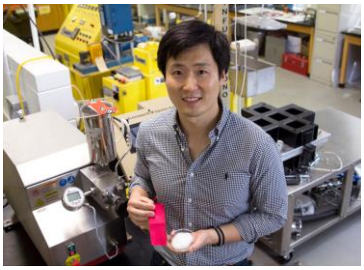


MacRae RO, Pask CM, Burdsall LK, Blackburn RS, Rayner CM, McGowan PC, *Angew. Chem. Int. Ed.* **2010**, *50*, 291.

Novel, Sustainable and Cost-Effective Textile Dyeing using Nanocellulosic Fibres

UNIVERSITY OF LEEDS

- Dr. Yunsang Kim *et al*., University of Georgia
- Innovative dyeing processes using coloured nanocellulose
- nano-sized cellulose fibrils (wood pulp) + dye → dyed nanocellulose dispersion



- Apply dyed nanocellulose dispersion onto the textile material using low water process
- Coloured nanocellulose permanently binds to textile surface
- Greatly reduces energy and water needed

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Criticism of Chemistry use for Repellency in Outdoor Apparel

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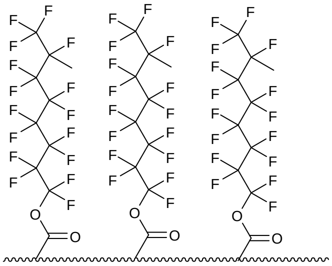
- Durable water repellents (DWR) applied to textiles to impart repellent functionality from water and oil
- For the last 60 years, per- and polyfluoroalkyl substances (PFASs) used in textile finishing



- Outdoor apparel industry has been directly targeted by Greenpeace
- The industry's PFAS use has been discussed in three reports since 2012
- **However, ratio of PFAS use in the outdoor apparel industry compared to whole textile industry unknown**

> *"...significant adverse effects have **not** been found in the general human population, however, significant adverse effects have been identified in laboratory animals and wildlife"*
> **US EPA**

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Significant Attention to Alternative Chemistries

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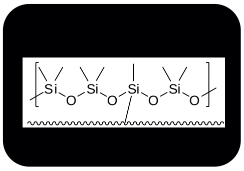
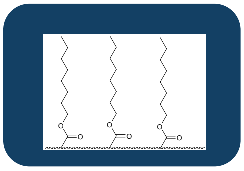
Suitable for Requirements?

- Mixed opinions on outdoor apparel requirements
- Involves wide range of activities, varying weather conditions, and demands on the wearer
- 'Wetting' of the fabric can cause detrimental cooling of the wearer – 'life protection'
- **Re-evaluation of consumer requirements**

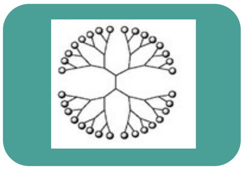
Surface terminal groups	Critical surface tension γ_c (mN/m) at 20°C
$-CF_3$	6
$-CF_2$	18
$-CH_3$	22
$-CH_2$	31



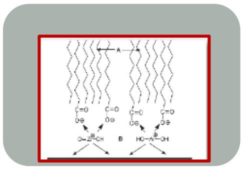
Silicones



Hydrocarbons



Dendritic/hyper-branched chemistry



Wax-based repellents

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Move to Fluorine-Free: Sufficient Functionality?

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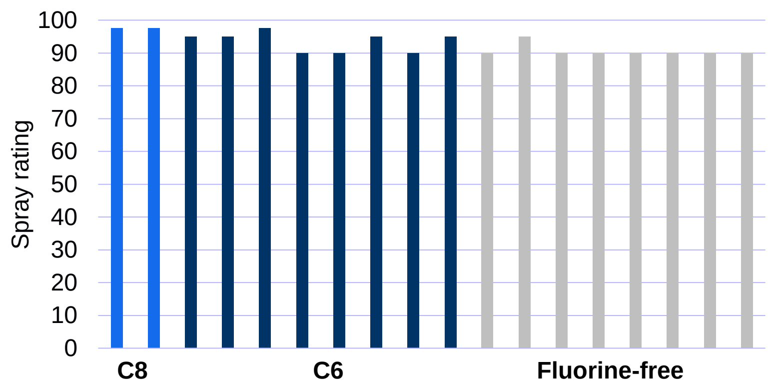
Characterisation of repellent fabrics currently in use from a number of brands



Spray test BS EN ISO 4920
Industry standard for testing resistance to surface wetting

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Fast Fashion

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- Fast, low price and disposable “supermarket” clothing
- Demand for apparel will double by 2025
- Environmental Impact
  - US imports >1 billion garments annually from China alone
  - 80% textiles end up in landfill (50 million tpa)
  - Dramatic increase in environmental damage caused by the textile industry
  - Safety compromised in evermore cost-cutting supply chain
- Human disasters (*e.g.* Rana Plaza, Bangladesh - 1,100 deaths, 2,500 injuries)
- **An enormous change is needed in the minds and attitudes of retailers and consumers**

Sustainable Textiles

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- Greater use of sustainable raw materials
- Lower energy & water consumption and pollution generation in production
- Lower impact in use
  - Water, energy, chemicals in cleaning/laundering
- Design for easy disassembly/disposal/ recycling
- **DESIGN FOR REDUCED CONSUMPTION AND LONGER LIFE**
  - **'Disposable' products unsustainable**

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Audience Survey Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Which is the most sustainable textile fibre?

- Cotton
- Polyester
- Something else

Sustainability Challenges for the Textiles Industry

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- Sustainability issues in the textiles industry have often been tackled in industry by tinkering and incremental change

- **Step-change solutions are needed to bring about truly sustainable apparel and footwear products**

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Further Reading…

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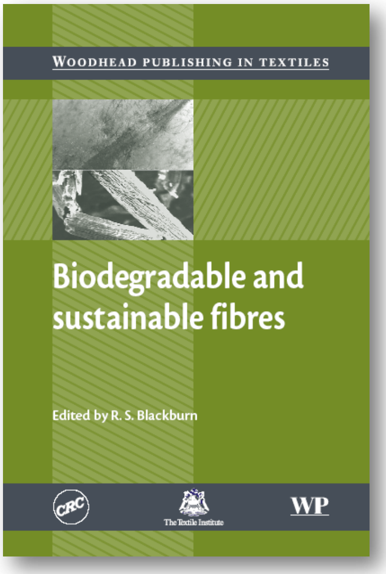

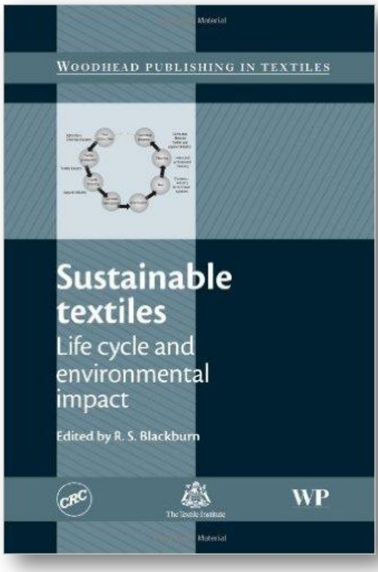

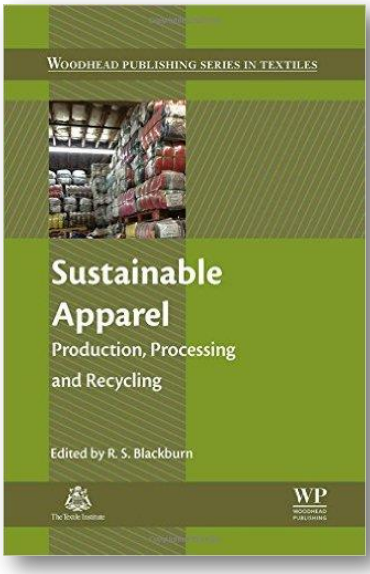

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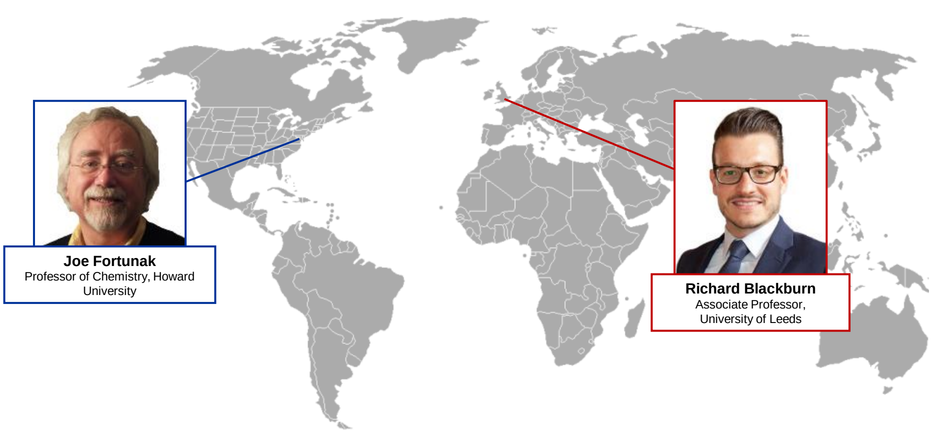

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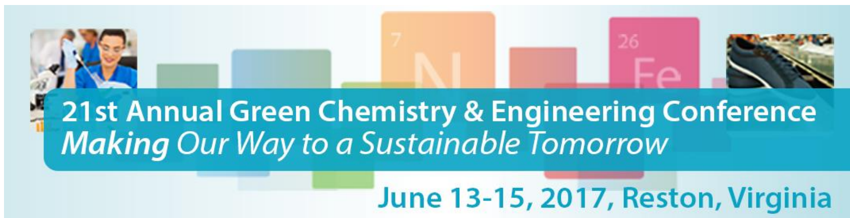

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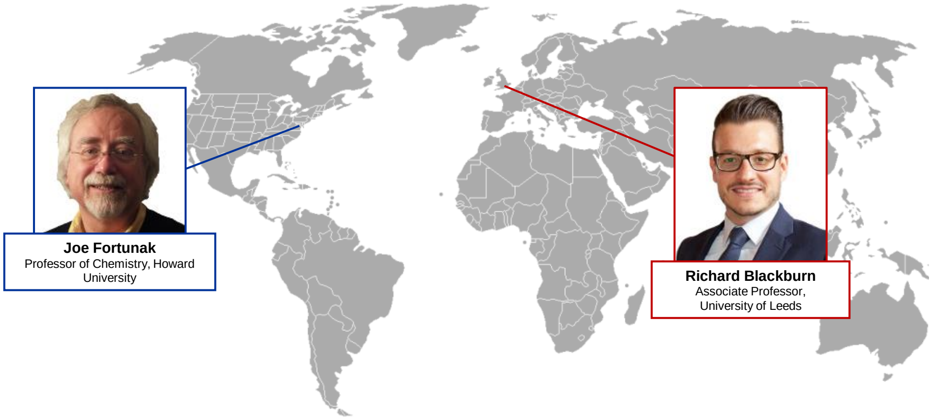

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- How green chemistry and nanoscience can be used together to develop innovative new products with environmental benefits

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