PRESENTATION

Session: **Sustainability from a Technical View**

Title: **Biodegradation Performance of Dyed and Finished Cotton in Various Natural Environmental Settings**

Speaker: **Mary Ankeny,** Cotton Incorporated, Cary, NC, USA

Presentations are available in the conference archive: https://baumwollboerse.de/en/competencies/international-cotton-conference/speeches/

Conference Organization

Faserinstitut Bremen e.V., Bremen, Germany. E-Mail: conference@faserinstitut.de
Bremer Baumwollboerse, Bremen, Germany. E-Mail: info@baumwollboerse.de









BIODEGRADATION PERFORMANCE OF DYED AND FINISHED COTTON IN VARIOUS NATURAL ENVIRONMENTAL SETTINGS.

By: Mary Ankeny, Cotton Incorporated

International Cotton Conference

September 29, 2022
Bremen, Germany

Presentation Overview

- Basis for this Study
- Study One:
  - Aquatic Degradation of Textile Fibers
- Study Two:
  - Effect of Dyes and Finishes on Aquatic Degradation of Cotton
- Study Three:
  - Effect of Finishes on Cotton's Degradation in Soil
- Study Four:
  - Simulated Landfill Degradation of Cotton

Microplastics, Nanoplastics, and Microfibers

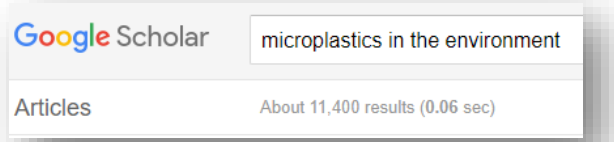
- "Microplastics" first appears in scientific literature in 2004 [1] (as an environmental pollutant) however a clear definition is not provided


BREVIA

Lost at Sea: Where Is All the Plastic?

Richard C. Thompson,[1]* Ylva Olsen,[1] Richard P. Mitchell,[1] Anthony Davis,[1] Steven J. Rowland,[1] Anthony W. G. John,[2] Daniel McGonigle,[3] Andrea E. Russell[3]

- Over 61,000 scientific journal articles published to date



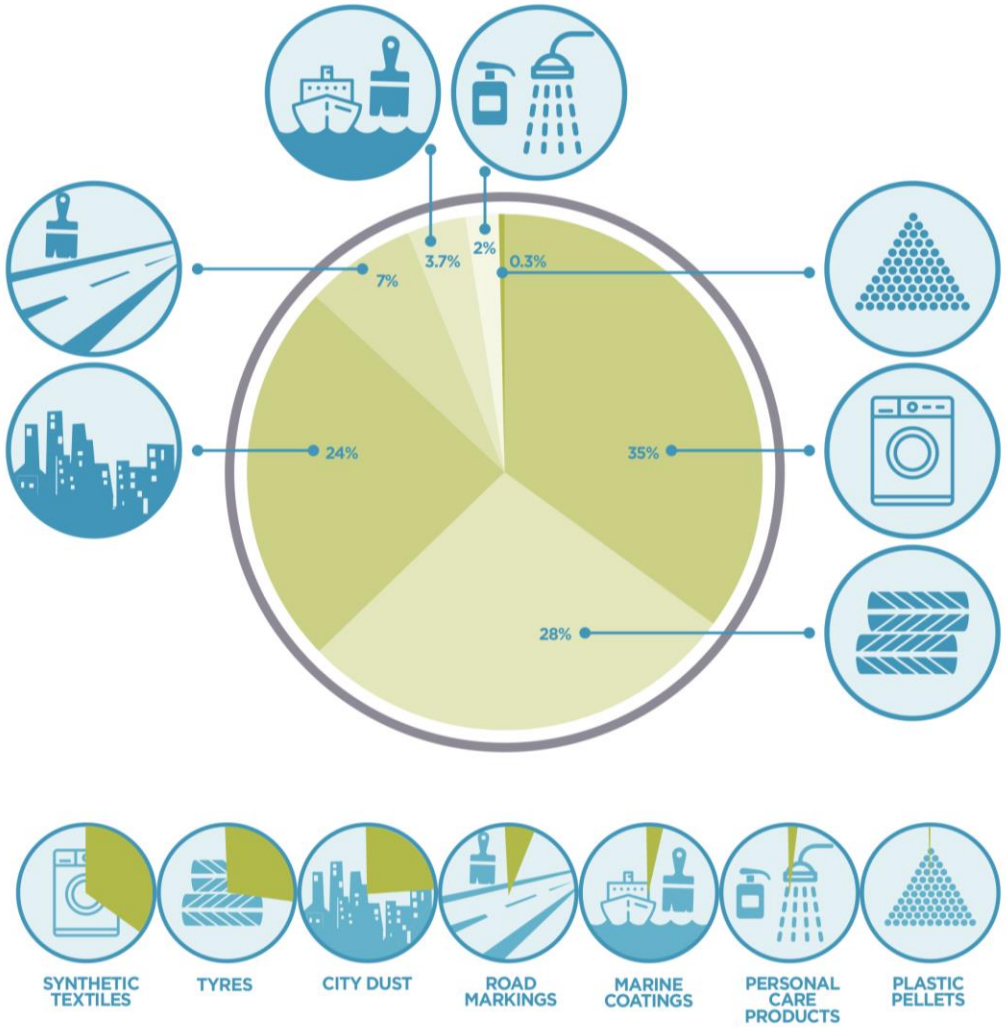
- **Microplastics** are any synthetic solid particle or polymeric matrix, with regular or irregular shape and with size ranging from 1 µm to 5 mm, of either primary or secondary manufacturing origin, which are insoluble in water [2]

- **Nanoplastics:** same as above but <1 µm [2]

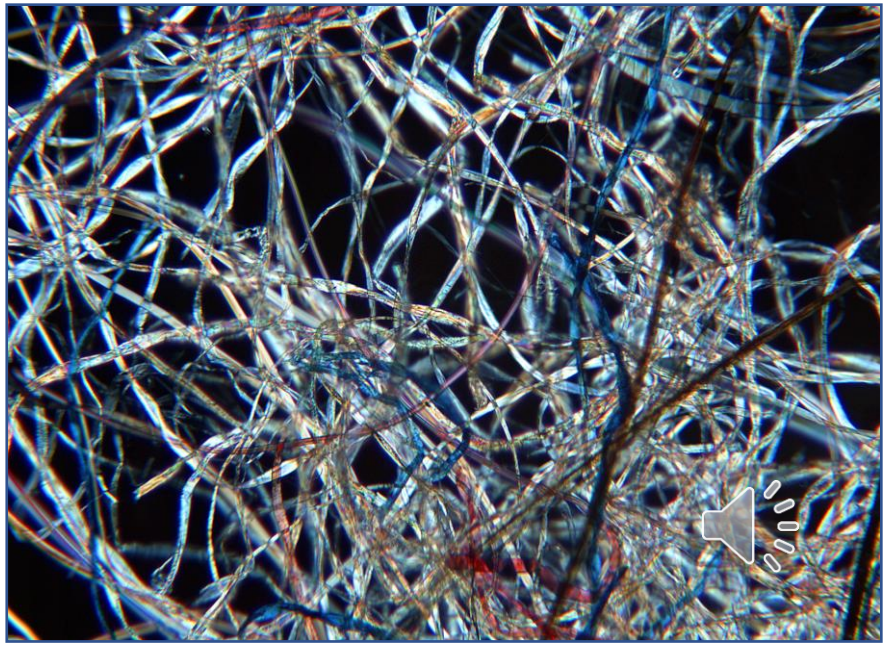
1: Thompson, R. C., Olson, Y., Mitchell, R. P., Davis, A., Rowland, S. J., John, A. W. G., … Russell, A. E. (2004). Lost at Sea: Where Is All the Plastic? Science, 304(5672), 838. https://doi.org/10.1126/science.1094559
2: Frias, J. P. G. L., & Nash, R. (2019). Microplastics: Finding a consensus on the definition. Marine Pollution Bulletin, 138(November 2018), 145–147. https://doi.org/10.1016/j.marpolbul.2018.11.022

Source: iStock.com/pcess609

Microplastics and Microfibers



- **Microfibers** are synthetic, man-made, and natural fibers (<5 mm) released from fabrics during laundering [1] or other physical processes such as wearing the garment

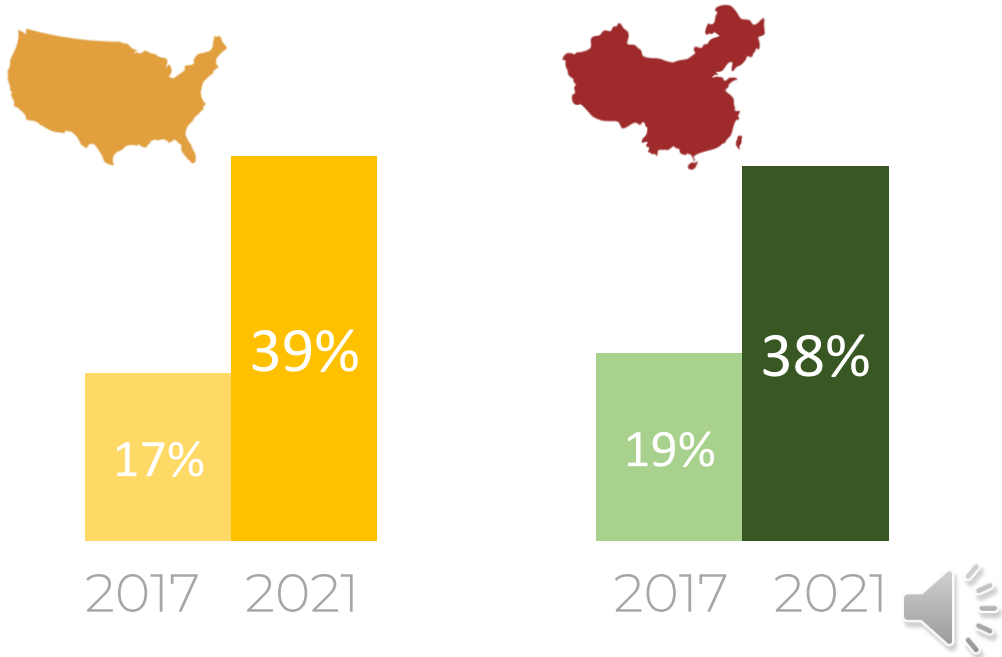


1. https://doi.org/10.1016/j.marpolbul.2019.02.062
2. Chart courtesy of EA and Quantis
3. Fiber image source: iStock.com/dwaugh

Awareness Grows

More consumers are aware of issues in textile production, especially for manmade fibers

Percentage of consumers who are aware of microplastic waste

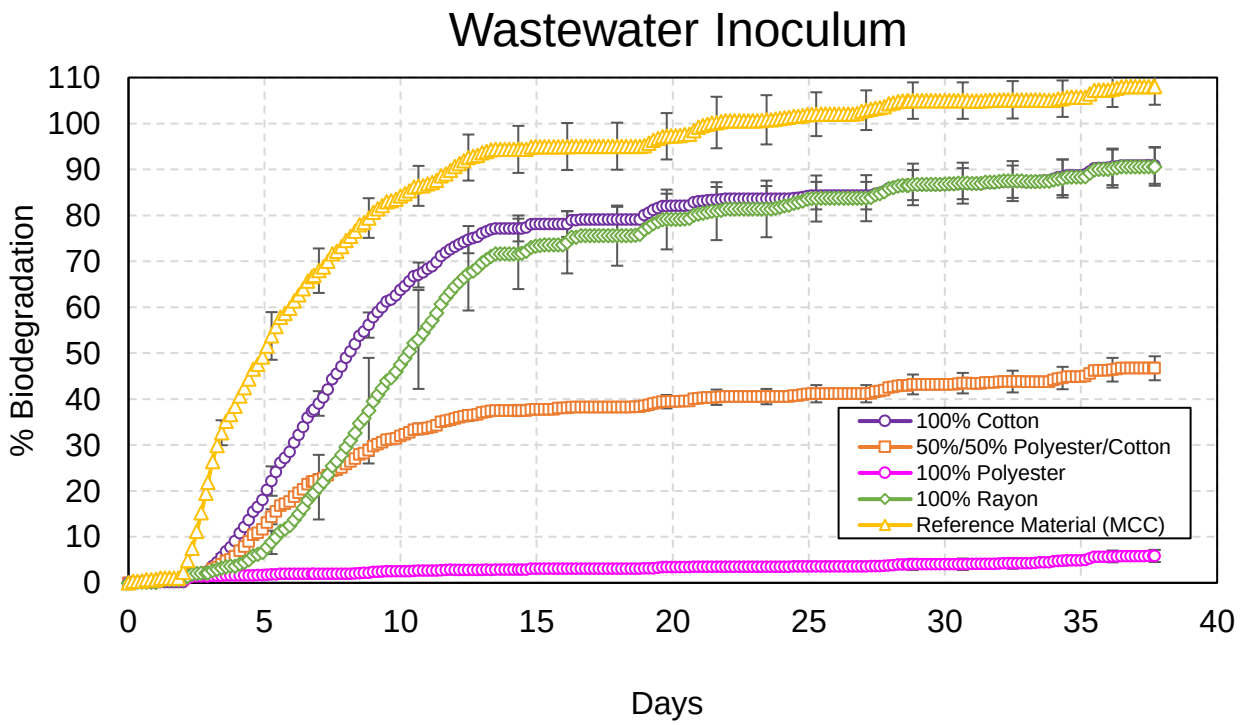


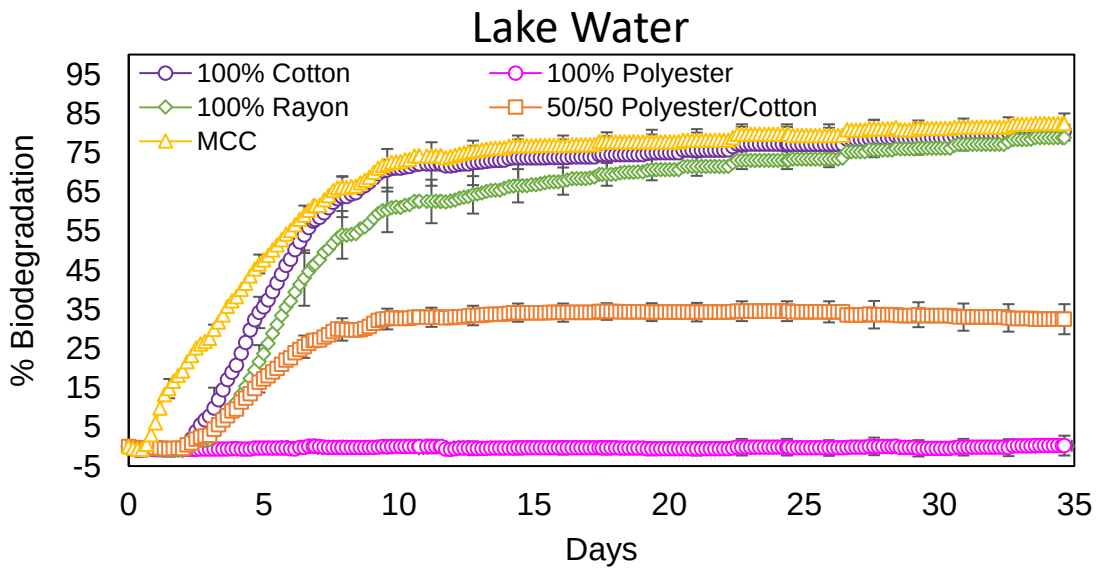
Source: CCI & Cotton Incorporated's 2017 and 2021 Global Sustainability Survey

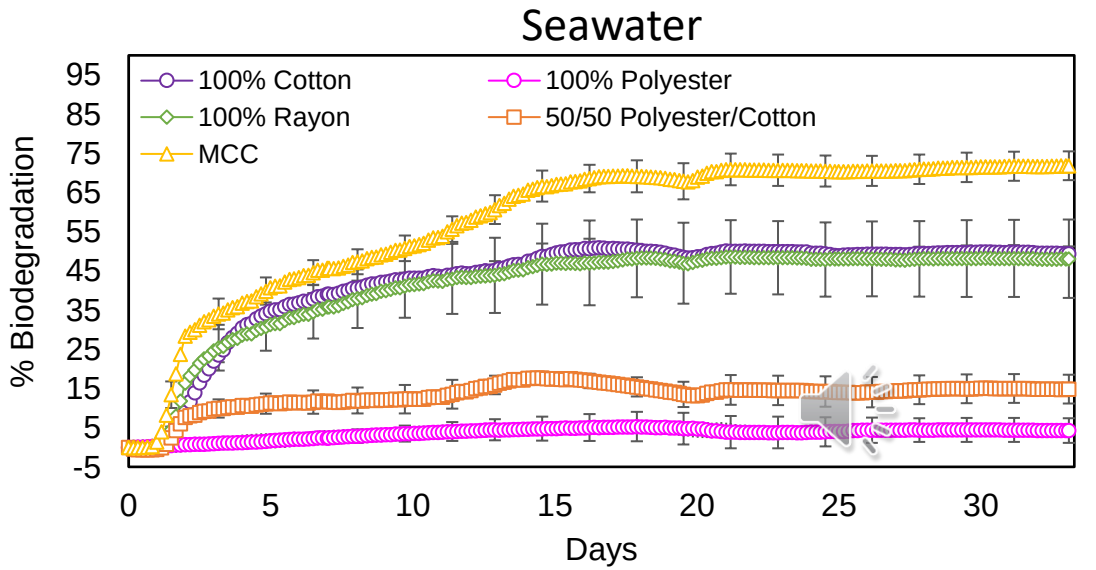
COTTON USA™

cotton®

Study 1: Aquatic Biodegradation of Textile Fibers







Zambrano, M.; Pawlak, J.; Daystar, J.; Ankeny, M.; Chen, J. J.; Venditti, R. Microfibers Generated from the Laundering of Cotton, Rayon and Polyester Based Fabrics and Their Aquatic Biodegradation. Mar. Pollut. Bull. 2019,

Aquatic Biodegradation of Textile Fibers from Spun Yarns

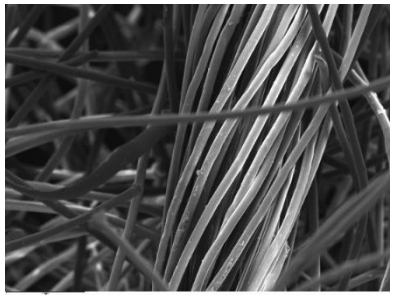
Biodegradation of textile yarns in different aquatic environment Plateau Phase Mean ± Standard Error			
Samples	**Biodegradation (%)**		
	Neuse River WWTP*	**Lake Water**	**Seawater**
MCC (Reference Material)	108.06 ± 0.04	79.63 ± 0.18	70.94 ± 0.38
100% Cotton Spun Yarns	90.88 ± 0.04	77.15 ± 0.37	49.3 ± 0.15
100% Rayon Spun Yarns	90.59 ± 0.04	73.43 ± 0.24	48.16 ± 0.93
50/50 Polyester/Cotton Spun Yarns	46.72 ± 0.03	33.86 ± 0.22	14.57 ± 0.36
100% Polyester Spun Yarns	5.83 ± 0.01	Not Appreciable	4.23 ± 0.34

*Prior to subtraction of nitrification reaction

Biodegradation in Lake Water

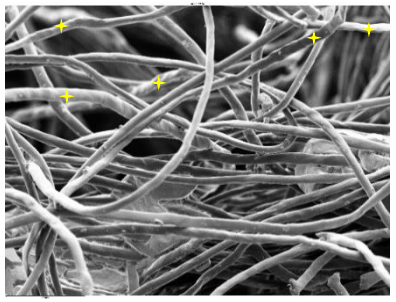
50/50 Polyester/Cotton Yarns

100% Polyester Yarns

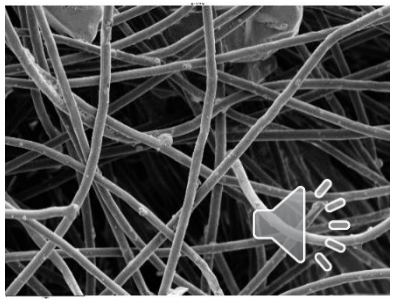


Biodegradation in Seawater

50/50 Polyester/Cotton Yarns



100% Polyester Yarns

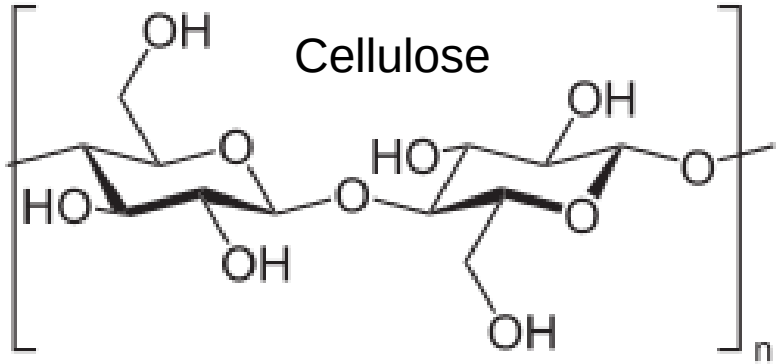


SEM images of residual solids after biodegradation experiments

Study 2: Effect of Dyes and Finishes on the Biodegradation of Cotton in Aquatic Environments

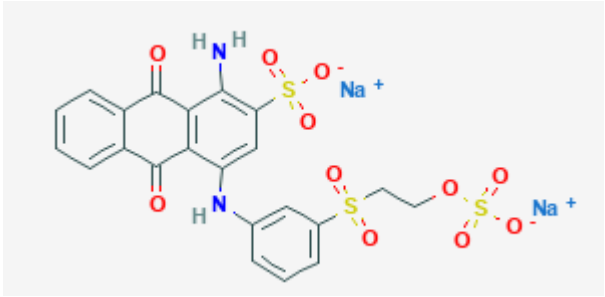
Hypothesis:

Cotton microfibers treated with typical dyes and finishes biodegrade in aquatic environments



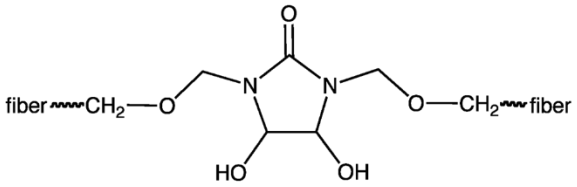
Cotton – Dyed

Reactive Blue 19



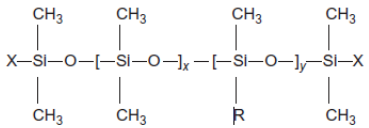
Cotton – Durable Press

DMDHEU & Catalyst



Cotton – Softener

Modified amino functional silicone



(A) $R = C_3H_6NH_2$

(B) $R = C_3H_6NHC_2H_4NH_2$

Cotton – Water Repellent

C6 & PBI

Non-PFOA fluorochemical

Polyfunctional blocked isocyanate crosslinker

Marine Pollution https://doi.org/10.1016/j.marpolbul.2021.112030

Study 2: Effect of Dyes and Finishes on the Biodegradation of Cotton Fabrics in Aquatic Environments

Samples

- Blank
- Cotton – No Finish
- Cotton – Dyed (Blue 19)
- Cotton – Durable Press
- Cotton Softener
- Cotton – Water Repellent
- Plant Material
- Reference Microcrystalline Cellulose

Inoculum

Activated Sludge
Neuse River WWTP, NC
ISO 14851

Lake Water
Lake Raleigh, NC
ISO 14851

Seawater
Wilmington, NC
ASTM D6691

Biodegradation Measurements

http://www.envitreat.com/rsa/

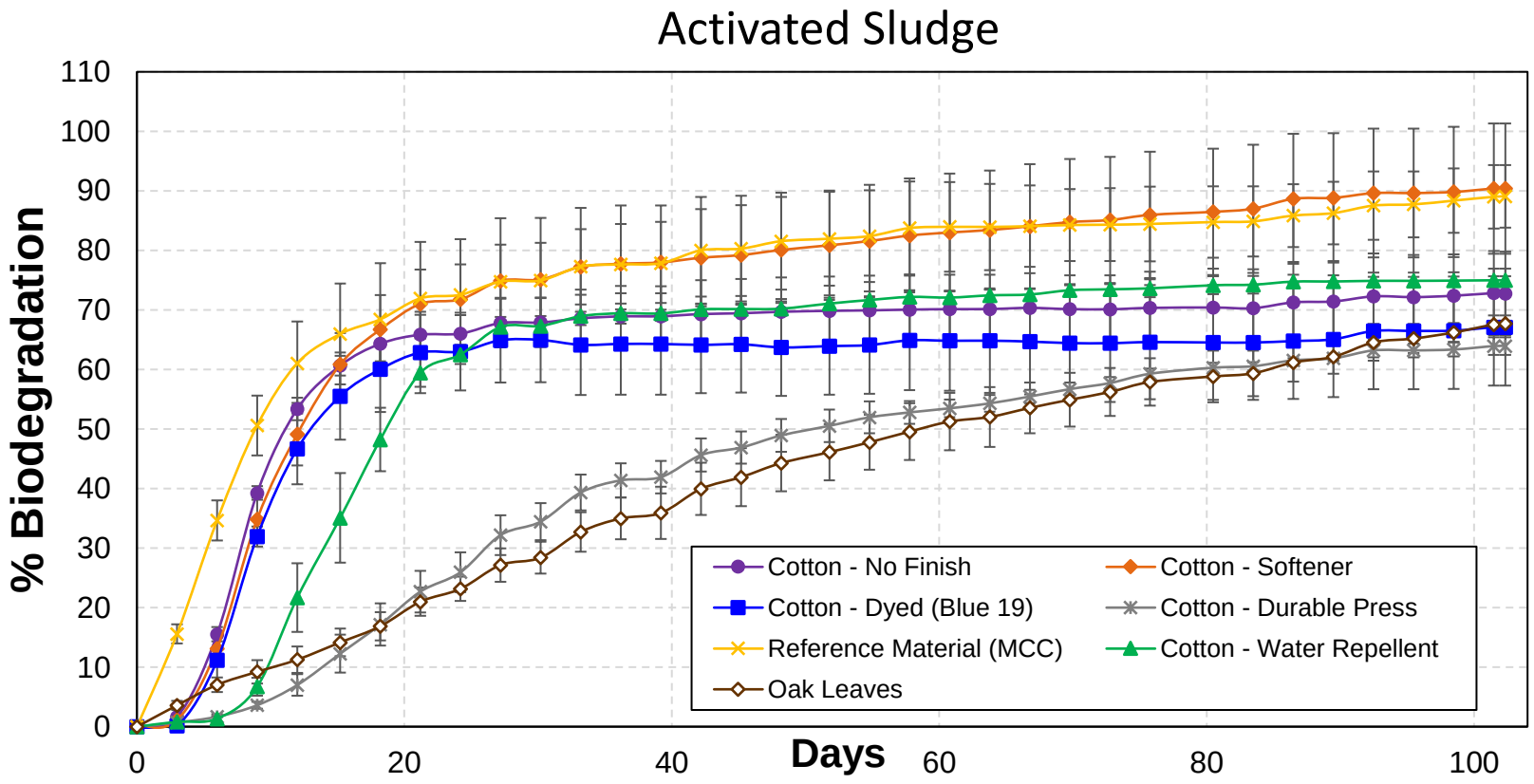
Respirometer System
RSA PF-8000

$$\% \text{ Biodegradation} = \frac{\text{Ou}}{\text{ThOD}} * 100$$

Ou - Oxygen Uptake
ThOD - Theoretical Oxygen Demand

ISO 14851:1999. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium -- Method by measuring the oxygen demand in a closed respirometer; 2005.
ASTM D6691 − 09. Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium; West Conshohocken, PA, 2009.

Study 2: Effect of Dyes and Finishes on the Biodegradation of Cotton Fabrics in Aquatic Environments



ISO 14851

Determination of the Ultimate Aerobic Biodegradability of Plastic Materials in an Aqueous Medium

N=3 all materials, except Oak Leaves (N=2)

Measurements – RSA PF-8000 (Oxygen Uptake)

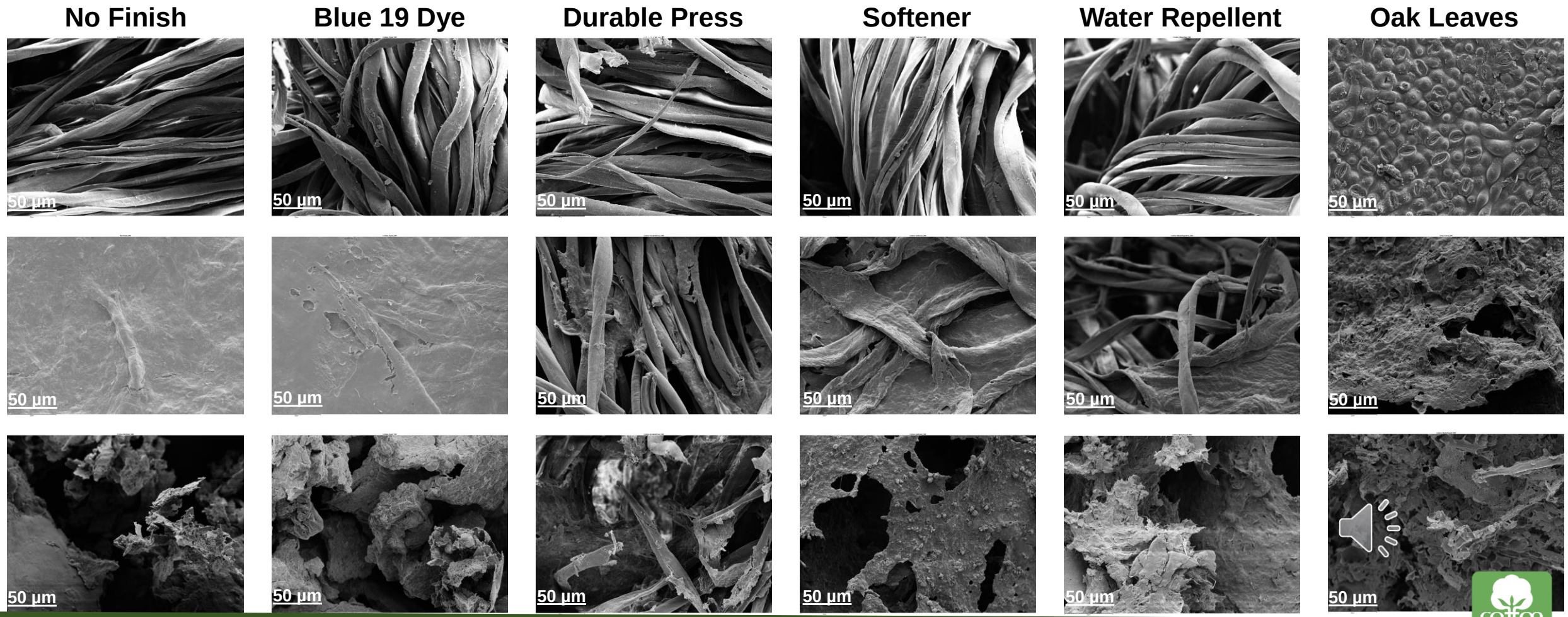
Material Added – 100 mg of yarns/500 ml Test Medium

ISO 14851:1999. Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium -- Method by measuring the oxygen demand in a closed respirometer; 2005.

Marine Pollution https://doi.org/10.1016/j.marpolbul.2021.112030

Study 2: Effect of Dyes and Finishes on the Biodegradation of Cotton Fabrics in Aquatic Environments

SEM images of the fibers during biodegradation using as inoculum 30 ppm of Activated Sludge solids from the Neuse River WWTP



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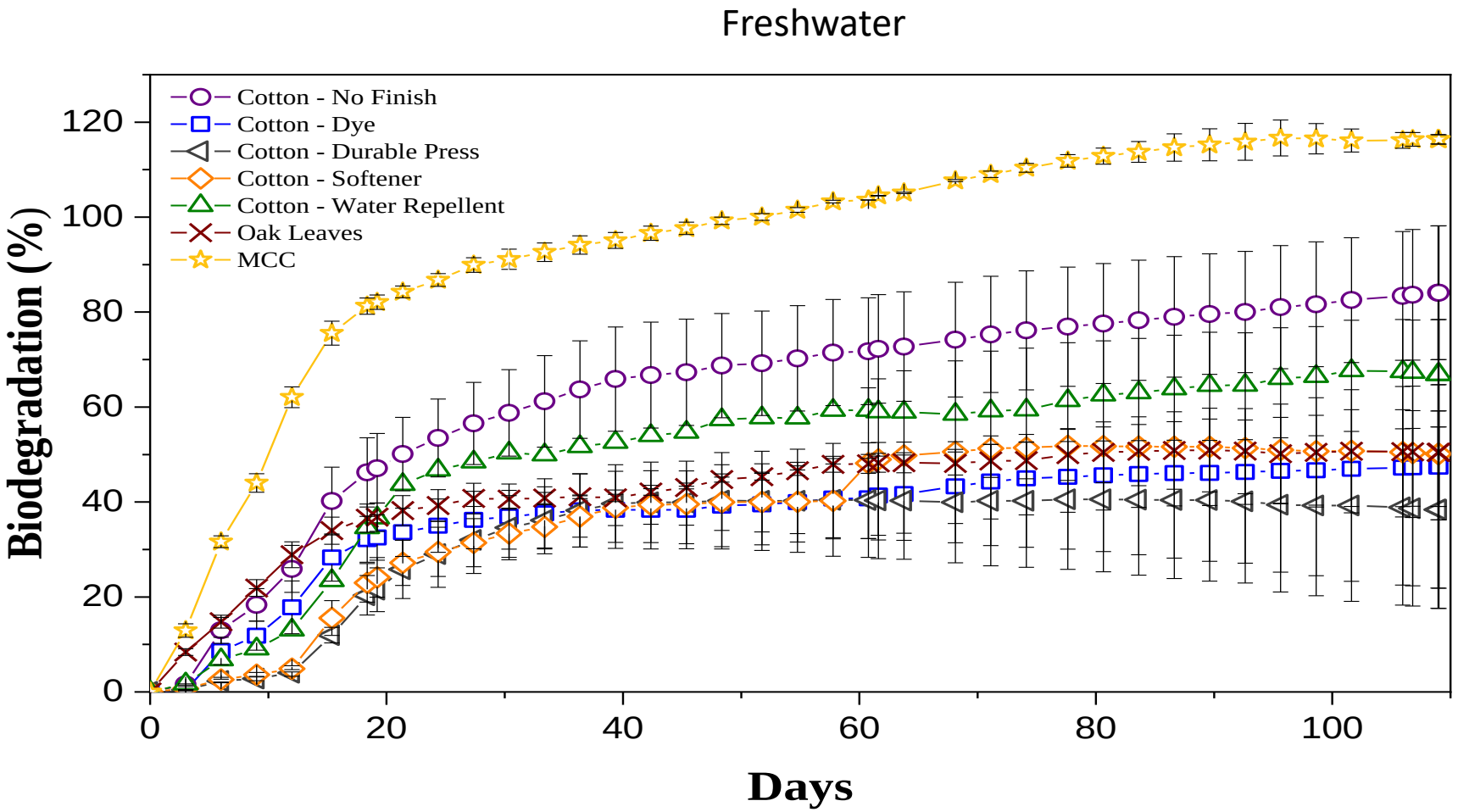

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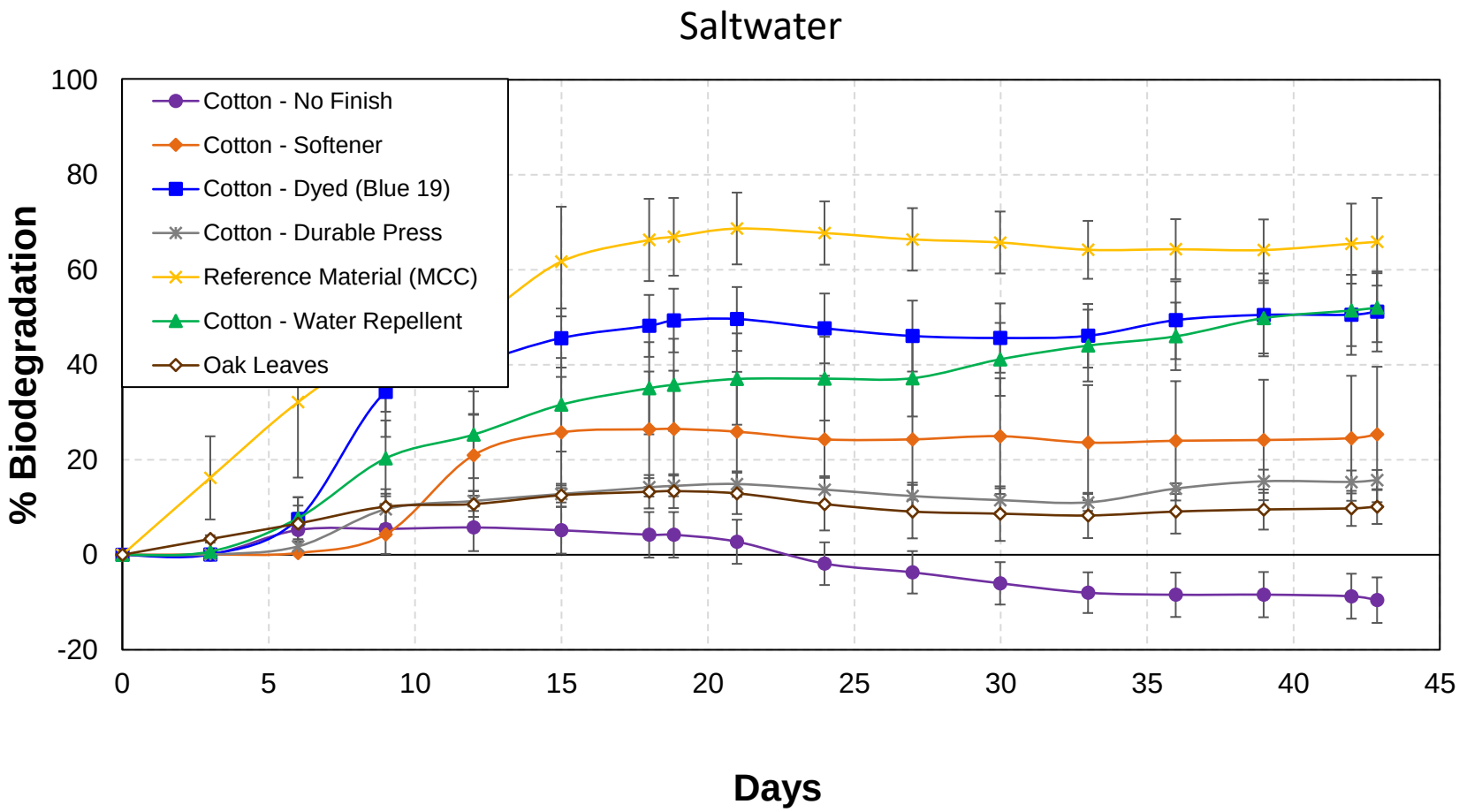

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Marine Pollution https://doi.org/10.1016/j.marpolbul.2021.112030

Summary of Freshwater and Seawater Inoculum

- The freshwater inoculum showed good activity during the experiment. MCC degraded completely during the 109 days of experiment.
- The finishes also affect the biodegradability in lake water conditions:
  - The control microfibers (no finish) degraded by 84%, followed by: water repellent (67%), softener (50%), dyed (47%), and durable press (38%).

- The seawater inoculum showed good activity for most of the samples in the study. MCC degraded > 60% during the 44 days of the experiment.
- The finishes also affect the biodegradability in seawater conditions:
  - The control cotton (no finish) did not degrade. This trial is being repeated
  - The other fibers degraded: water repellant (52%), dyed (51%), softener (25%), durable press (16%).

Marine Pollution https://doi.org/10.1016/j.marpolbul.2021.112030

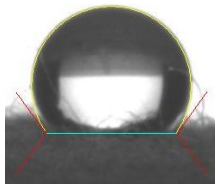
Effect of Finishes on Cotton Biodegradation in Aquatic Environments

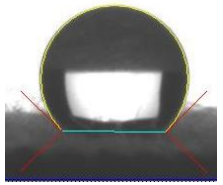
Surface Properties/Characteristics Related with Biodegradation

Surface Chemical Composition by XPS

Sample	C 1s (%)	O 1s (%)	Si 2p (%)	F 1s (%)	N 1s (%)	Cl 2p (%)
No Finish	66	34	0	0	0	0
Dyed	63	35	2	0	0	0
Durable Press	64	33	0	0	2	1
Softener	54	37	9	0	0	0
Water Repellent	42	8	0	50	0	0

Water Absorbency of Textiles and Hydrophilicity

Softener 

Water Repellent 

Sample	Wet-out Time N=5	Water Contact Angle N=3
No Finish	Zero	NA
Dyed	Zero	NA
Durable Press	Zero	NA
Softener	3.5±0.6 s	127°±1°
Water Repellent	60 + s	134°±1°

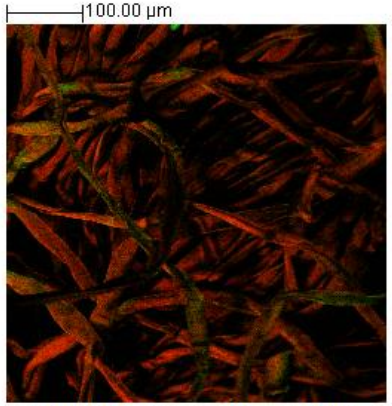
Aquatic Biodegradability of Textile Materials: Impact of Dyes and Finishes Project Number: 19-936 2020 Annual Report. M. Zambrano, R.Venditti, and J.Pawak. Forest Biomaterials Department, North Carolina State University

Effect of Finishes on Cotton Biodegradation in Aquatic Environments

Surface Properties/Characteristics Related with Biodegradation

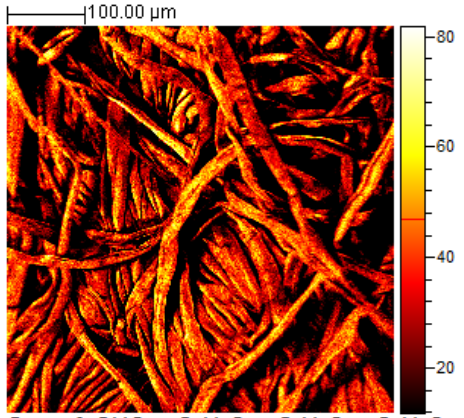
Distribution of Finishes of the Surface of the Fabric by ToF SIMS

Blue 19 (Dye)



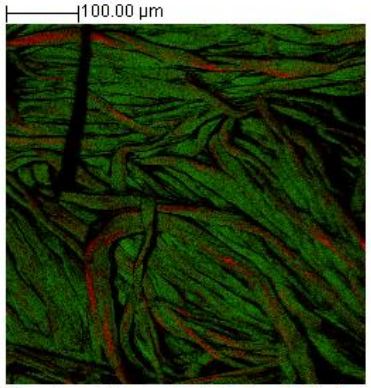
Overlay of Sum of: CHO_2-, $C_2H_3O_2$-, $C_3H_3O_2$-, $C_4H_3O_3$-, SO_3-,

No Finish



Sum of: CHO_2-, $C_2H_3O_2$-, $C_3H_3O_2$-, $C_4H_3O_3$-
MC: 82; TC: 1.583e+006

Water Repellent



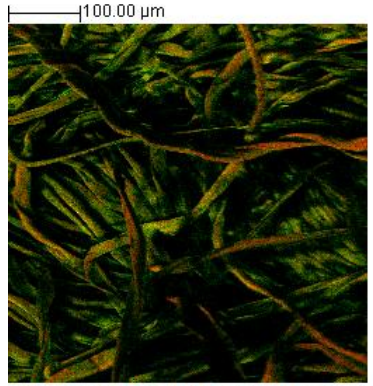
Overlay of Sum of: $C_2H_3O_2$-, $C_2H_3O_2$-, $C_3H_3O_2$-, $C_4H_3O_3$-, C_7F_{11}-,

Durable Press

Overlay of Sum of: $C_2H_3O_2$-, $C_3H_3O_2$-, $C_4H_3O_3$-, CHO_2-, CN-,

Red - Cellulose
Green - Finishes

Softener



Overlay of Sum of: CHO_2-, $C_2H_3O_2$-, $C_3H_3O_2$-, $C_4H_3O_3$-, Sum of: $SiC_5H_{13}O_3$-, $Si_2C_7H_9O$-, $Si_3C_5H_{15}O_4$-,

Aquatic Biodegradability of Textile Materials: Impact of Dyes and Finishes Project Number: 19-936 2020 Annual Report. M. Zambrano, R.Venditti, and J.Pawak, Forest Biomaterials Department, North Carolina State University

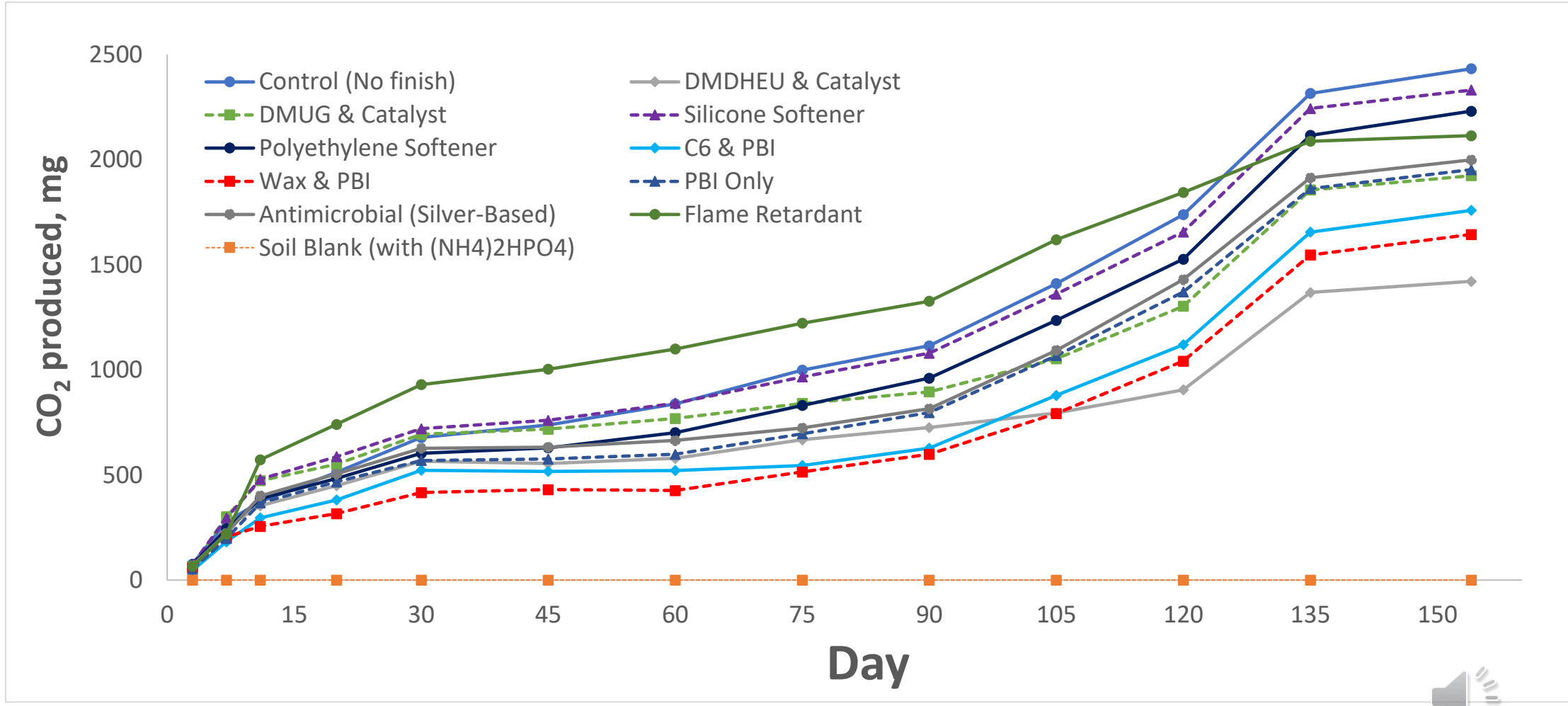
Study 3: Effect of Finishes on Cotton's Degradation in Soil

Composting simulation study conducted at Cornell University

Soil Blank	Wax + PBI
Control (no finish)	C6 +PBI
Polyethylene Softener	Antimicrobial (silver based)
Silicone Softener	DMDHEU + Catalyst
Partially Blocked Isocyanite (PB)	DMUG + Catalyst
	Flame Retardant

Smith, S., Ozturk, M. & Frey, M. Soil biodegradation of cotton fabrics treated with common finishes. *Cellulose* **28**, 4485–4494 (2021). https://doi.org/10.1007/s10570-020-03666-w

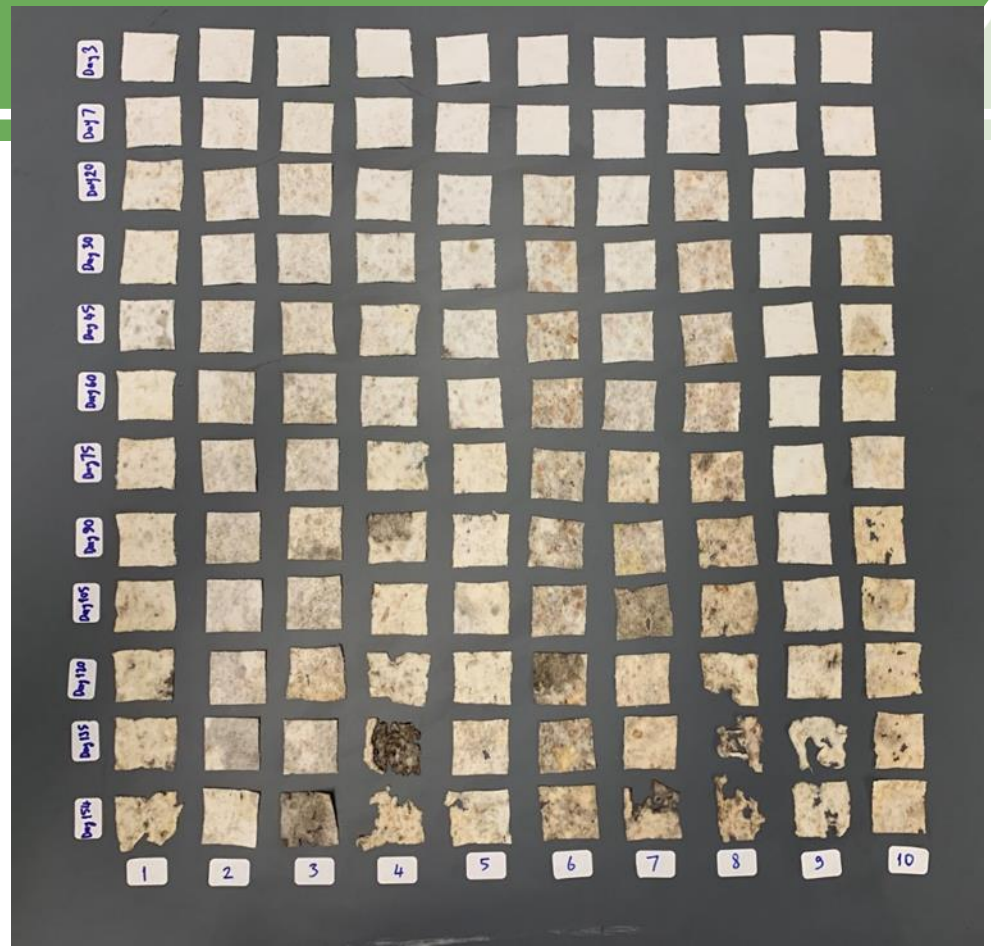
Study 3: Effect of Finishes on Cotton's Degradation in Soil



Smith, S., Ozturk, M. & Frey, M. Soil biodegradation of cotton fabrics treated with common finishes. *Cellulose* **28**, 4485–4494 (2021). https://doi.org/10.1007/s10570-020-03666-w

Summary of Compost Study

- By appearance
  - PBI Only, Wax & PBI, and Silicone softener look **most** degraded after 154 days
  - DMDHEU & Catalyst and Flame Retardant look **least** degraded after 154 days
- By weight loss
  - PBI Only, Silicone Softener, and Antimicrobial lost the **most** weight
  - DMDHEU & Catalyst and DMUG & Catalyst lost the **least** amount of weight
- By total CO2 production
  - Control, Silicone softener, and Polyethylene softener produced the **most** CO_2 after 154 days
  - DMDHEU & Catalyst and Wax & PBI produced the **least** CO_2 after 154 days



1) Control
2) DMDHEU & Catalyst
3) DMUG & Catalyst
4) Silicone Softener
5) Polyethylene Softener
6) C6 & PBI
7) Wax & PBI
8) PBI Only
9) Antimicrobial
10) Flame Retardant

Smith, S., Ozturk, M. & Frey, M. Soil biodegradation of cotton fabrics treated with common finishes. *Cellulose* **28**, 4485–4494 (2021). https://doi.org/10.1007/s10570-020-03666-w

U.S. Disposal Statistics: Textile Waste

istock photo: Ziga_Plahutar

In 2018 the U.S. generated
17 Million Tons of Textile Waste

Of that waste

11.3 Million Tons were Landfilled

Clothing and Footwear Subset

- Generated: 13 M Tons
- Landfilled: 9.1 M Tons
- Recycled: 1.7 M Tons
- Incinerated: 2.2 M Tons

https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/nondurable-goods-product-specific-data#ClothingandFootwear

Study 4: Simulated Landfill Environment Decomposition

Objectives:

1. Determine if cotton fabric, that has been dyed and finished, will decompose in a simulated landfill environment.

2. Determine if polyester fabric will decompose in a simulated landfill environment.

Anaerobic Decomposition of Cotton Fabric Under Simulated Landfill Conditions, Project Number: 20-705 2020 Annual Report. Komal Charania, Dr. Florentino de la Cruz, and Dr. Morton A. Barlaz - all NC State University

istock photo: tarras79

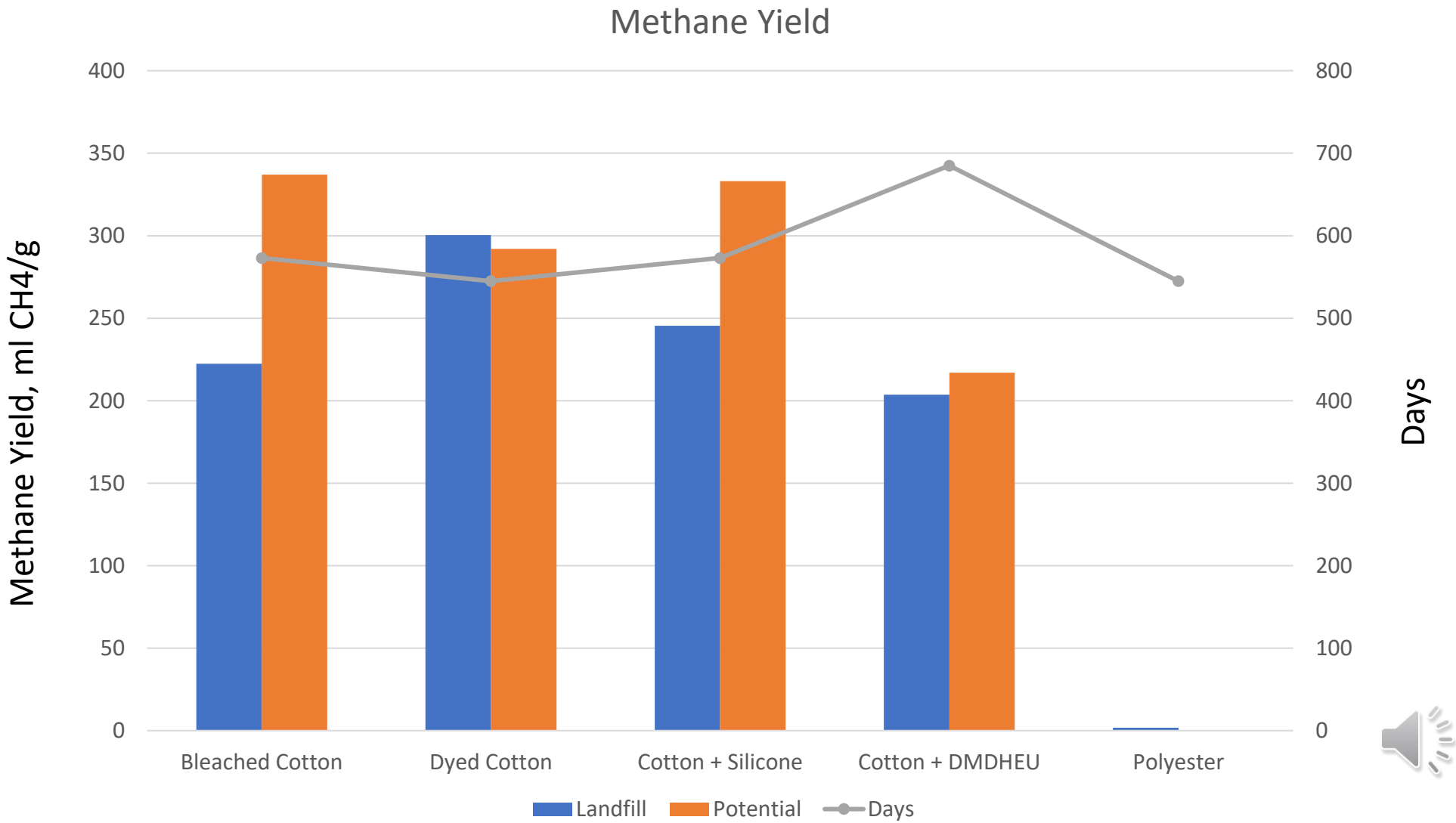
Study 4: Simulated Landfill Environment Decomposition

Samples Tested

Treatment	Description
1	inoculum + dyed cotton fabric (Reactive Black 5)
2	inoculum + bleached cotton fabric
3	inoculum + cotton fabric with silicone softener finish
4	inoculum + cotton fabric with durable press finish (DMDHEU)
5	inoculum + polyester fabric
6	inoculum (background methane)

Anaerobic Decomposition of Cotton Fabric Under Simulated Landfill Conditions, Project Number: 20-705 2020 Annual Report. Komal Charania, Dr. Florentino de la Cruz, and Dr. Morton A. Barlaz - all NC State University

Study 4: Simulated Landfill Environment Decomposition



Anaerobic Decomposition of Cotton Fabric Under Simulated Landfill Conditions, Project Number: 20-705 2020 Annual Report. Komal Charania, Dr. Florentino de la Cruz, and Dr. Morton A. Barlaz - all NC State University

Preliminary Summary of Landfill Study

- All cotton fabrics underwent biodegradation in the simulated landfill environment.
- Similar to other environments, the cotton with the DMDHEU finish degraded more slowly than its counterparts.
- The polyester fabric did not degrade and behaved similar to the blank.

Anaerobic Decomposition of Cotton Fabric Under Simulated Landfill Conditions, Project Number: 20-705 2020 Annual Report. Komal Charania, Dr. Florentino de la Cruz, and Dr. Morton A. Barlaz - all NC State University

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Product Evaluation Lab
Color Services Lab

Mary Ankeny, MSc
Dr. Jesse Daystar

Australian Government
Cotton Research and Development Corporation

Cornell University

Dr. Margaret Frey
Dr. Mehmet Ozturk

NC STATE UNIVERSITY Bio&Ag ENGINEERING

Environmental Analysis Lab

Dr. Jay Chen
Dr. Cong Tu

CCEE NC STATE UNIVERSITY

Dr. Morton Barlaz
Dr. Florentino de la Cruz

BIOTECHNOLOGY NC STATE UNIVERSITY

Dr. Carlos Goller
Dr. Robert M. Kelly