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“Riding the Wave of Green Chemistry: How to Enhance Awareness of Plastics in the Ocean”

Jane Wissinger
Professor of Chemistry, University of Minnesota, and Senior Principle Investigator, Center for Sustainable Polymers

Reuben Hudson
Research Professor, Colby College

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This ACS Webinar is co-produced with ACS Green Chemistry Institute, ACS Professional Education, and Chemists Celebrate Earth Week
Riding the Wave of Green Chemistry: How to Enhance Awareness of Plastics in the Ocean

Jane E. Wissinger
University of Minnesota
Reuben Hudson
Colby College

Overview

• Experiments developed for the K-12 & college curriculum which introduce:
  – Plastics in society
  – Polymer basics
  – Green/sustainable chemistry solutions
  – (New) sustainable materials

• Feedback from students/teachers

• Resources
Today, how many kilograms of plastics does an average person in North America consume each year?

- 5 kg (11 lbs)
- 25 kg (55 lbs)
- 50 kg (110 lbs)
- 75 kg (165 lbs)
- 100 kg (220 lbs)

Plastics in Society – Attention Grabbers

World Economic Forum: “Rethinking the future of plastics” January 2016

- Today, **95% of plastic packaging** material value, or $80-120 billion annually, is **lost to the economy after a short first use**.

- More than 40 years after the launch of the first universal recycling symbol, only **14% of plastic packaging is collected for recycling**.

- In a business-as-usual scenario, the ocean is expected to contain 1 ton of plastic for every 3 tons of fish by 2025, and **by 2050, more plastics than fish (by weight)**.

http://www3.weforum.org/docs/WEF_The_New_Plastics_Economy.pdf

Plastics in the Ocean – Attention Grabbers

- Currently 250 million metric tons of plastic in the ocean; 5 trillion pieces

- Hazardous to marine life

- Studies show birds are ingesting (Midway-CNN video report)

- Studies show fish are ingesting

- We are ingesting marine life with microplastics

https://cen.acs.org/materials/polymers/Fighting-ocean-plastics-source/96/16
Plastics in the Ocean

Sperm Whale had 64 pounds of plastic & waste in its stomach

- Typical diet of giant squid
- This whale:
  - Plastic bags
  - Netting
  - Plastic water container
- Died of peritonitis and rupture of digestive system


POLYMER CHEMISTRY GREEN/SUSTAINABLE CHEMISTRY
Polymer Basics and Unique Properties

**High School**
- Definitions
- Size, variety
- Representations
- Tensile testing
- UV/Smartphone apps

**Higher Education**
- Classification of polymers
- Representations
- Copolymers (block)
- Calculation of $M_n$
- $^1H$ NMR spectroscopy
- IR and $^{13}C$ NMR
- UV spectroscopy

Green Chemistry Solutions

- 12 Principles – Prevent pollution!
- Use of renewable feedstocks
- Safer solvents/reaction conditions
- **Design for degradation** (biodegradable; compostable)

Corn starch or sugar cane $\rightarrow$ lactide $\rightarrow$ polylactide (PLA) $\rightarrow$ consumer product

http://makingsociety.com/2013/08/materialmatters-series-n1-pla-plastic/
Renewable Triblock Polymer Experiment

- Based on publication\(^1\) and modified for organic chemistry laboratory
- Renewable monomers\(^2\)
- Triblock for tunability and discovery-based\(^3\)
- Interesting mechanical properties

Renewable Triblock Polymer Experiment

Day 1: Synthesis of 2 different homopolymers

- Diphenyl phosphate (DFP)
  - 1 M HCl, 2 days, room temp.
  - or
  - 7 days, room temp.

Monomer
- \( \delta \)-deca lactone, \( x = 4 \)
- \( \delta \)-dodeca lactone, \( x = 6 \)

Homopolymer
- poly(\( \delta \)-deca lactone), \( x = 4 \)
- poly(\( \delta \)-dodeca lactone), \( x = 6 \)

Day 2: Triblock formation adding L-Lactide

- Sn(Oct)_2
- 130 °C, 1 hr

L-lactide

Renewable Triblock Polymer Experiment

- Use initiator peaks to approximate \( M_n \) and integrations to determine size of each block polymer
  - IR – distinct C=O
  - \(^{13}\)C NMR – distinct C=O
Renewable Triblock Polymer Experiment

Students design mechanical/physical property testing

• **Flexibility (%) PLLA**

• **Strength** - 1 inch x 0.5 inch strip (~0.5 g) could hold 290 g of clamps and others

• **Degradation** - place in aqueous NaOH solution for minutes, retest strength

• **Adhesion**

Dyeing to Degrade: A Bioplastics Experiment

• Renewable, non-toxic components
• Citric acid, glycerol, tapioca root starch
• Three combinations results in three different structural polymers
• FDA approved yellow dye 5 allows degradation studies

<table>
<thead>
<tr>
<th>Sample 1: Starch and Citric Acid</th>
<th>Sample 2: Starch and Glycerol</th>
<th>Sample 3: Glycerol and Citric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Sample 1" /></td>
<td><img src="image2" alt="Sample 2" /></td>
<td><img src="image3" alt="Sample 3" /></td>
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</tbody>
</table>

*manuscript in preparation*
Dyeing to Degrade: A Bioplastics Experiment

- Degradation in aqueous 1 M NaOH (dye stable)
- Release of dye followed by UV Spectrometer or Smartphone App
- Beer’s Law plots, graphing, Le Chatelier’s principles, polymer structures, plastics in society

Polymeric Medical Sutures: An Exploration of Polymers and Green Chemistry

Part 1: Drawing Sutures Using Polycaprolactone (PCL)

Part 2: Tie-Ability and Tensile Strength Testing

Part 3: Testing Degradability of Sutures

Connection:
Absorbable sutures → biodegradable polymers
Non-absorbable sutures → non-degradable polymers


https://csp.umn.edu/labs/
Student Feedback

“I enjoyed learning about renewable and degradable polymers by performing this experiment.” (Fall 2017, 256 responses)

“The material associated with the sustainable polymer experiment enhanced my awareness of plastics in the ocean.” (Spring 2018, 230 responses)

“I think this was an interesting way to introduce the concept of sustainability as increased waste and plastic use is a current issue that is good for us to learn about.” – Ochem student 2014

Green & Sustainable Chemistry Workshop for High School Teachers – Summer 2017

Which green chemistry/sustainability lecture content are you likely to add to your curriculum?

- Pillars of Sustainability
- 12 Principles of Green Chemistry
- Biomimicry
- Plastics in the Environment
- Toxic Release Inventory (TRI) exercise
- Green Chemistry Challenge Awards
- Other
K-12 Outreach: Lobster Shells to Plastic Objects
Of the 320 million tons of plastic produced each year, what percent is sourced from biomass?

- 1 percent
- 2 percent
- 5 percent
- 10 percent
- 25 percent

https://www.european-bioplastics.org/market
Chitin and Chitosan

![Chitin and Chitosan](image)

**Durable Polymer**

![Durable Polymer](image)
Earth Abundant

Inexpensive
Audience Challenge Question

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Which of the following polymers is most expensive (kilogram scale, Alibaba):

- low density poly propylene
- polystyrene
- chitin
- poly lactic acid

Economics of Bioplastics
**Processing – in the lab**


**Processing – in the classroom**

Green Chemistry Perspective

Renewable Resources

Molding Process

Durable Pieces

Compostable

Design For Degradation

Benign Solvent: dilute, aqueous acetic acid

Drying

Chain Extraction

Small, single layer chitosan piece

Small, triple layer chitosan piece

Small, saw dust-filled chitosan piece

Large, single layer chitosan piece
Why we care

How does trash make it to the ocean?

How can the ocean stem tide of trash?
Conclusions: Polymer content for all levels

• Topic **relevant and engaging** to all levels
• **ACS major accreditation** includes macromolecules
• Tunable properties enable **inquiry based pedagogies**
• Exploring mechanical properties covers **engineering principles** (next generation science standards)
• Awareness → Science → Solutions

More to think about

• Reduction of single-use items
• More infrastructure for collecting/recycling waste
• ‘Mining’ oceans for discarded plastic to recycle or recover energy
# Acknowledgements

## Experiment Development:

<table>
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## Funding:

- MN Pollution Control Agency - Green Chemistry & Design Curriculum & Environmental Assistance Program
- Center for Sustainable Polymers (NSF Center for Chemical Innovation)
- Margaret A. Cargill Scholarship Fund (Augsburg College)
- Department of Chemistry, University of Minnesota
- NSF Science, Education and Engineering for Sustainability Fellowship
- Department of Chemistry, Colby College

## Photography Credits:

Jennifer Henderson, Eileen Harvala, Laura Seifert, Samantha Meyer, Amaia Alvarez

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