University at Buffalo
The State University of New York

Valorization of Plastic Waste: Research Advances in Molecular Recycling

Paschalis Alexandridis

Department of Chemical and Biological Engineering
Department of Civil, Structural, and Environmental Engineering (*adjunct*)
New York State Center on Plastics Recycling Research & Innovation
University at Buffalo, The State University of New York (SUNY)

palexand@buffalo.edu
www.cbe.buffalo.edu/alexandridis

Outline

- definition of the problem: too much plastic waste
- negative impacts of plastic
- how we currently recycle plastics: mechanical recycling and chemical recycling
- research to improve recycling of plastic waste: “molecular” (physical) recycling
- molecular recycling of plastics: dissolution/precipitation thermodynamics
- molecular recycling of plastics: polyolefin dissolution kinetics
- molecular recycling of plastics: delamination of multilayer films
- closing remarks

Plastics are useful, even indispensable

Plastics packaging is essential for food safety, storage, distribution, and reduces food waste.

In climate protection polymeric thermal insulators and lightweight engineering plastics contribute to significant energy savings accompanied by reduced emission of the greenhouse gas carbon dioxide.

In health care functional polymers enable controlled drug release, protect humans against bacterial attack, and are components of implants, dental fillings, artificial hips, disposable syringes, blood bags, cosmetics, and numerous medical devices-like sensors.

Durability and safety rely on corrosion protection by coatings which safeguard metals even in a maritime environment.

Polymer membranes are being employed in blood purification by artificial kidneys, water desalination and purification, recovery of metal wastes, separation of chemicals, and even in energy harvesting by means of fuel cells.

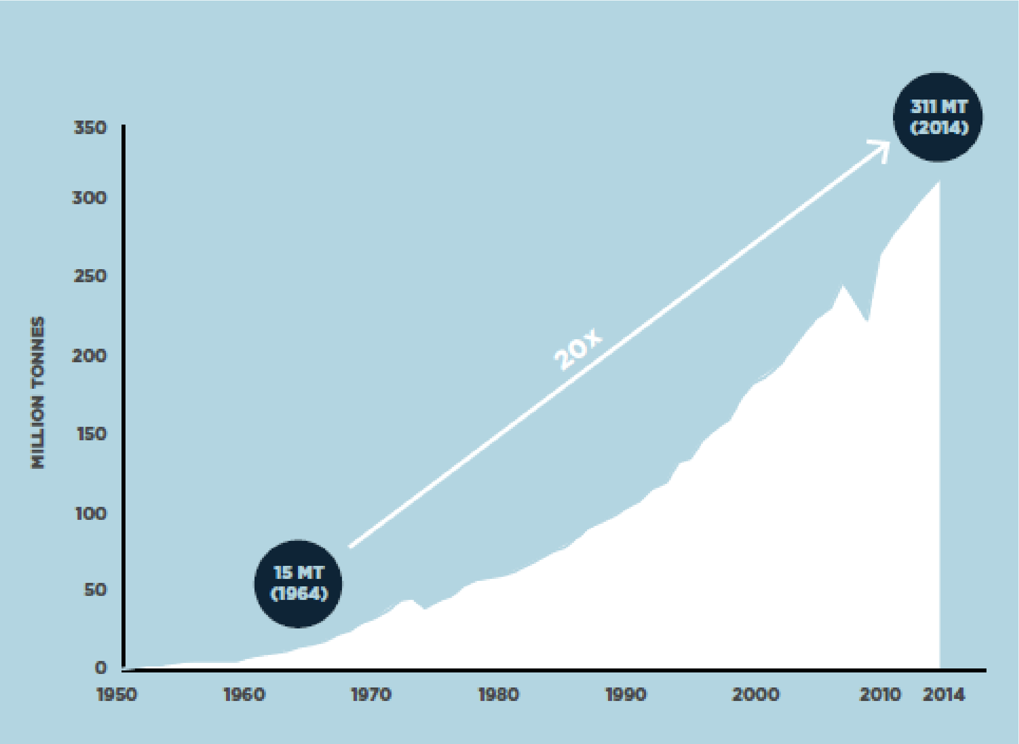
Without polymers as electrical insulators transportation of electrical energy would not be feasible.

Moreover, human comfort and leisure strongly benefits polymer innovations like functional textiles, lightweight engineering plastics, and formulated systems.

Tailoring Hydrocarbon Polymers and All-Hydrocarbon Composites for Circular Economy

We consume a lot of plastic

FIGURE 1: GROWTH IN GLOBAL PLASTICS PRODUCTION 1950–2014



Source: PlasticsEurope, *Plastics – the Facts 2013* (2013); PlasticsEurope, *Plastics – the Facts 2015* (2015).

The growth of plastics consumption closely follows the rapid growth of the world population.

Since people living in developing countries aspire high living standards of industrialized countries the demand for plastics will continue to rise at a rapid pace from around **15 million tons in 1965 and today's 450 million tons (1 trillion pounds)** to well above 1 billion tons in 50 years.

THE NEW PLASTICS ECONOMY:
RETHINKING THE FUTURE OF PLASTICS & CATALYSING ACTION

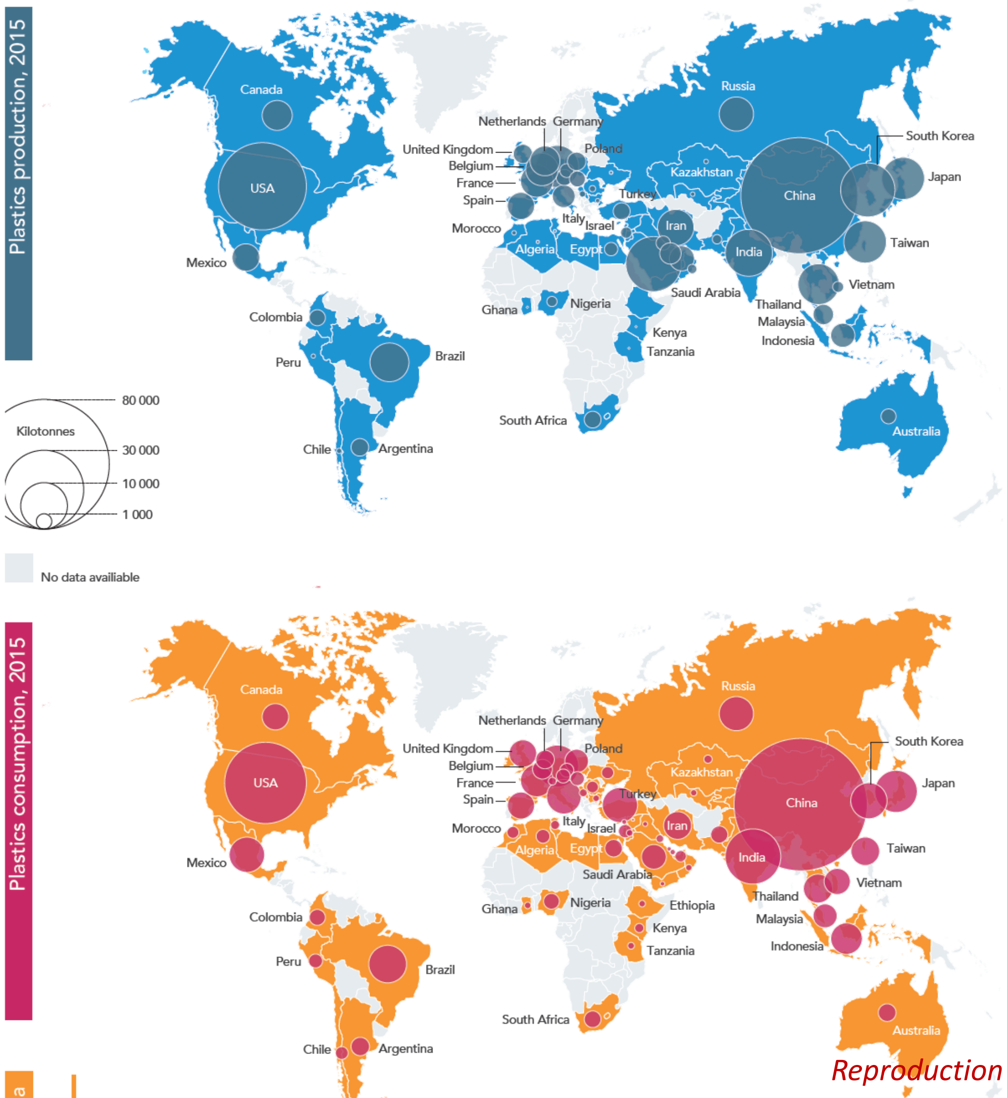
www.ellenmacarthurfoundation.org

Plastic is a global issue

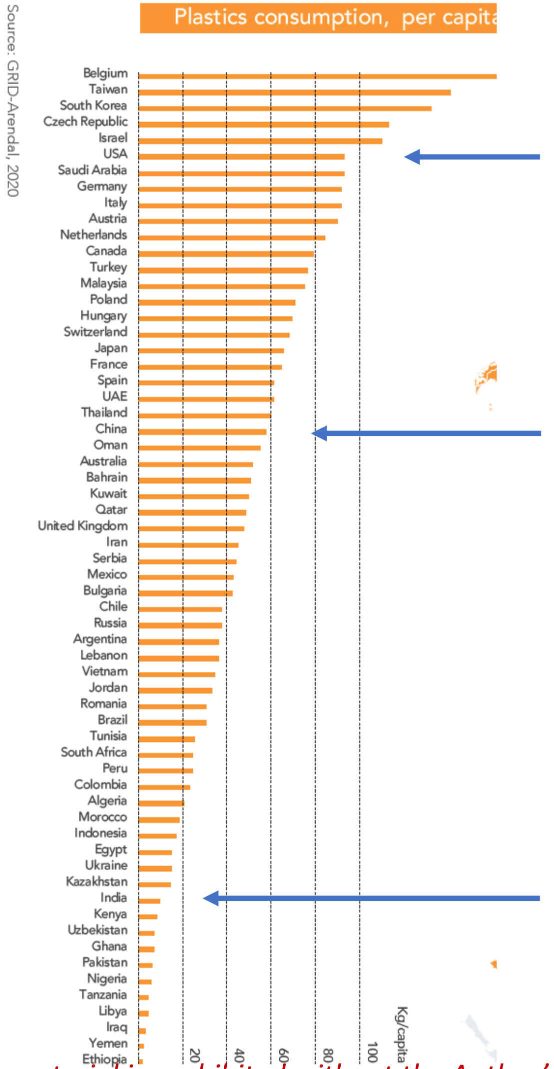
Figure 2 – Global plastics production and consumption

production

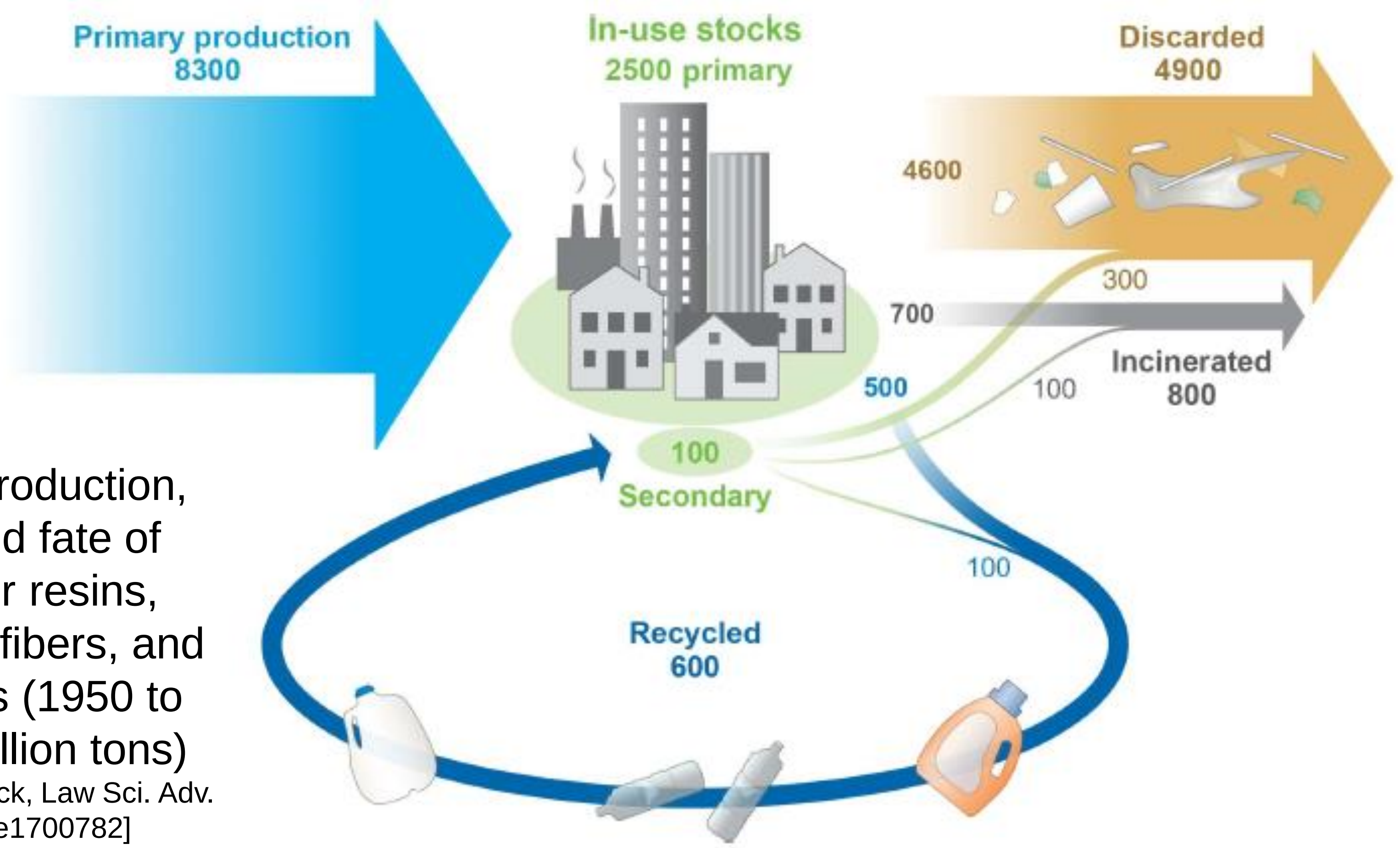
consumption



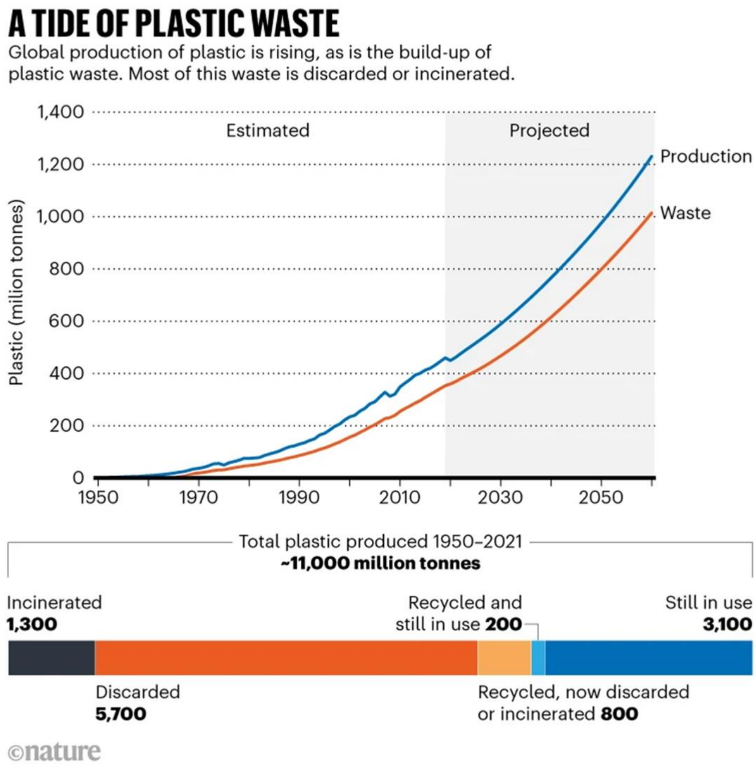
consumption per capita



The majority of plastic is discarded



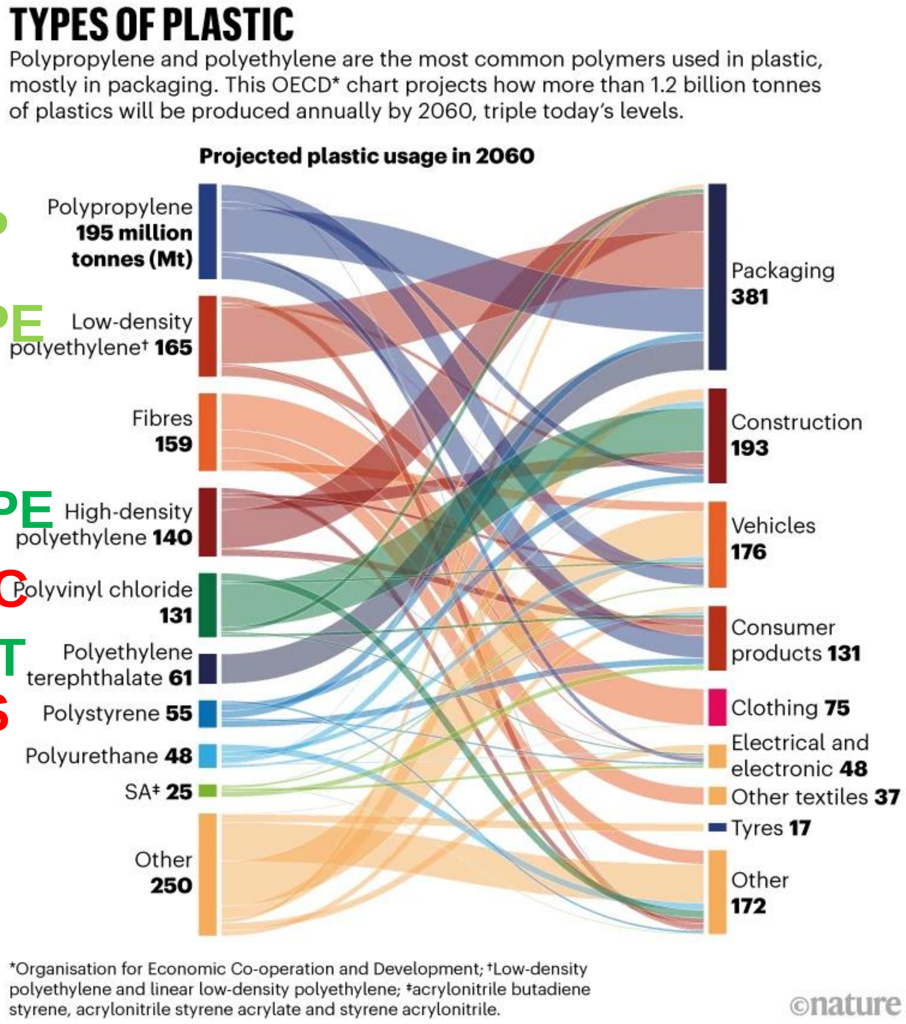
Global production, use, and fate of polymer resins, synthetic fibers, and additives (1950 to 2015; million tons)
[Geyer, Jambeck, Law Sci. Adv. 2017;3: e1700782]



Plastics Recycling

Challenges and Opportunities

Common types of plastics and % recycled in US



	PET	HDPE	PVC	LDPE	PP	PS	
	1 Polyethylene terephthalate	2 High-density polyethylene	3 Polyvinyl chloride	4 Low-density polyethylene	5 Polypropylene	6 Polystyrene	7 Other
Common applications of virgin plastic	Carbonated beverage bottles, water bottles, heatable food trays	Noncarbonated beverage (e.g., milk) containers, grocery bags, household chemical bottles	Pipe, windows, synthetic leather, medical tubing, automotive product bottles	Flexible films (e.g., trash bags, bread bags, dry cleaning garment bags); squeeze bottles	Straws, cups, yogurt containers, ketchup bottles, hangers, automobile battery casings	To-go containers, hot and cold cups, flatware, foam packing, trays for meat or fish	Nylon, polycarbonate, polylactic acid, multilayer packaging, safety glasses, lenses
Mass discarded in US, 2017 (billion kg)	4.54	5.58	0.87	7.33	7.26	2.13	Data not available
Percentage recycled in US, 2017	18.2%	9.4%	Negligible	4.2%	0.6%	0.4%	Data not available
Common applications of recycled plastic	Clothing, carpet, carbonated beverage and water bottles, clamshell containers	Decking, flower pots, crates, pipe, detergent bottles	Pipe, siding, carpet backing, flooring	Trash bags, decking, shipping envelopes, compost bins	Paint cans, speed bumps, plant pots, toothbrush holders, hangers	Picture frames, crown molding, tape dispensers, hangers, toys	Electronic housings, auto parts

Plastics Recycling

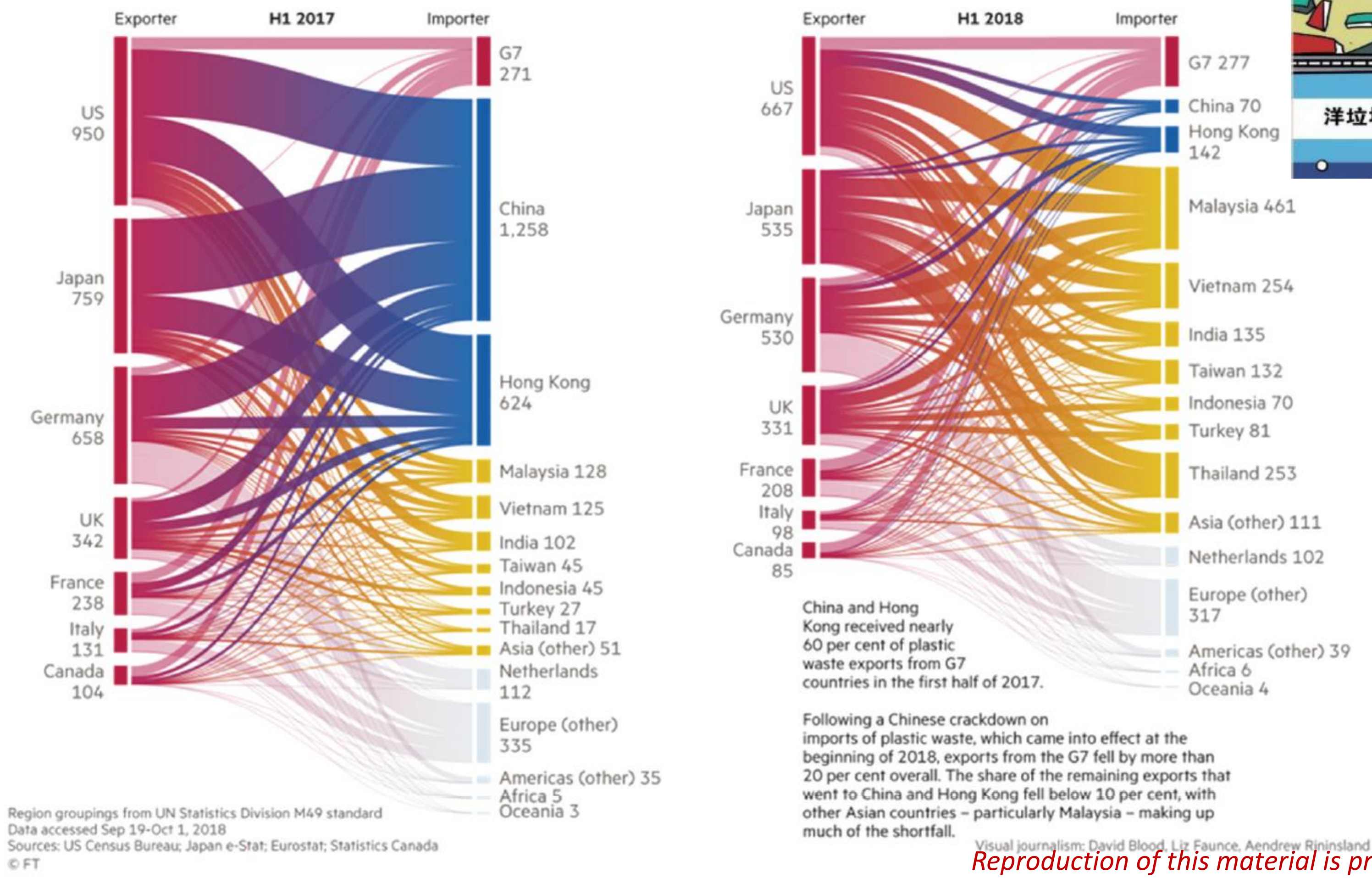
Challenges and Opportunities

Disruption in plastic waste flow: "National Sword"

Figure 17 – Change in plastic trade flows between 2017 and 2018

How the global river of plastic waste changed course in just 12 months

Exports of plastic waste and scrap from G7 countries ('000 tonnes)



Plastic use increased during COVID

- Medical waste generation has increased significantly with the ongoing Covid-19 pandemic

- Covid-19 has increased medical waste generation by 18 to 425%, and increased the ratio of hazardous (infectious) waste by 9% to 125%. [data from international studies; no relevant data found for the US] [Kalanrary et al.; Liang et al.]

Kalantary, R. R.; Jamshidi, A.; Mofrad, M. M. G.; Jafari, A. J.; Heidari, N.; Fallahizadeh, S.; Hesami Arani, M.; Torkashvand, J., Effect of COVID-19 pandemic on medical waste management: a case study. *J Environ Health Sci Eng* **2021**
Liang, Y.; Song, Q.; Wu, N.; Li, J.; Zhong, Y.; Zeng, W., Repercussions of COVID-19 pandemic on solid waste generation and management strategies. *Frontiers of Environmental Science & Engineering* **2021**

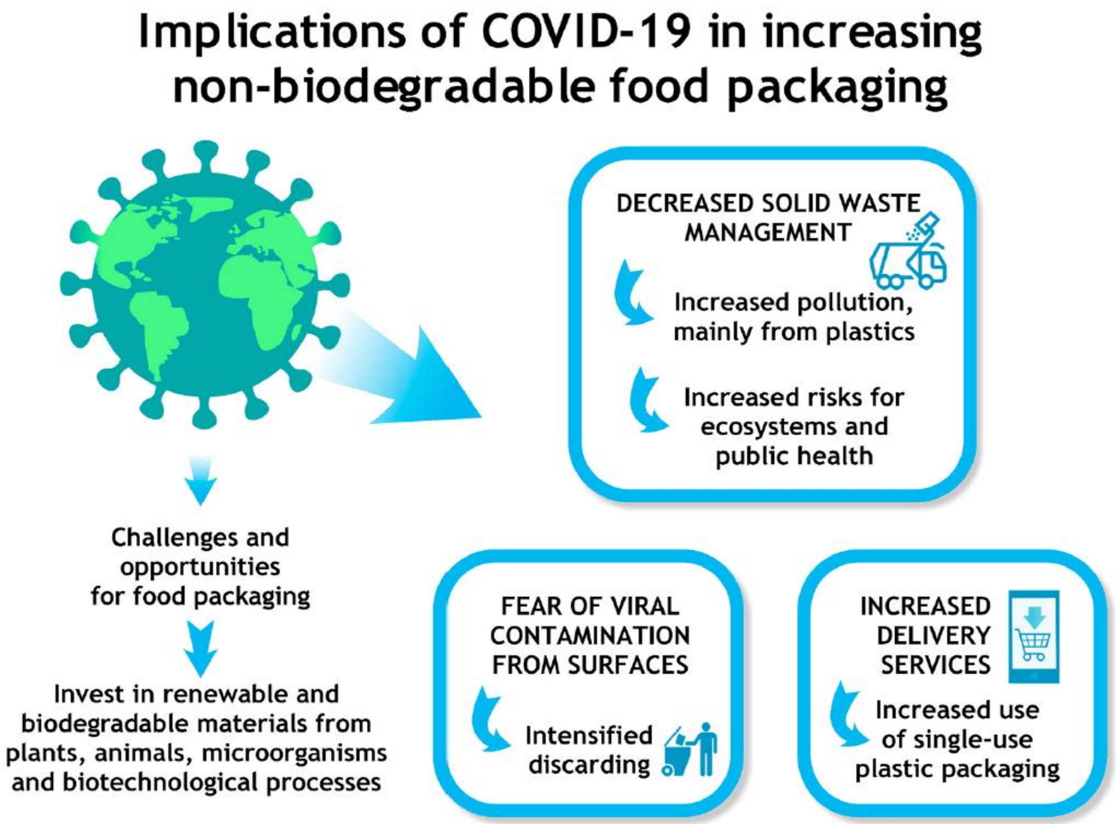


Fig. 1. Crisis of COVID-19 and increase in non-biodegradable food packaging.

Trends in Food Science & Technology 116 (2021) 1195–1199

- Consumption of packed food, fresh food, and food delivery increased during lockdown

- Highest generation of waste was observed for plastic packaging and food waste


Science of the Total Environment 777 (2021) 145997

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

ELSEVIER

COVID-19 and waste production in households: A trend analysis

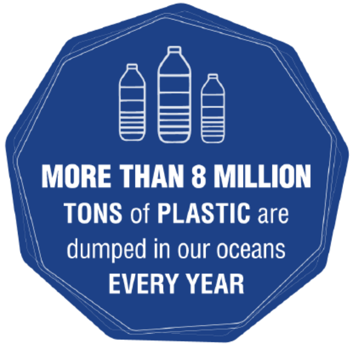
Walter Leal Filho[a,g], Viktoria Voronova[b], Marija Kloga[b], Arminda Paço[c], Aprajita Minhas[a,*], Amanda Lange Salvia[d], Celia Dias Ferreira[e,h], Subarna Sivapalan[f]

Plastics Recycling

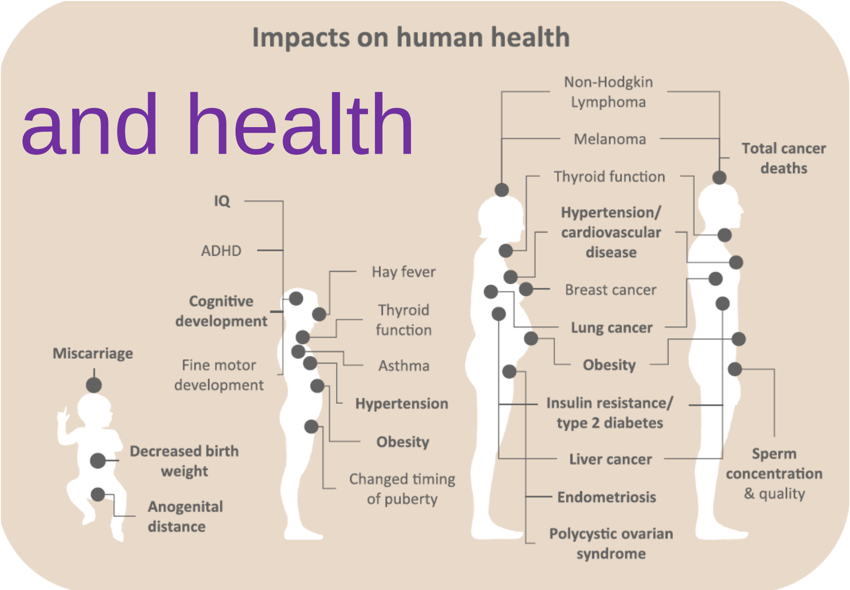
Challenges and Opportunities

Negative impacts of plastic

Plastic pollution and oceans



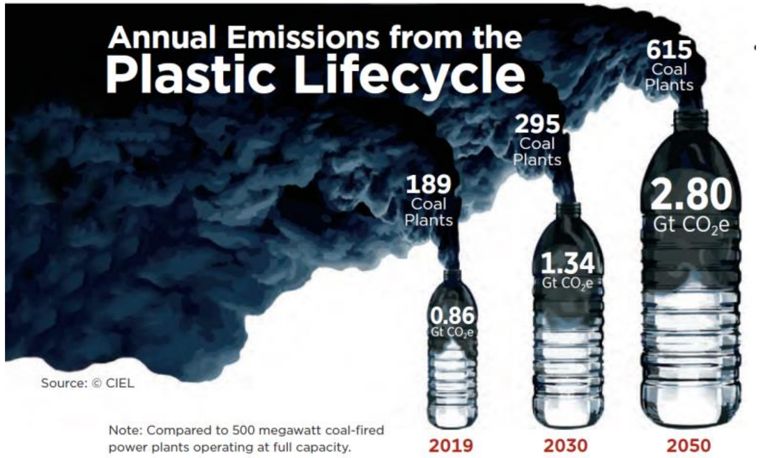
Plastics and health



Plastic pollution and soil

Microplastics

Plastics and climate



Global agreement to control plastic

Plastic pollution: Green light for 'historic' treaty

By Helen Briggs
Environment correspondent

2 hours ago | Comments

March 2, 2022

GETTY IMAGES

An international committee will look at options for reducing plastic pollution

The world is set to get a global treaty to tackle plastic pollution.

A treaty controlling plastic is coming

Countries also plan to form a global science panel on chemicals

MARCH 7, 2022 | **CEN.ACS.ORG**

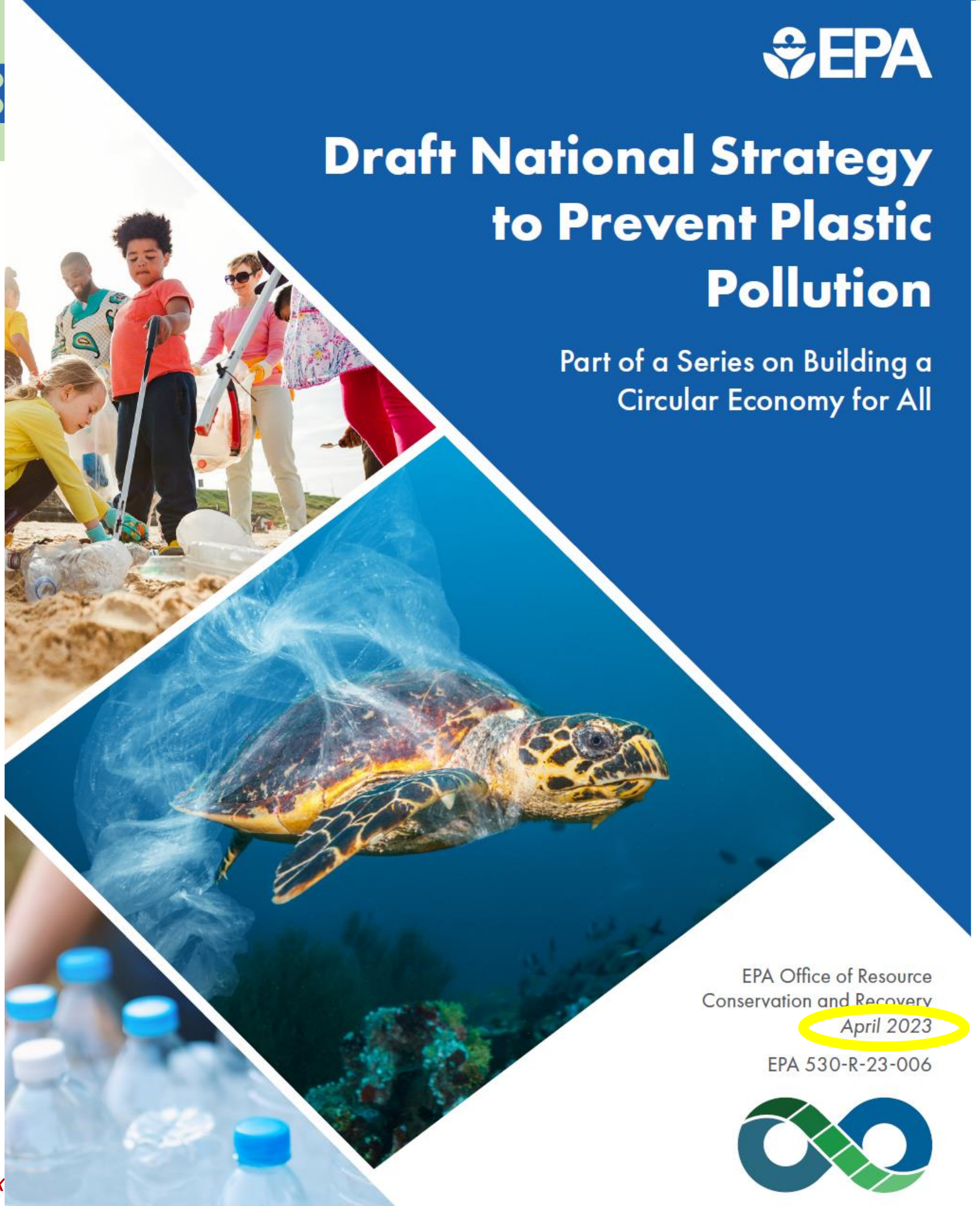
Countries around the world agreed March 2 to negotiate a global treaty aimed at controlling plastic, from production to disposal.

"Plastic pollution has grown into an epidemic," Espen Barth Eide, Norway's minister for climate and the environment, says in a statement. But with the backing for a treaty from 175 countries, "we are officially on track for a cure." Eide presided at a meeting of the United Nations Environment Assembly (UNEA), the UN's top decision-making body on environmental issues, in Nairobi, Kenya, where governments endorsed the creation of the plastic pact.

The planned accord, expected to be completed by the end of 2024, will cover the life cycle of plastics and foster the design of reusable and recyclable products and materials, according to the United Nations Environment Programme (UNEP). The agreement would also call for international collaboration to help developing countries access technology as well as promote scientific and technical cooperation.

The global chemical industry, the producers of plastic, backs the plan for a treaty. In a statement, the International Council of Chemical Associations says UNEA's mandate for the accord "provides governments with the flexibility to identify binding and voluntary measures across the full lifecycle of plastics, while recognizing there is no single approach to solving this global challenge."

Environmental advocates are enthusiastic about the treaty. Yet they also express concern that industry will oppose efforts to curb the production and widespread recycling of plastic. "We have two years to negotiate an entirely new treaty—an ambitious time frame—and a powerful plastics and petrochemical lobby will fight it all the way," Christina Dixon of the Environmental Investigation Agency says in a statement.


EPA

Draft National Strategy to Prevent Plastic Pollution

Part of a Series on Building a Circular Economy for All

EPA Office of Resource Conservation and Recovery
April 2023
EPA 530-R-23-006

Table of Contents

It hasn't been easy to replace plastic…

The Washington Post
Democracy Dies in Darkness

CLIMATE SOLUTIONS

Why glass, paper and other options aren't the simple alternative to plastic that they seem to be

Finding a good alternative to plastic — a ubiquitous material that's inexpensive, robust and versatile — hasn't been easy

By Allyson Chiu

June 7, 2023 at 6:30 a.m. EDT

Why ‘Biodegradable’ Isn’t What You Think - The New York Times

Biodegradable plastics have way to go…

Why Biodegradable Isn’t What You Think

By John Schwartz
Oct. 1, 2020

“There is a place for biodegradable materials” as a way to cut down the sheer amount of mismanaged plastic waste the world is dealing with, said Jenna Jambeck, a professor of environmental engineering at the University of Georgia who has studied the accumulation of plastics in the world’s oceans and the ability of PHA to degrade. However, she worries about the consequences of developing products that are seemingly environmentally friendly without planning for disposal and recycling. “You have to think about end of life when you’re designing things,” she said.

Features

Danimer Scientific is expanding this polyhydroxyalkanoate plant in Winchester, Kentucky.

BIOBASED CHEMICALS

Will PHA finally deliver?

Producers of the biodegradable polymer say they are gaining traction, but others have doubts

ALEX TULLO, C&EN STAFF

In April, Daniel Carraway, founder of the polyhydroxyalkanoate start-up RWDC Industries, found himself in an unusual forum for someone trying to sell plastic. Carraway was being interviewed by the *Iron Man* actor Robert Downey Jr. on the FootPrint Coalition’s YouTube channel. The FootPrint Coalition is Downey’s venture capital firm and also an RWDC investor. The FootPrint Coalition’s other investments include a bamboo toilet paper company and an outfit developing mealworm protein.

Encouraged by Downey, Carraway pitched his biodegradable biopolymer as the solution to the plastic waste crisis. “We have to clean up the mess we made,” Carraway said. “But we also have to stop making the mess.” The plastic industry has been trying to establish a recycling infrastructure since the 1970s, he noted, but it “just doesn’t work.”

Carraway and other proponents are hyping polyhydroxyalkanoates, known collectively as PHA, as the next big thing, but they are hardly new. Nature has used this class of polymers to store cellular energy for millions of years. Companies have been trying to commercialize them—via industrial fermentation—for several decades. But despite what should be a strong selling point—biodegradability in a wide range of environments—they haven’t taken off. The list of companies that have tried and failed to bring PHA to market keeps growing.

This time, boosters of the polymer maintain, will be different. The world has changed, they say. Cities are banning plastic straws and take-out containers, and PHA is a responsible alternative. Large consumer product companies are clamoring for biodegradable packaging. Indeed, PHA Skittles bags and Bacardí rum bottles are due out in stores soon.

Danimer Scientific, the firm responsible for those applications, puts the addressable PHA market at 230 million metric tons (t) per year—more than half the world’s plastic demand. Meanwhile, the PHA industry is still in its infancy, with capacity of less than 1 million t.

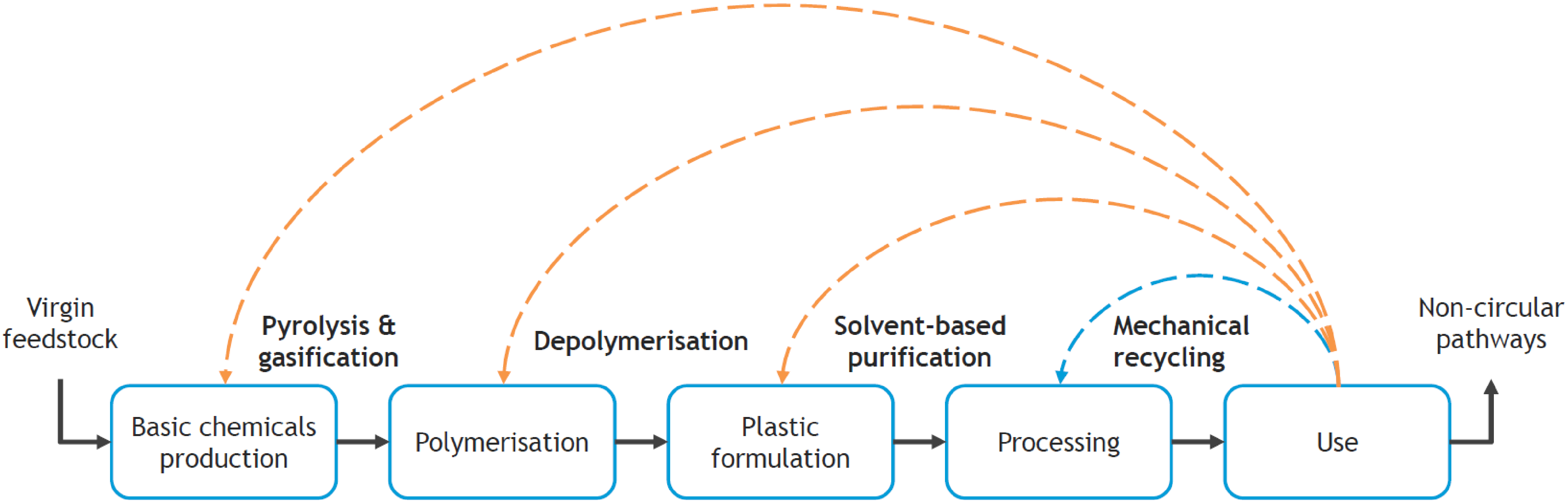
Detractors, however, warn that it won’t be easy for PHA to compete with the likes of polyethylene and polypropylene. PHA’s biodegradability is overhyped, they say. And the biopolymer is too expensive to compete with petrochemicals on a large scale. Regardless, all eyes are on PHA.

The company leading the current charge for PHA is Danimer. The firm, based in Bainbridge, Georgia, started as a polylactic acid compounder and bought its PHA fermentation technology from Procter & Gamble back in 2007.

Only recently has the PHA business begun to gain significant traction for Danimer. The company opened its first commercial plant, in Winchester, Kentucky, last year. It can make 9,000 t per year and is being expanded to about 30,000 t by next year.

Danimer says it is struggling to keep up with forecast demand. The first plant, it projects, will be running at full capacity by the end of this year. Danimer is close to having the output for the expansion reserved by customers as well, CEO Steve Croskrey says. “If you count pending contracts, we’re there.”

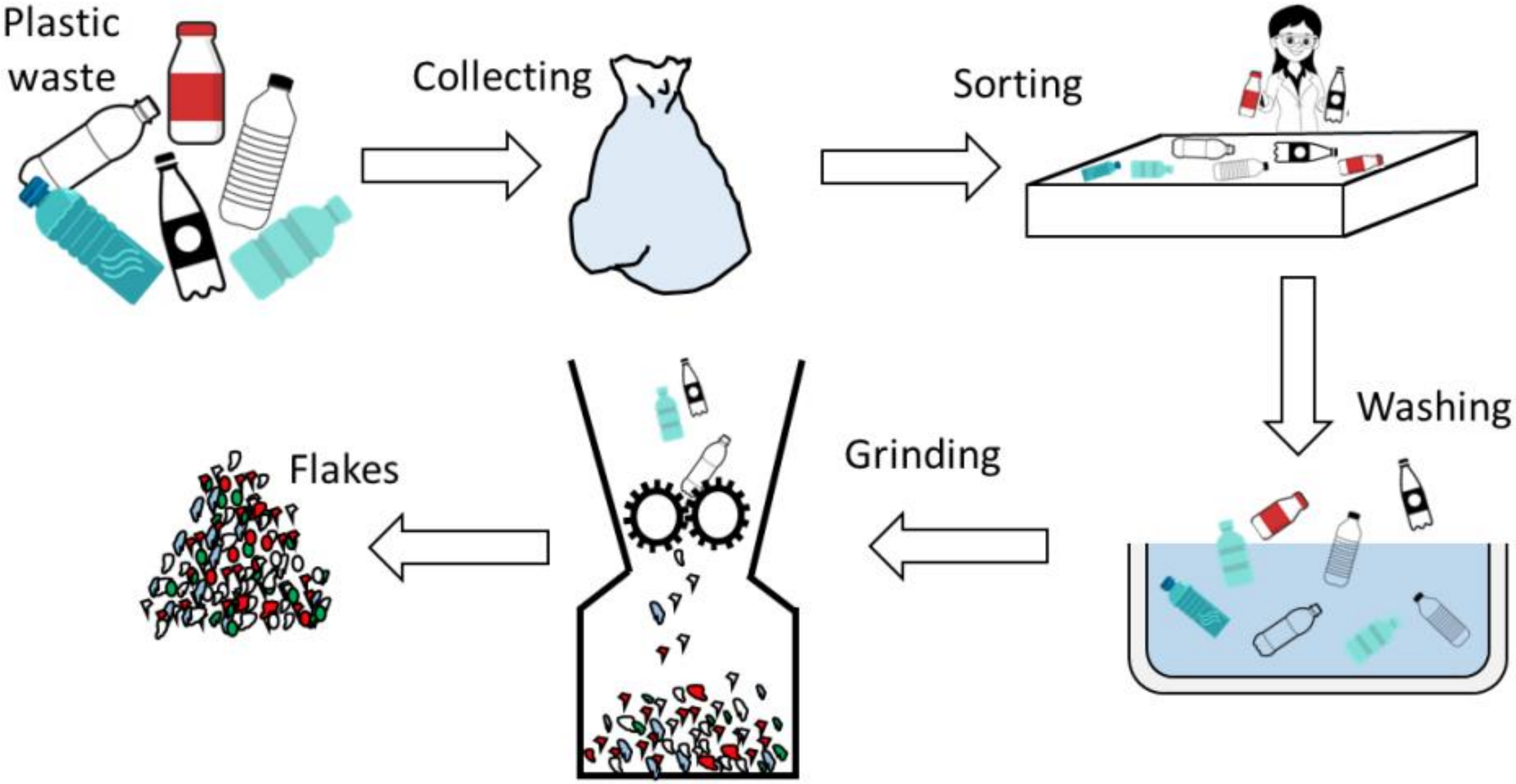
Recycling of plastic waste



Plastic value chain

Image based on Crippa et al., 2019, *A circular economy for plastics - Insights from research and innovation to inform policy and funding decisions*, European Commission

Mechanical recycling of plastic waste



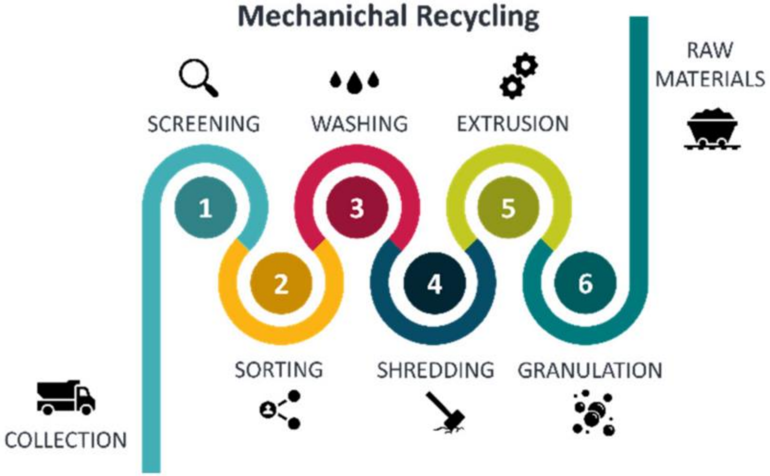
https://ubuntoo.com/blogs/mechanical-recycling-for-dummies

Visit to local Materials Recovery Facility (MRF)

Automated sorting for mechanical recycling of plastic waste

https://www.simsmunicipal.com/recycling-education-center/school-tours/

Mechanical recycling of plastics is not enough



WILL PLASTICS RECYCLING MEET ITS DEADLINE?

Consumer product companies have set lofty goals for recycling but have so far made only modest progress

ALEX TULLO, C&EN STAFF

28 C&EN | CEN.ACS.ORG | OCTOBER 11, 2021

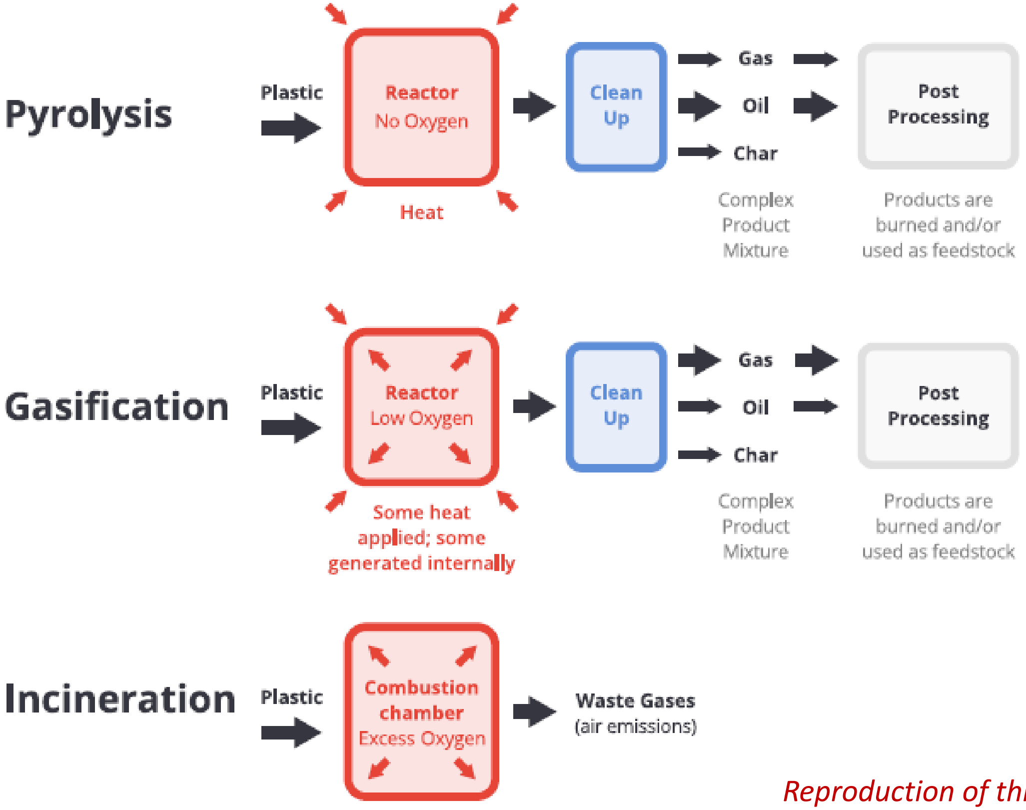
"There has been this history of making big, grand promises on recycling and not following through."

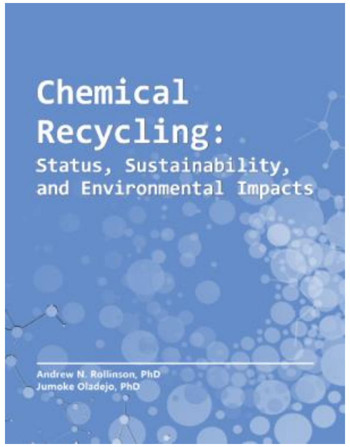
—**Conrad MacKerron,** senior vice president, As You Sow

Chemical recycling of plastic waste

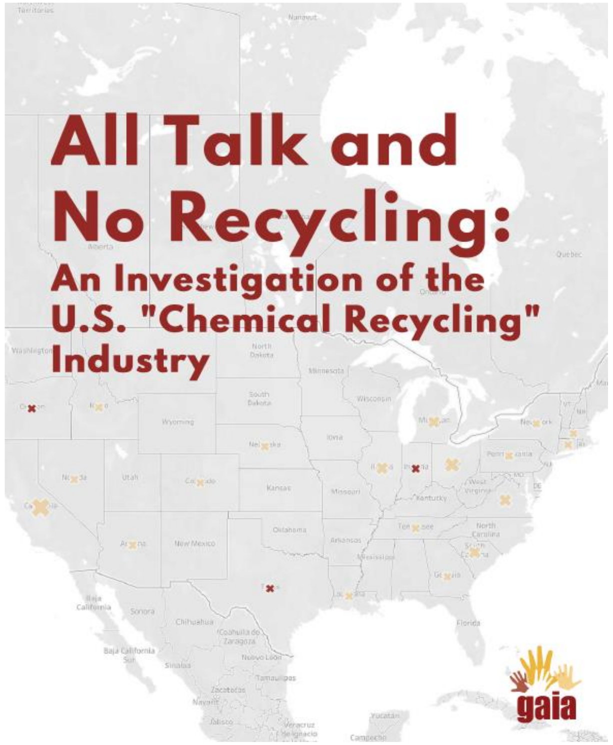
Gasification and Pyrolysis

Gasification and pyrolysis are, at face value, very simple concepts. They were devised over one hundred years ago as technologies for converting woody biomass and coal into gaseous and liquid chemicals along with producing carbon-rich solids. Their names derive from these historical applications.





Chemical "recycling" (?)




WASTEDIVE

DIVE BRIEF

ISRI rejects 'advanced recycling' label, says plastic-to-fuel projects should not count as recycling

Published Aug. 10, 2022

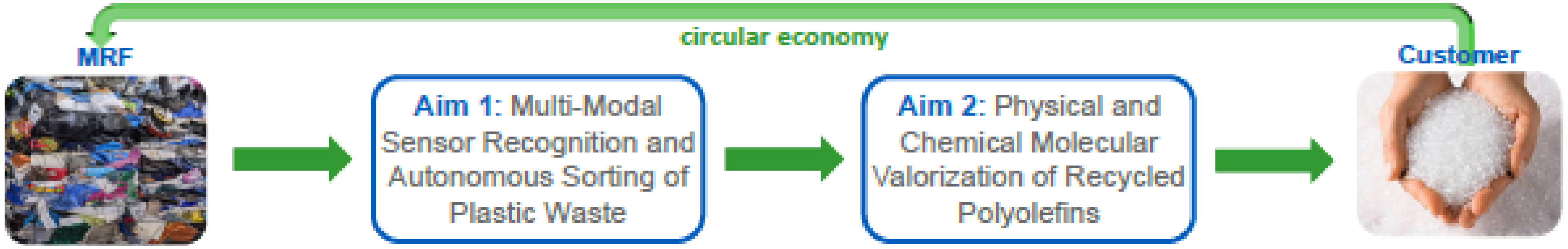
- "Chemical recycling" releases toxic chemicals into the environment.
- "Chemical recycling" has a large carbon footprint.
- "Chemical recycling" has not yet been proven to work at scale.
- "Chemical recycling" cannot compete in the market.
- "Chemical recycling" does not fit in a circular economy.

EFRI E3P: Valorization of Plastic Waste via Advanced Separation and Processing

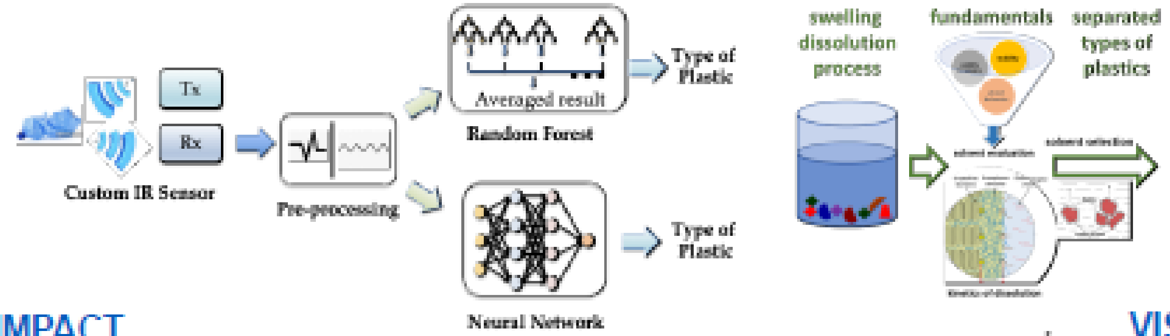
Ways to improve mechanical & chemical recycling of plastic waste

PROJECT TEAM

Luis Velarde: *Spectroscopy*
Thomas Thundat: *Sensors*
Karthik Dantu: *AI & Robotics*
Marina Tsianou: *Dissolution*
Paschalis Alexandridis (PI): *Separations*
Javid Rzayev: *Synthesis*
John Atkinson: *Waste Management*
Michael Shelly: *Economic Impacts*
Amit Goyal: *Commercialization*
ALL: *Education and Outreach*



On-line sensor recognition • advanced sorting • novel solvent treatments • high-value materials



- PE wax applications > 1 USD Billion market
- Degradable PE improved recycling
- Resins for 3D printing additive manufacturing

NOVELTY

- Fast on-line molecular recognition of plastics
- Advanced machine learning of spectral data for different plastics types and additives
- Autonomous robotics for sorting plastics
- Separation and purification of plastics using environmentally responsible solvents in a swelling/dissolution process
- Telechelic waxes and new materials

IMPACT

- Paradigm shift in real-time, high-throughput sorting via a combination of novel sensors, machine learning, vision-based recognition and tracking
- Fundamental upcycling of plastic waste with minimal CO_2 emissions
- Developed technologies: (i) readily integrated in Materials Recovery Facilities (MRF), (ii) adaptable to variable plastic waste composition, (iii) upgradable, (iv) scalable and transferable to other industries
- Student and community engagement via industry expert lectures, museum exhibit, diverse recruitment plan, and course development

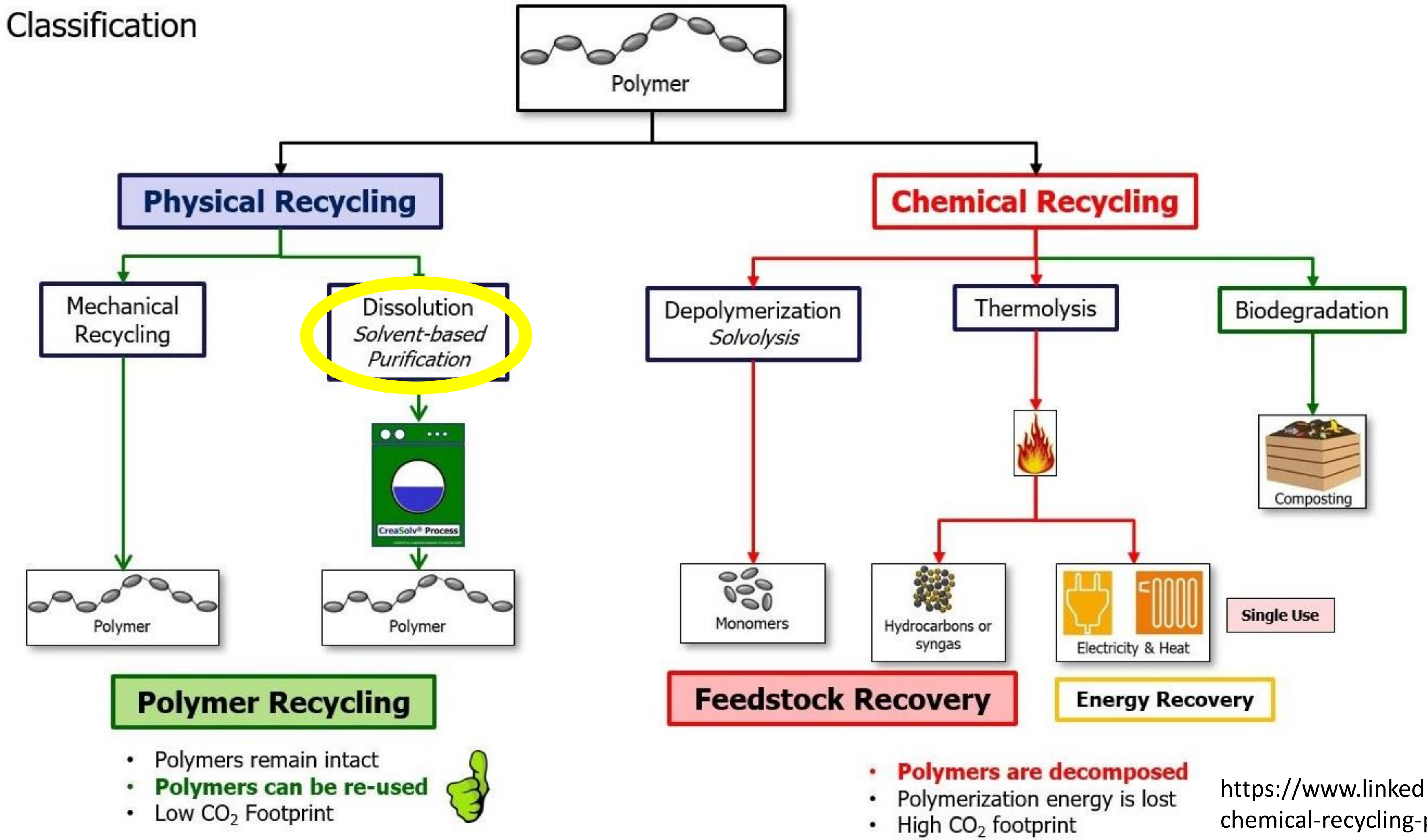
VISION

- Less plastic in landfills and incinerators
- More recycled plastic back into products
- Inspire innovation in plastics recycling industry
- Increase employment in waste management

RESPONSIBLE INNOVATION

- Environmentally-friendly sorting and solvents
- Oversight by "Responsible Innovation" and 'Broadening Participation' advisory committees

“Molecular” (physical) recycling of plastic waste



https://www.linkedin.com/pulse/dissolution-chemical-recycling-plastic-waste-gerald-altnau

EFRI E3P: Valorization of Plastic Waste via Advanced Separation and Processing

Dissolution/Precipitation Recycling of Polyolefins

Christian Ferger
cmferger@buffalo.edu
Mentors:
Prof. Marina Tsianou
Prof. Paschalis Alexandridis

MOTIVATION

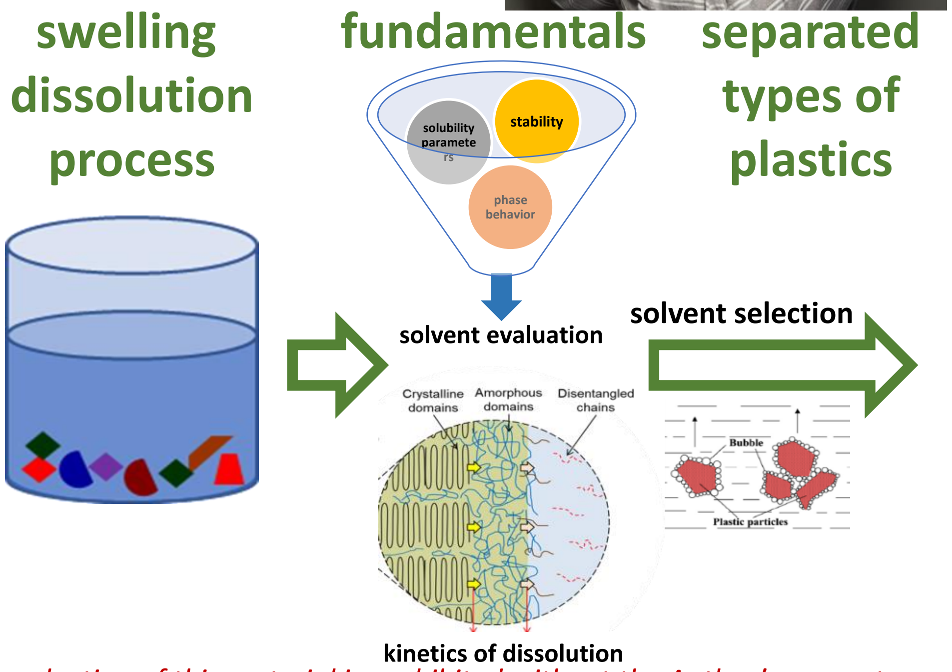
Dissolution/precipitation recycling, a method in which a polymer is dissolved in a solvent and reprecipitated after the removal of insoluble contaminants, offers the opportunity to **generate near-virgin quality polymers** from plastic waste. However, the few solvents that can dissolve polyolefins are hazardous.

PROJECT DESCRIPTION

Evaluate polyolefin phase behavior in environmentally responsible "green" solvents and solvent-antisolvent mixtures.
A**nalyze polymer-solvent thermodynamic interactions** to identify solvents and conditions under which selective dissolution/precipitation recycling can be successfully applied.

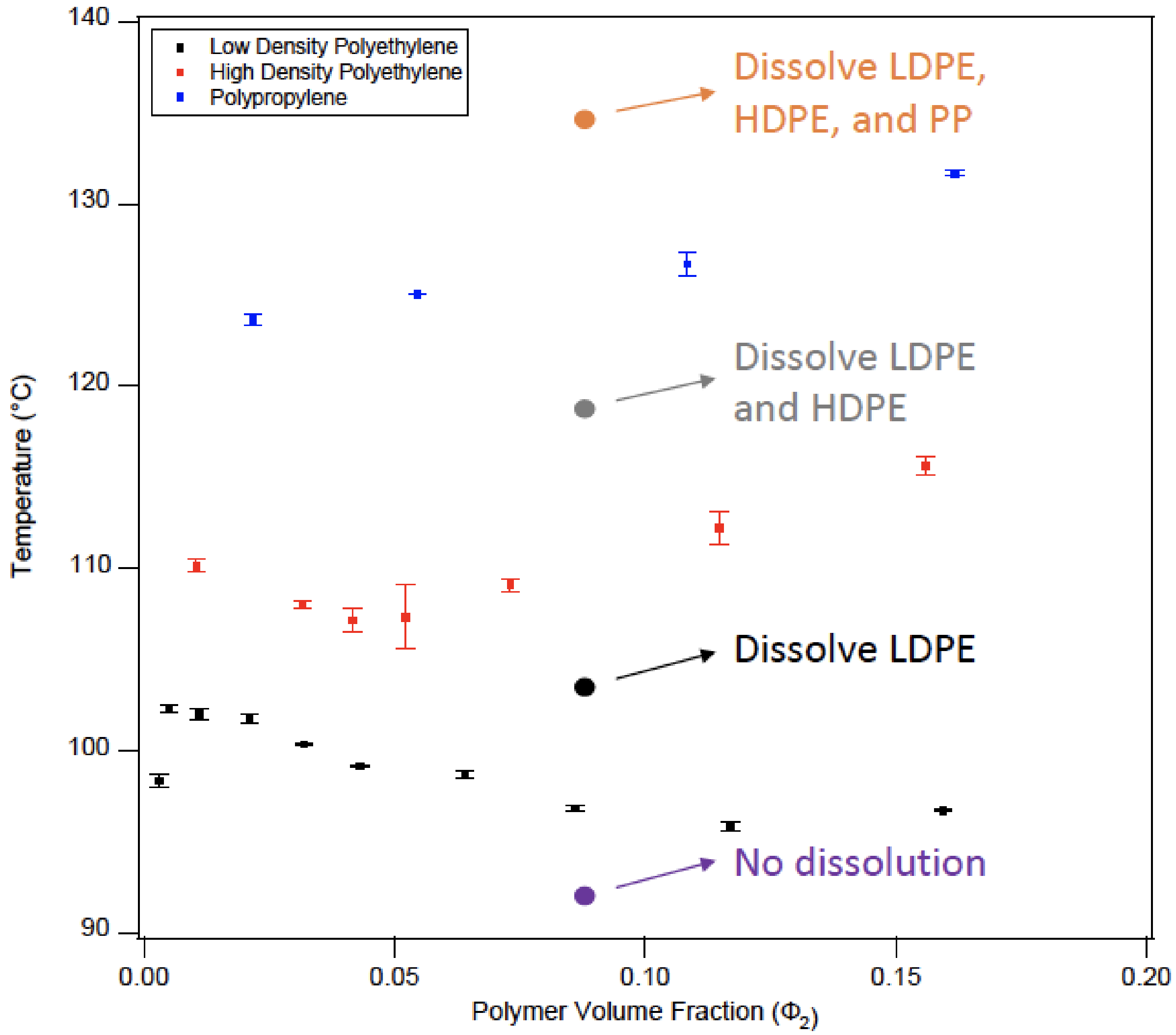
METHOD OF APPROACH

Identify "green solvents" using solvent selection guides. Polymer-solvent phase behavior data is then generated through observing the onset of phase separation at a particular volume fraction by lowering the solution temperature (cloud point measurements).



EFRI E3P: Valorization of Plastic Waste via Advanced Separation and Processing

Phase Diagram for Polyolefins in Green Solvent



RESULTS/FINDINGS:

- ✓ Polyolefin (HDPE, LDPE, and PP) phase behavior in five different "green solvents"
- ✓ Influence of antisolvent (precipitating agent) on polyolefin solubility- negligible up to a certain concentration (dependent on antisolvent)

IN PROGRESS:

- ❑ Analysis of polymer-solvent thermodynamic interactions using Flory-Huggins theory

PRACTICAL IMPLICATIONS:

- ❖ The generated phase diagrams can be applied in the dissolution/precipitation recycling of polyolefins in order to isolate and purify a target polymer

EFRI E3P: Valorization of Plastic Waste via Advanced Separation and Processing

Polyolefin Dissolution Kinetics

Ali Ghasemi
alighase@buffalo.edu
Mentors: Prof. Marina Tsianou and Prof. Paschalis Alexandridis

MOTIVATION

- Recycling of polyolefins via dissolution/precipitation can increase both the fraction of plastics that is being recycled and the value of the plastics recovered.
- Understanding the underlying phenomena which govern the dissolution behavior of polyolefins is critical in the design and optimization of chemical recycling processes involving plastic dissolution/precipitation.

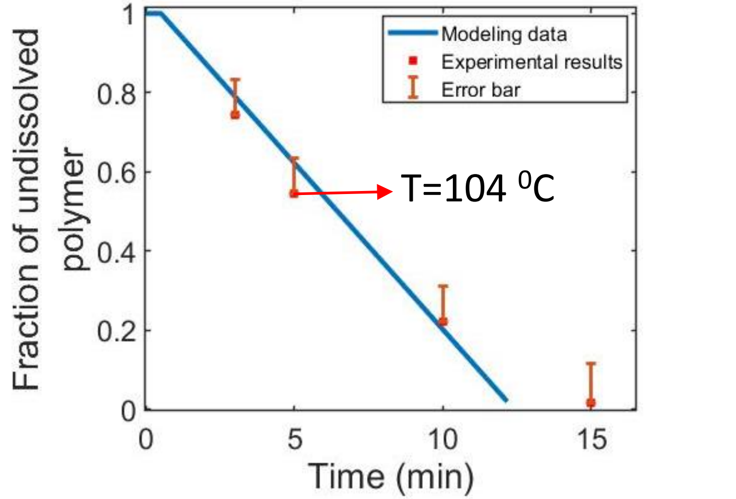
PROJECT DESCRIPTION

- Achieve a comprehensive understanding on the dissolution kinetics of polyolefins, the most popular type of plastics

METHOD OF APPROACH

- A phenomenological model is developed to describe the swelling and dissolution of polyolefins by capturing the underlying transport phenomena.
- Dissolution kinetics experiments are performed to validate the model and obtain the key fitting parameters.

Dissolution of HDPE in p-xylene at T=104 ^{0}C



Fitting model to experimental data to obtain the fitting parameters (K_{dec} & r_{dis})

$K_{dec} = 38.5\times10^{-3}$ (1/s)

$r_{dis} = 1.75\times10^{-8}$ m/s

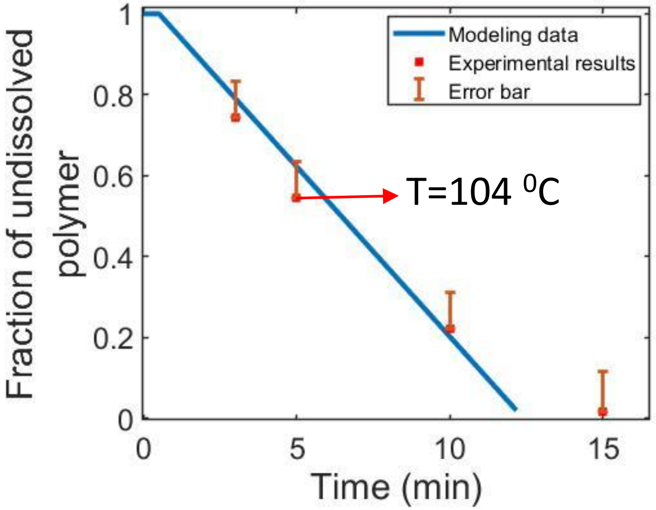
EFRI E3P: Valorization of Plastic Waste via Advanced Separation and Processing

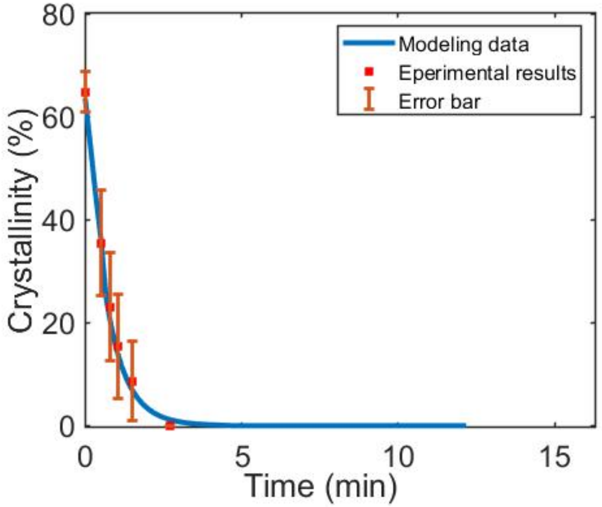
Fit model to experimental data to obtain the fitting parameters K_{dec} & r_{dis}

- Dissolution of HDPE in p-xylene (T=104 ^{0}C)
- HDPE samples: 1cm×1cm×0.1mm

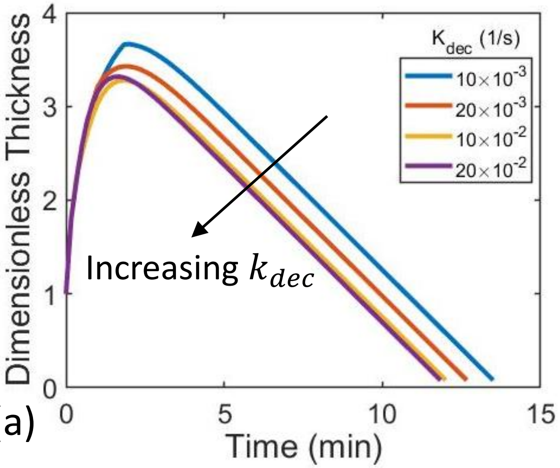
$r_{dis}=1.75\times10^{-8}$ (m/s)

$K_{dec}=38.5\times10^{-3}$ (1/s)

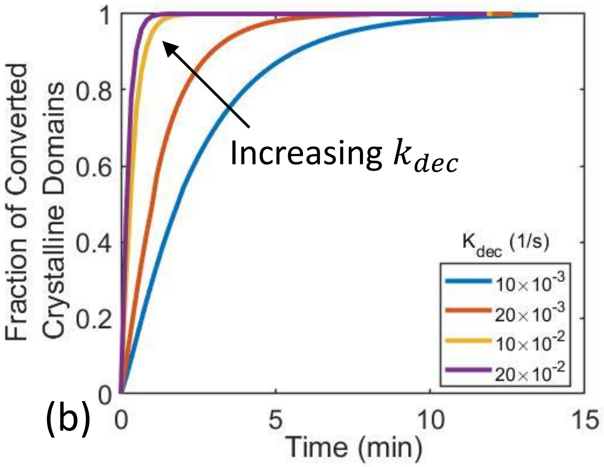




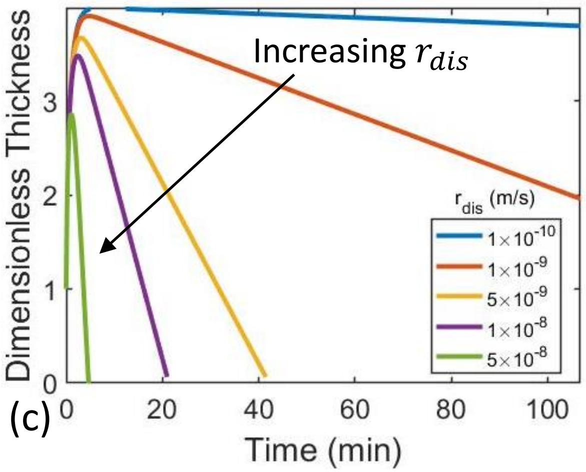
Effects of k_{dec} (a) & (b), and r_{dis} (c) & (d) on the dissolution process



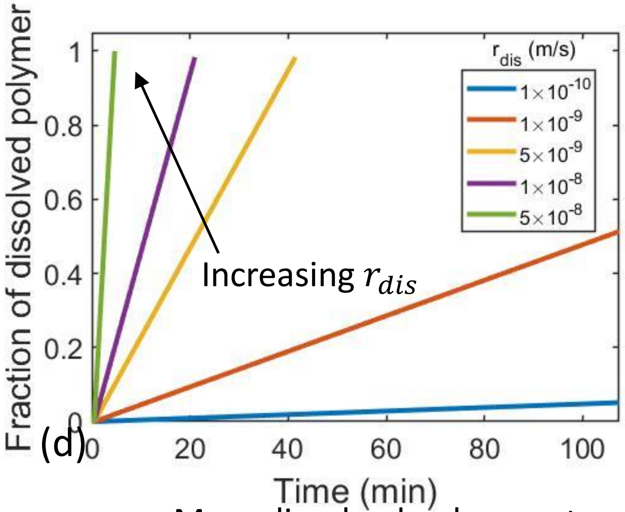
(a)



(b)



(c)



(d)

k_{dec} ↑ ⇒ Crystalline domains will decrystallize more, less swelling will happen

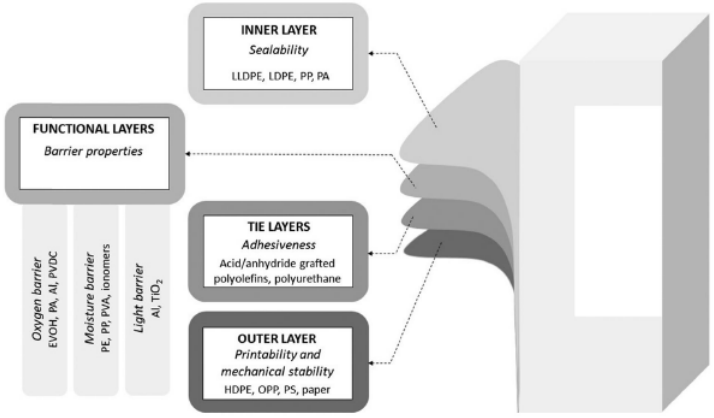
k_{dec} ↑ ⇒ Crystalline domains will decrystallize sooner

r_{dis} ↑ ⇒ Less swelling and less time for full dissolution

r_{dis} ↑ ⇒ More dissolved polymer at a specific time and less time for full dissolution

REMADE: Recycling of Polymer-based Multilayer Packaging by Delamination

Packaging consumes 40% of plastics used world-wide. Half of plastic flexible packaging comprises multilayer films.



1 Various layers of multilayer packaging
Dixon, 2011; Ebnesajjad, 2012; Morris, 2016)

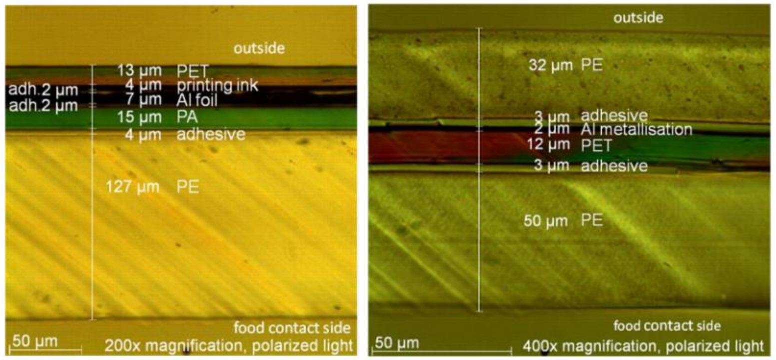
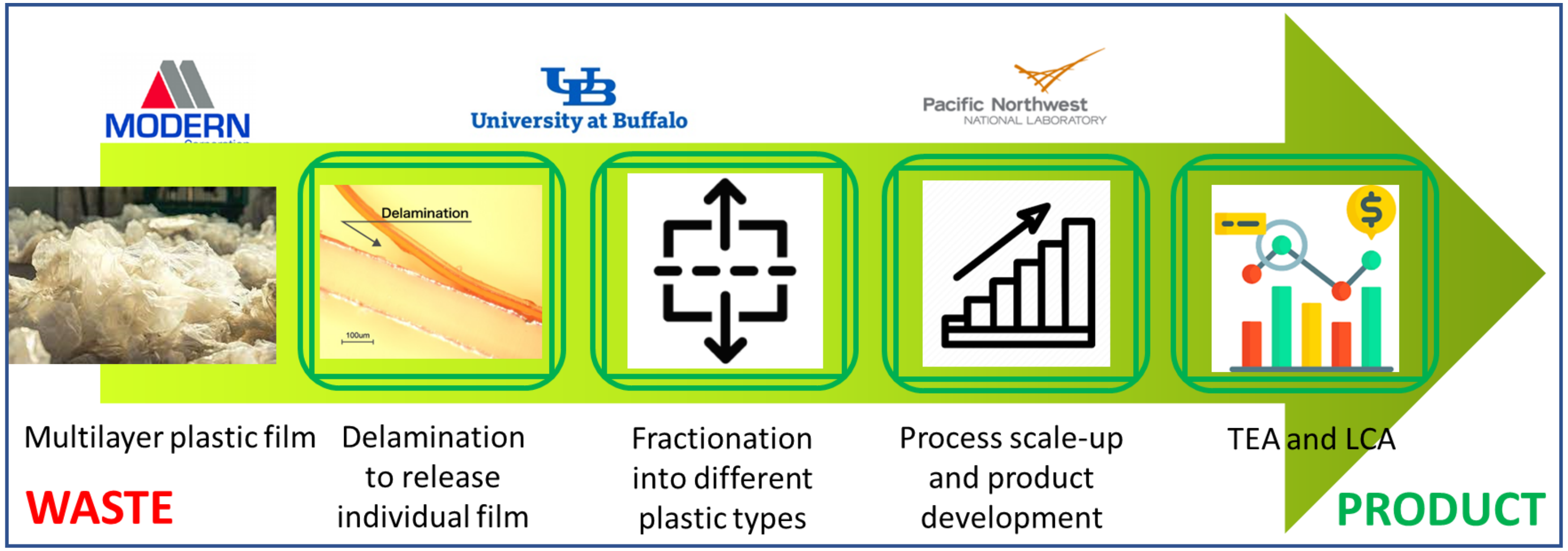


Figure 3 Microtome sections of multilayer plastic laminates in polarised light

This project aims to deconstruct flexible films and multilayer packaging utilizing delamination, to recover polyolefin films using separation processes, and to validate that the recovered plastics can replace primary materials without loss of properties or performance.



supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Advanced Manufacturing Office Award Number DE-EE0007897

University at Buffalo
Initiative for Plastics Recycling Research and Innovation

NEW YORK STATE OF OPPORTUNITY | Department of Environmental Conservation

https://www.buffalo.edu/iprri.html

Our Research

In addition to developing secondary recyclable markets and streamlining the recycling process, our researchers are focused on six specific tasks.

- Map the reverse supply for plastics in New York State, and conduct a deep dive into the structure of the collection, disposal and recycling industries.
- Improve the efficiency of businesses involved in collecting and processing plastics in New York State.
- Research plastics i… natural environment…
- Research plastics in New York agriculture/food and medical industries.
- Understand contemporary attitudes toward recycling and current recycling behaviors.
- Develop advanced high-speed plastic sorting by molecular contrast infrared imaging.

Task led by
Prof. Alexandridis

Closing remarks

- *Problem*: plastic is an invaluable material, but too much plastic waste generates concern
- *Negative impacts of plastic*: environment (water, soil, GHG generation, climate) and health (additives in plastic, microplastics)
- *How we currently recycle plastic*: primarily with mechanical recycling; chemical recycling receives negative publicity and limited utilization
- *Emerging trends*: bans of certain plastic products, EPR, reusable containers, bioplastics, new chemistries for recyclable plastics, plastics from CO_2 from air, etc.
- But can these handle 450 million metric tons annual plastics production? (slated to go up)
- *In the meantime*: plenty of room for improved sortation and for molecular re/up-cycling
- *Molecular Recycling of Plastics*: environmentally responsible solvents for dissolution of polyolefins; solvent-polyolefin phase behavior; mechanism and kinetics of polymer dissolution; solvent-assisted delamination of multilayer films

University at Buffalo
The State University of New York

Valorization of Plastic Waste: Research Advances in Molecular Recycling

Thank You!

palexand@buffalo.edu
www.cbe.buffalo.edu/alexandridis
https://scholar.google.com/citations?user=AHDBpe8AAAAJ&hl=en