DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

Cellulose-Chitin Composites for Performance Advantaged Barrier Products

March 10, 2021
Technology Area Session

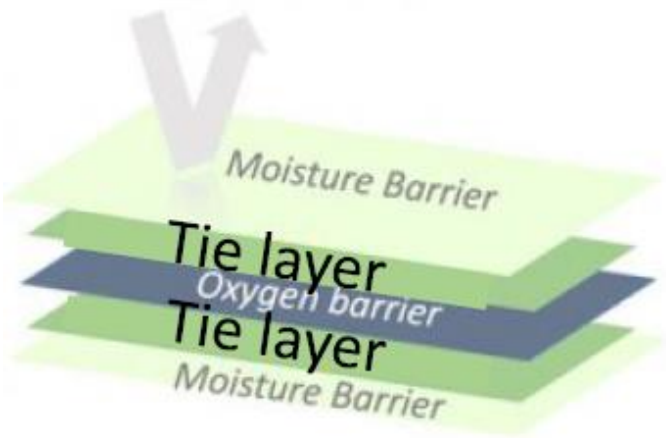
Carson Meredith
Georgia Tech

Project Overview

DE-FOA-0001916
Topic 3: PABP

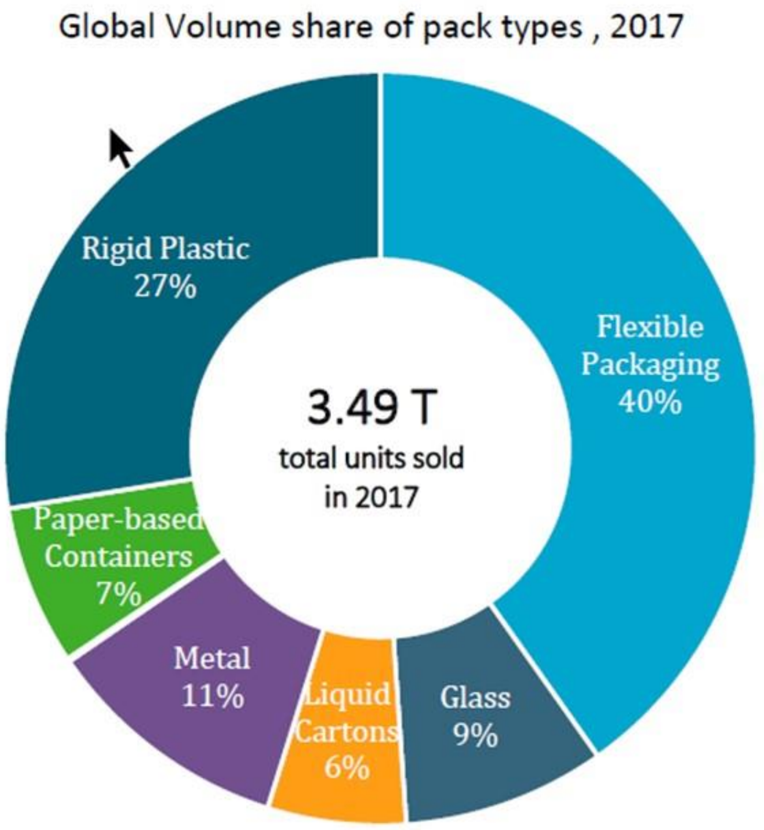
What: Develop a performance advantaged bioproduct (PABP) alternative to petroleum-based flexible packaging
How: Scalable coating biomass-based multilayer films with at least 10% improvement in O_2 permeability vs. PET

State-of-art: multilayer flexible packaging
-critical to food safety & supply
-multimaterial petroleum derived
-unrecyclable/nondegradable



Why - Impact:
-valuable by-products from biorefineries
-reduced landfill use and ocean leakage
-circular packaging alternative – reuse of carbon

Risks: cost to produce, achieving performance advantage in manufacturable format, biomass availability



Total 2017 market size	3.49 Tn
Total 2022 market size	3,93 Tn
Forecast Absolute Growth (2017-2022)	12.7%

packworld.com

1 – Management

Task 1: Initial Verification (M1-M3) → **GNG**

Task 2: PABP Design and Prototyping (M4-M18) → **GNG**

Task 3: PABP Optimization for Food and Device Packaging (M19-36)

Task 4: PABP Manufacturability (M19-36)

C. Meredith (ChBE): chitin extraction, spray coat, transport props., TEA

M. Shofner (MSE): mechanical properties & rheology

T. Harris (ME): interface properties & slot die coating

J. Reynolds (CHEM): electrochromic device packaging & testing

1 – Management

Year 1 – bi-weekly meetings whole team; weekly subteam meetings

Year 2/3 – tri-weekly whole team; weekly subteams

Whole team meetings focus on interdisciplinary feedback, data and material exchange, and maintaining focus on task objectives

Changes in student or post-doc staffing are discussed and agreed by PI/coPIs

Challenges in student/post-doc performance handled by PI and CoPI involved

1 – Management

Industrial stakeholder engagement

- Tidal Vision – Chitin producer in North America
- Sugino – Japan-based chitin nanofiber producer

(evaluation of commercially available materials)

- Winpak, Ltd. – N.A. flexible packaging converter – evaluation of material for commercial coating.
- Nestle – global food brand – selection of compatible products

Collaboration

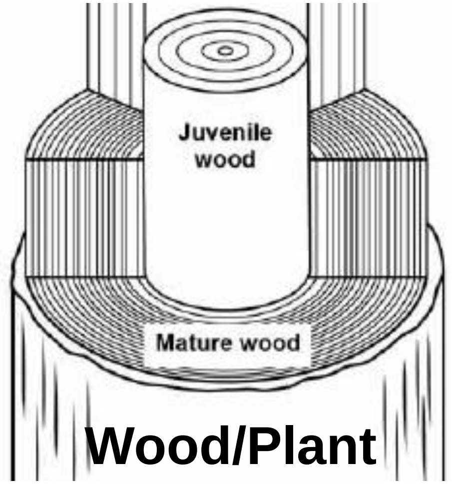
- Georgia Tech RBI-funded project overlap
- NREL Peter Ciesielski – SEM EDS profiling for concentration profiles
- UGA Jason Locklin – biodegradation trial underway

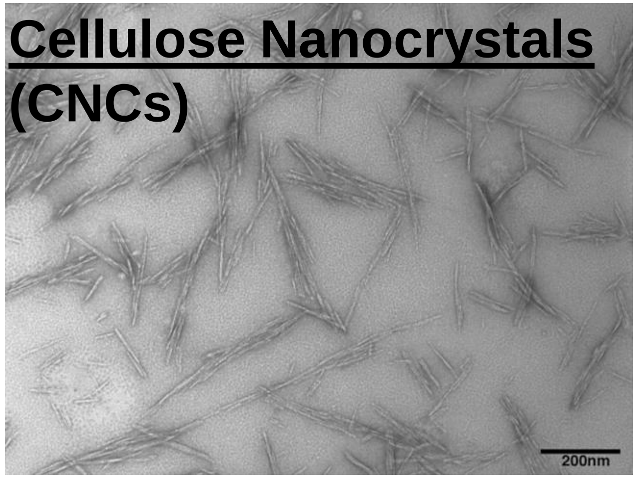
1 – Management

Risk	Mitigation
Compatibility with converters	Focus on scalable coating technology available to converters
Feedstock availability	cellulose: 137 million tons annual chitin: 3-6 million tons annual
Process costs	Process design and optimization
Mechanical properties/durability	Subtask dedicated to optimization and durability testing
Biodegradability / compostability	Trial with University of Georgia facility

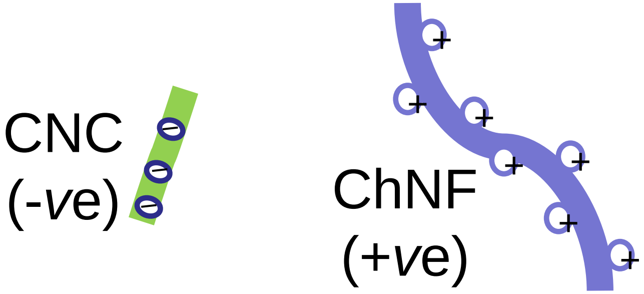
2 – Approach

Biomass sources with potential to exceed oxygen barrier properties of PET

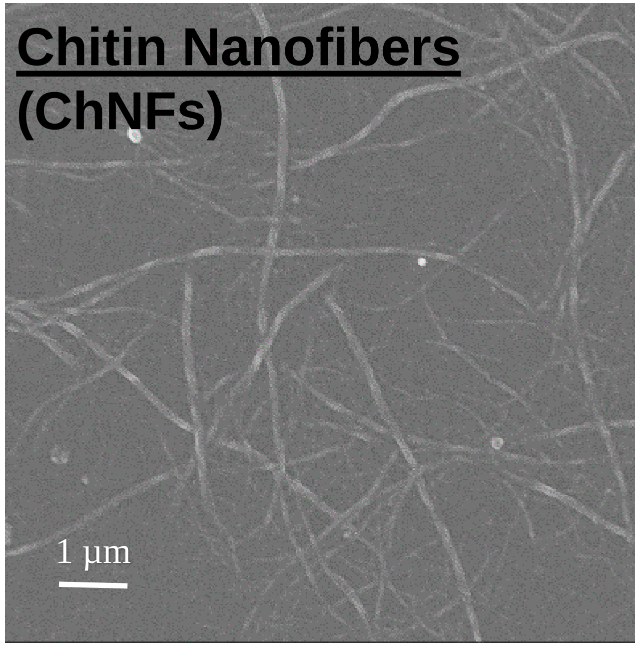




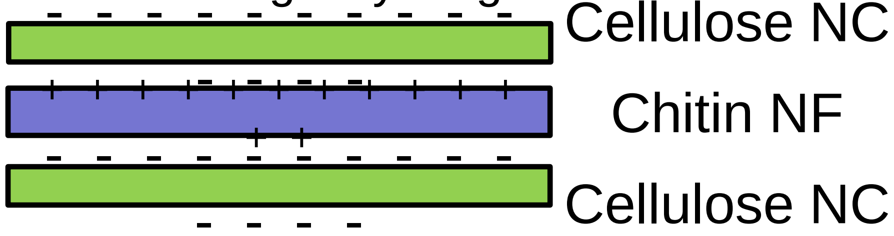
Exploit synergism between chitin and cellulose-based nanofibers



Crustacean food waste/ Fungi



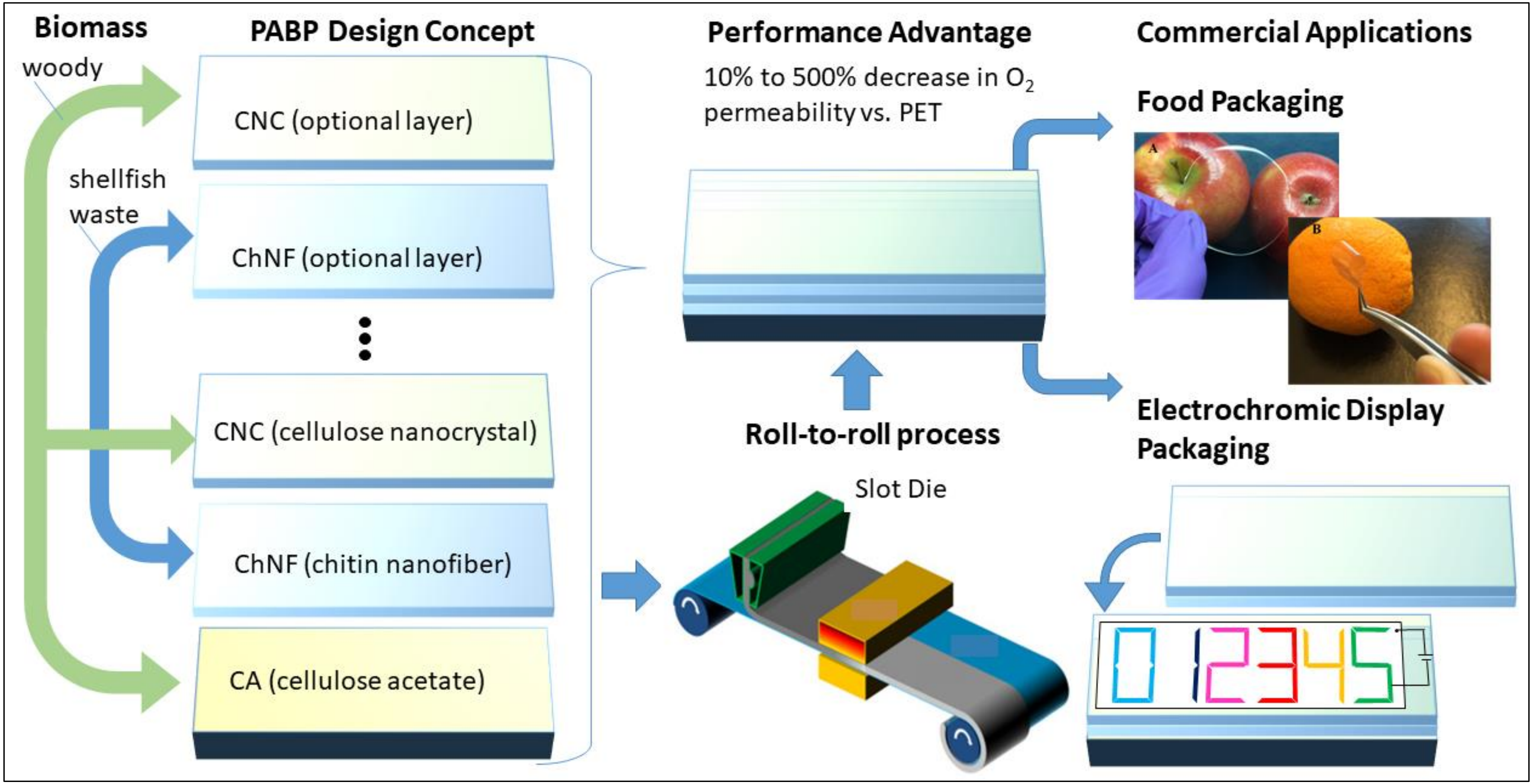
Produce dense, well-adhered interfaces through layering



Achieve barrier performance, mechanical and optical properties

2 – Approach

Develop Roll-to-roll Manufacturing of PABP



2 – Approach

Challenges

-Proposal baseline was spray-coated with OP 2.5x > PET

-Manufacturing in single coating pass by dual-layer slot-die

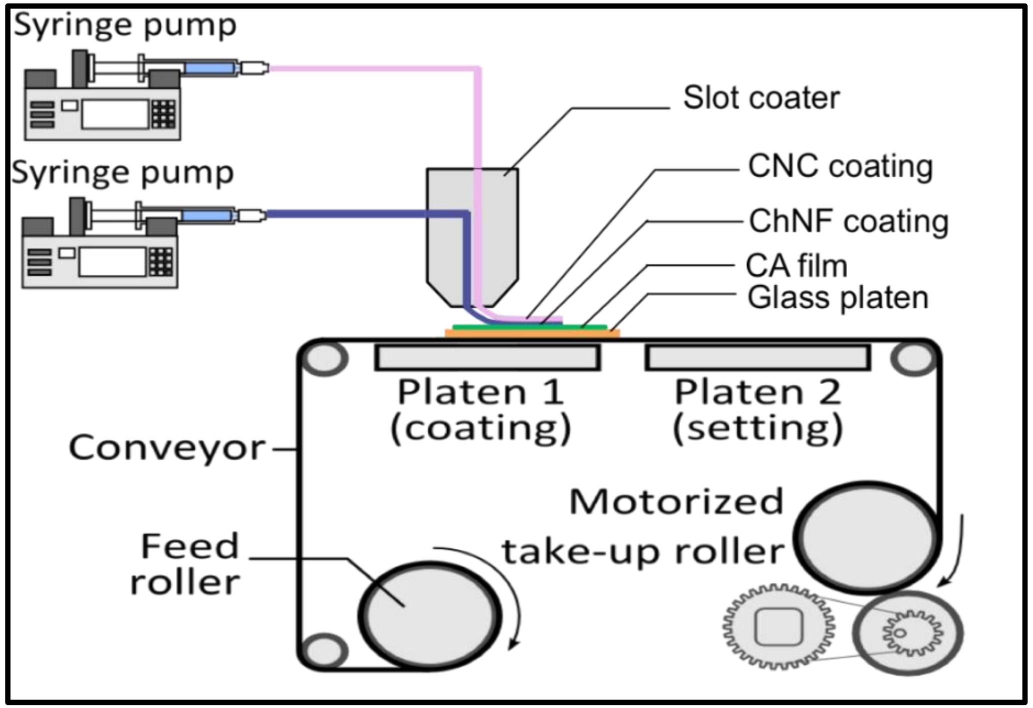
-Achieving O_2 Permeability (OP) below PET with manufacturable process

-Sensitivity of OP to drying environment humidity

-Water vapor sensitivity of OP

-Mechanical properties

-Cost of ChNF production



2 – Approach

GNG 1 – Initial Verification at Month 3 (January 2019)

- Established capability to produce adequate supply of material
- Established baseline for benchmark PET and for starting point of bilayer coatings on new substrate, cellulose acetate (CA)
- Identified critical hand-offs in information and materials amongst coPIs

GNG 2 – Intermediate Verification at Month 18 (July 2020)

- Verification of PABP OP 10% improvement versus PET
- Identification of challenges to reproducibility
- Identification of project priorities for budget period 3 (final 18 months)

2 – Approach

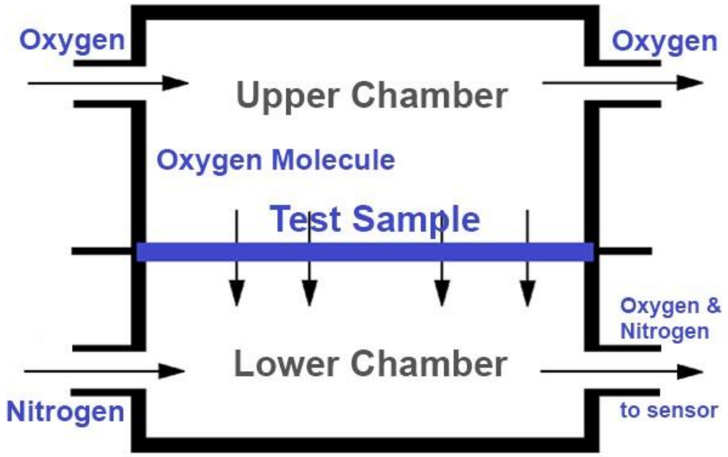
Technical Metrics

-O_2 Permeability (OP) – normalized barrier performance, measured at room T and 50% relative humidity

-Water vapor transport rate (WVTR)

-Puncture strength, Elongation at break

-Electrochromic device performance (switching time, photostability)



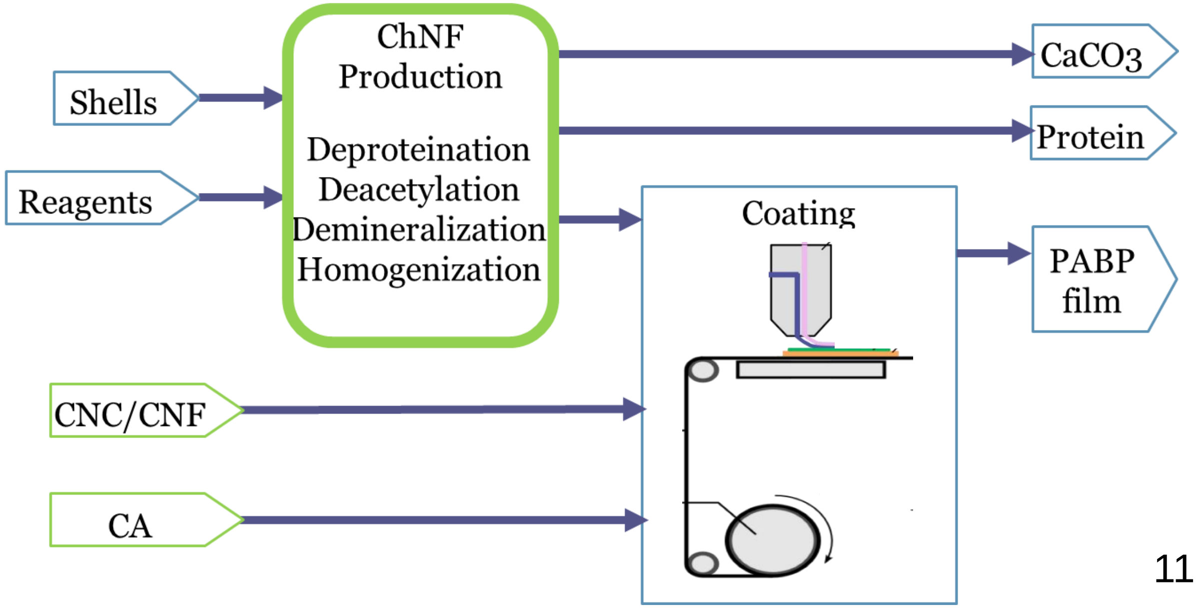
Economic Metrics

-First-pass process design

-cost per kg to produce ChNFs exploring pulp mill integration

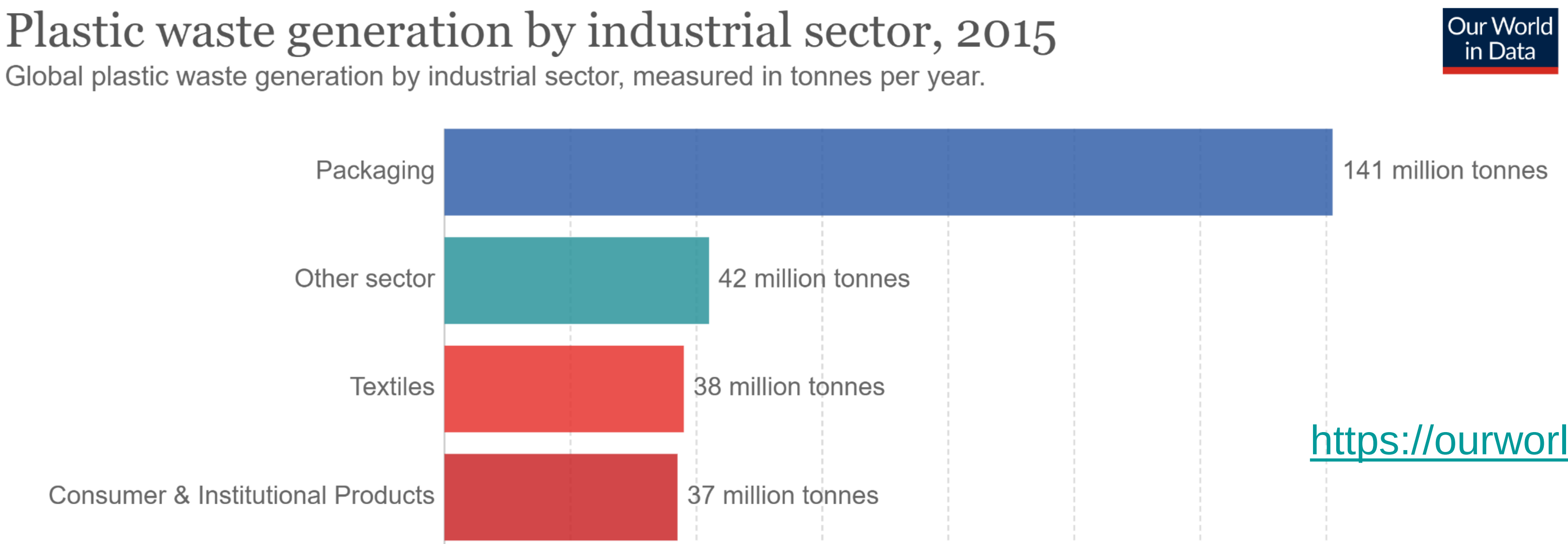
-energy utilization per kg ChNF

-cost and energy per m^2 to coat and dry



3 – Impact

Our PABP is a biomass-derived, degradable alternative to current unrecyclable / nondegradable flexible packaging → about 1 trillion units of plastic waste per year



https://ourworldindata.org/faq-on-plastics

CNCs and chitin are biodegradable → a solution for food packaging to biodegrade or compost with waste food.

Circular return of CO_2 back to biomass production – carbon regeneration

Addresses landfill use, environmental leakage (oceans) and microplastic accumulation

Meets industry-driven demand for alternative single-use plastic package designs.

re: New Plastics Economy Global Commitment

3 – Impact

Publications

1 article in *ACS Sustainable Chem. & Eng.* (IF=7.6)

ASAP 2021 doi.org/10.1021/acssuschemeng.0c09121

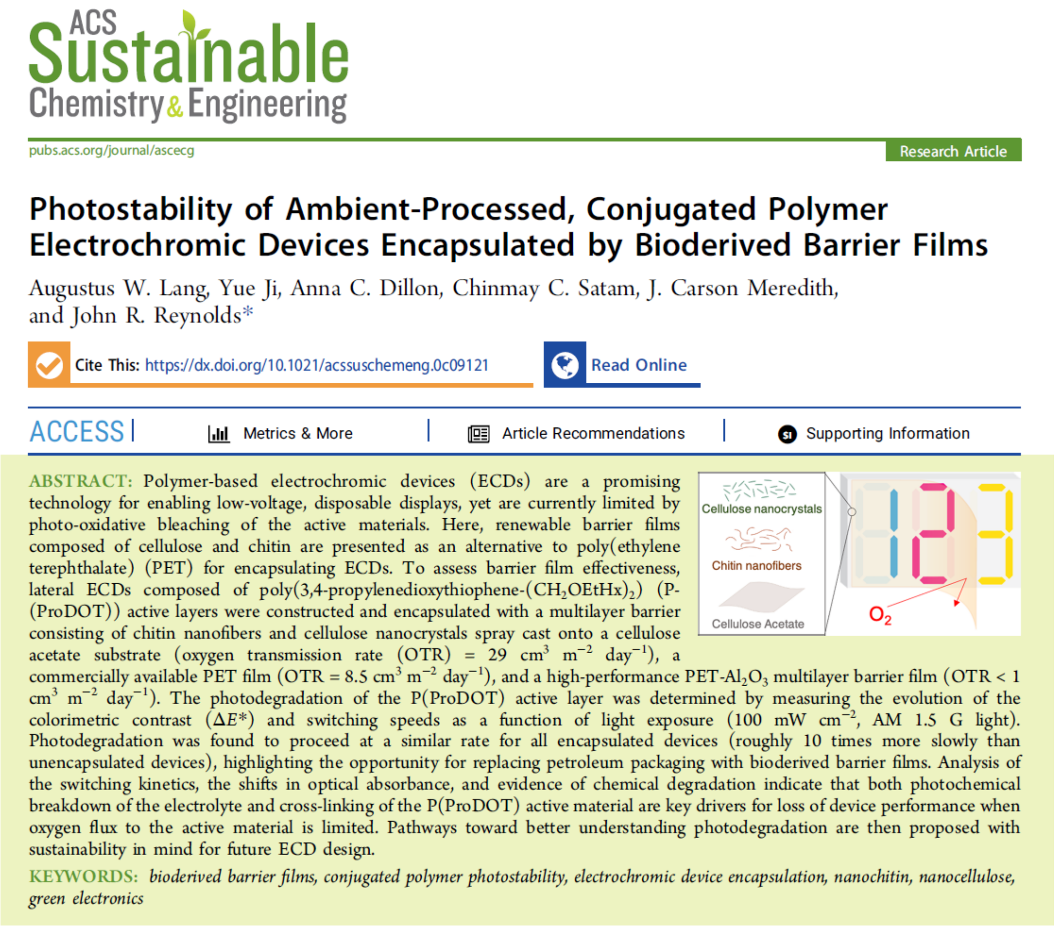
1 article in *Emergent Materials* (no IF)

[*Emergent Materials*](Emergent Materials) **3** 919–936 (2020)

2 articles in preparation

ACS Sustainable Chemistry & Engineering (IF = 7.6)

ACS Applied Materials & Interfaces (IF = 8.76)



ACS Sustainable Chemistry & Engineering

pubs.acs.org/journal/ascecg Research Article

Photostability of Ambient-Processed, Conjugated Polymer Electrochromic Devices Encapsulated by Bioderived Barrier Films

Augustus W. Lang, Yue Ji, Anna C. Dillon, Chinmay C. Satam, J. Carson Meredith, and John R. Reynolds*

Cite This: https://dx.doi.org/10.1021/acssuschemeng.0c09121 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Polymer-based electrochromic devices (ECDs) are a promising technology for enabling low-voltage, disposable displays, yet are currently limited by photo-oxidative bleaching of the active materials. Here, renewable barrier films composed of cellulose and chitin are presented as an alternative to poly(ethylene terephthalate) (PET) for encapsulating ECDs. To assess barrier film effectiveness, lateral ECDs composed of poly(3,4-propylenedioxythiophene-$(CH_2OEtHx)_2$) (P-(ProDOT)) active layers were constructed and encapsulated with a multilayer barrier consisting of chitin nanofibers and cellulose nanocrystals spray cast onto a cellulose acetate substrate (oxygen transmission rate (OTR) = 29 $cm^3\ m^{-2}\ day^{-1}$), a commercially available PET film (OTR = 8.5 $cm^3\ m^{-2}\ day^{-1}$), and a high-performance PET-Al_2O_3 multilayer barrier film (OTR < 1 $cm^3\ m^{-2}\ day^{-1}$). The photodegradation of the P(ProDOT) active layer was determined by measuring the evolution of the colorimetric contrast (ΔE^*) and switching speeds as a function of light exposure (100 mW cm^{-2}, AM 1.5 G light). Photodegradation was found to proceed at a similar rate for all encapsulated devices (roughly 10 times more slowly than unencapsulated devices), highlighting the opportunity for replacing petroleum packaging with bioderived barrier films. Analysis of the switching kinetics, the shifts in optical absorbance, and evidence of chemical degradation indicate that both photochemical breakdown of the electrolyte and cross-linking of the P(ProDOT) active material are key drivers for loss of device performance when oxygen flux to the active material is limited. Pathways toward better understanding photodegradation are then proposed with sustainability in mind for future ECD design.

KEYWORDS: *bioderived barrier films, conjugated polymer photostability, electrochromic device encapsulation, nanochitin, nanocellulose, green electronics*

Commercialization Developments

Proposal to USDA/US Endowment for Forests for commercialization with Mars, Inc.

Piloting project with a major packaging converter to explore adaptation to other commercial coating operations.

4 – Progress and Outcomes

Task	Description	Planned Completion	% Complete	Actual Completion
1	Initial Verification	31-Mar-19	100%	31-Mar-19
2	PABP Design and Prototyping	30-Jun-20	100%	1-Aug-20
2.1	Chitin and cellulse stock material production	30-Jun-20	100%	1-Aug-20
2.2	Optimization of suspensions for single layer slot die	1-Mar-20	100%	1-Mar-20
2.3	Lab-scale exploration of PABP design and composition	31-Dec-19	100%	31-Dec-19
2.4	Produce slot-coated PABPs / characterize barrier	30-Jun-20	100%	1-Aug-20
2.5	Intermediate verification task	30-Jun-20	100%	1-Aug-20
3	Optimization for food and device packaging	31-Dec-21	20%	
3.1	Barrier property optimization	30-Jun-21	30%	
3.2	Mechanical property optimization	30-Jun-21	20%	
3.3	Optical property optimization	30-Jun-21	10%	
3.4	Apply PABP to electrochromic display packaging	31-Dec-21	20%	
4	PABP Manufacturability	31-Dec-21	15%	
4.1	Implement multilayer slot die processing	31-Dec-21	20%	
4.2	Cost estimation for chitin-cellulose PABP production	31-Dec-21	10%	
4.3	Final Verification and Reporting	31-Dec-21	0%	

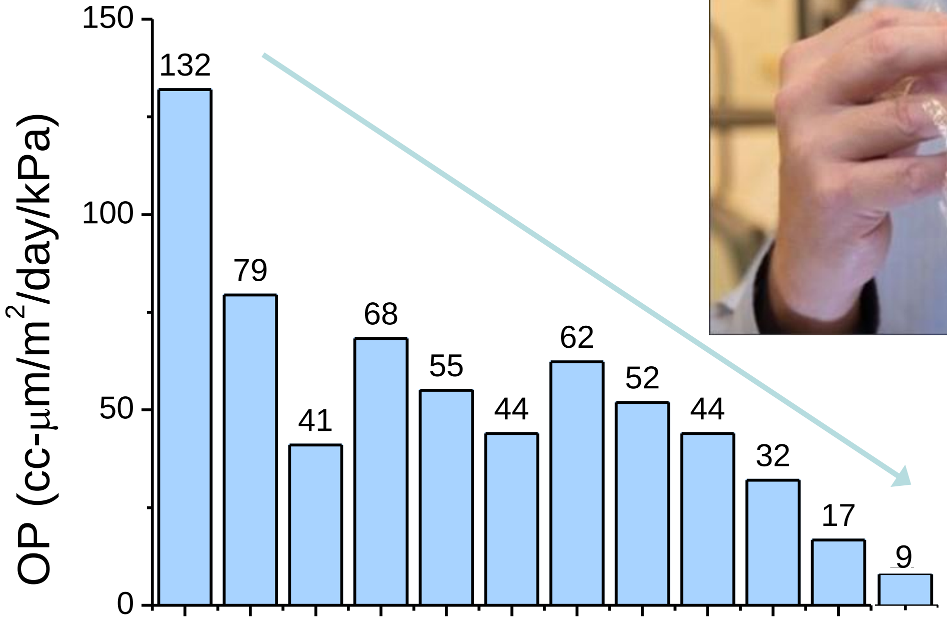
4 – Progress and Outcomes

Subtask 2.1 – Supply CNC and ChNF suspensions via biomass extraction
Subtask 2.3 - Lab-scale exploration of PABP design and composition

We discovered that the ChNFs can be optimized through their extraction processing.

The resulting fiber size and charge leads to widely different performance in a bilayer coated with CNCs.

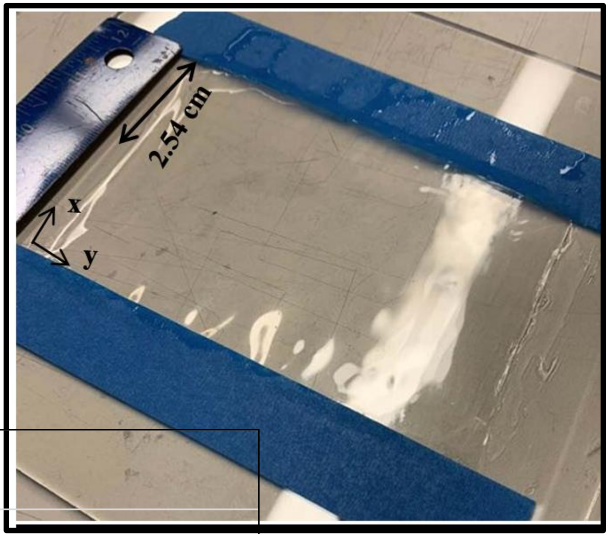
Sprayed ChNF + CNC on cellulose acetate (CA)



ChNF process intensity
→changes to size and charge

chitosan additive

4 – Progress and Outcomes



Subtask 2.4 – Produce slot-coated PABPs

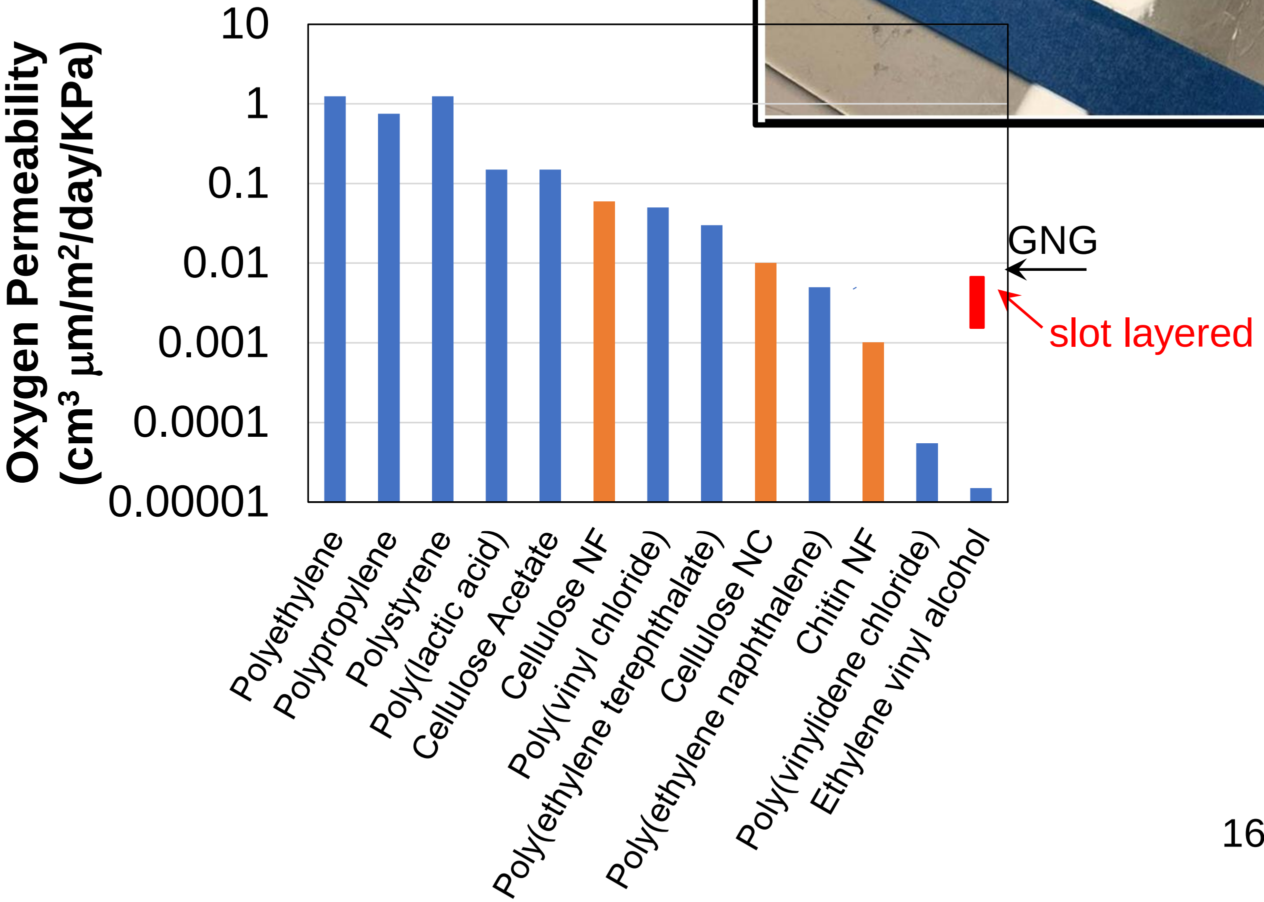
Subtask 4.1 – Optimize dual-layer slot-die

Dual-chamber slot die produced.

Films with OP values from 1.7 to 7.2 cm^{3}μm m^{-2}d^{-1}kP^{-1} produced, depending on conditions.

Exceeds GNG target of 9 cm^{3}μm m^{-2}d^{-1}kP^{-1}.

The 'best' oriented PET on the market is 10 cm^{3}μm m^{-2}d^{-1}kP^{-1}.



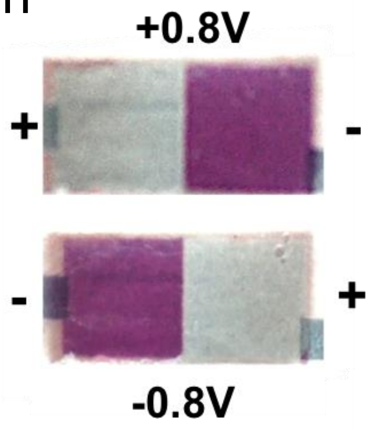
4 – Progress and Outcomes

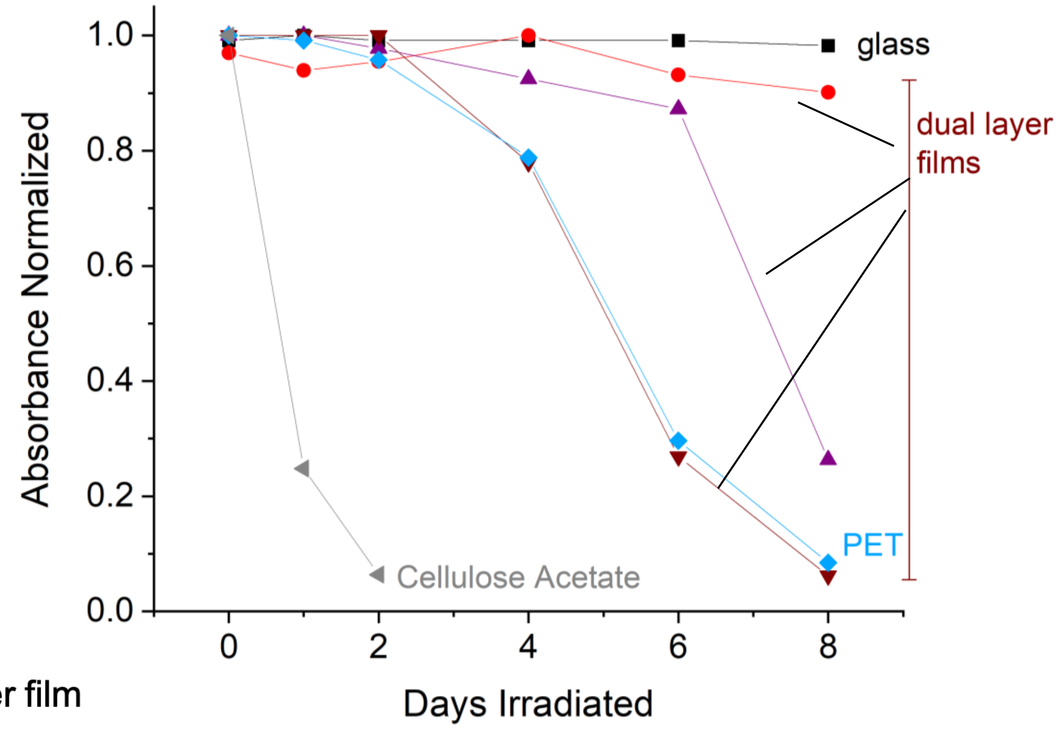
Photostability

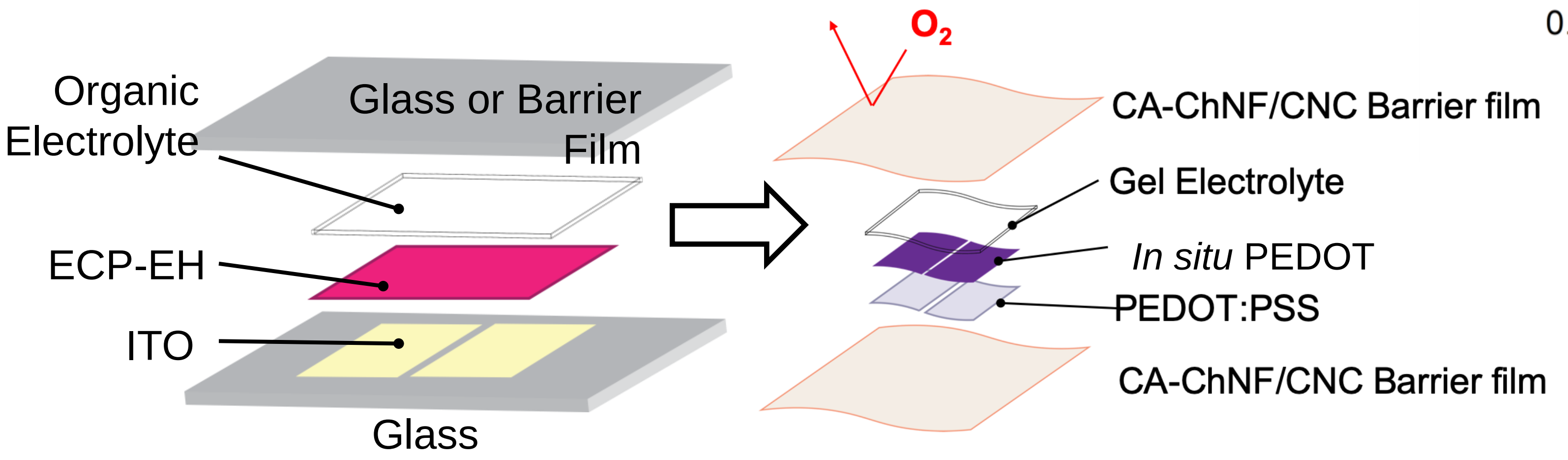
Subtask 2.3 – Encapsulation of ECDs

Subtask 3.4 – ECD packaging optimization

Performance of ECDs packaged in CNC/ChNF/CA barriers is near 3M FTB and better than PET.







4 – Progress and Outcomes

Milestone	Description	Planned Completion	% Complete	Actual Completion
2.1.ML.1	Production of required quantities of ChNF and CNC	30-Jun-19	100%	30-Jun-19
2.2.ML.1	Measure wetting properties of suspensions from 2.1	3-Jun-19	100%	30-Jun-19
2.2.ML.2	Measure rheological properties / lower boundary limit	30-Sep-19	100%	30-Sep-19
2.3.ML.1	Produce spray-dried prototypes and report O2	31-Dec-19	100%	31-Dec-19
2.4.ML.1	Design multilayer slot die	31-Mar-20	100%	31-Mar-20
2.5.ML.1	Chitin-cellulose PABP produced with 10% PO2	30-Jun-20	100%	30-Jun-20
2.5.ML.2	PABP films have at least 10% PO2 improvement	30-Jun-20	100%	17-Aug-20
3.4.ML.1	Identify gel electrolyte with acceptable performance	30-Sep-20	100%	31-Dec-20
4.1.ML.1	Fabricate bilayer or multilayer PABP on CA with multilayer	31-Dec-20	100%	31-Dec-20
3.4.ML.2	Achieve optical performance with PABP coating intact	31-Mar-21	50%	
3.2.ML.1	Determine process conditions that optimize mechanical	30-Jun-21	10%	
3.4.ML.3	Attain increase in bleaching time with PABP	30-Sep-21	10%	
4.3.ML.1	Verification of final performance for PABP	31-Dec-21	0%	

Summary

- This project is developing a performance advantaged bioproduct
  - -biomass alternative to petroleum products utilized in flexible packaging for oxygen barriers
  - -intermediate target 10% reduction in O_2 permeability vs. PET
  - -final target 80% reduction in O_2 permeability vs. PET
- Focus on manufacturable approach by slot-die coating → simultaneous deposition of chitin-cellulose nanomaterial bilayers
- We have achieved a 28% to 83% reduction in O_2 permeability reduction relative to biaxially oriented PET film
- Impact: expands range of byproducts of biomass biorefining; reduces landfill; regenerates carbon in packaging (#1 source of plastic waste)
- Final year in project is focusing on optimization of O_2 permeability, effects of humidity, mechanical properties, process design and cost analysis.

Quad Chart Overview (Competitive Project)

Timeline
- 10/1/2018
- 3/31/2022

	FY20 Costed	Total Award
DOE Funding	$334,012	$1,015,501
Project Cost Share	$70,614	$285,075

Project Partners*

N/A

Project Goal

This project will produce a performance advantaged bioproduct for flexible plastic food and electronics packaging, formed from biomass sources, which exceeds the O_2 barrier performance of oriented poly(ethylene terephthalate)(PET) by 10% to 500%.

End of Project Milestone

Oxygen Permeability	2	cm^3 µm / (m^2 kPa d)
Water Vapor Transmission Rate	1	g mm/(m^2 d)
Puncture strength	50	Mpa
Strain % at break	35	%
Light Transmission	90	%

Funding Mechanism

BEEPS DE-FOA-0001916
Topic 3
2018

*Only fill out if applicable.

Additional Slides

Responses to Previous Reviewers' Comments

- Highlights from Initial Verification Go/No-Go Review
  - Encouragement to carry out experimental design
    - Our team carried out a design of experiments on ChNF preparation, exploring a 3-factorial design and discovering an optimal preparation of ChNFs minimizing OP
  - Focus on solving difficulties spray-coating cellulose acetate (CA) and establish a new project baseline for CNC/ChNF/CA coated films.
    - Issues faced at verification visit with CA deformation during spraying were resolved shortly afterwards. A new baseline was established.
  - The project would benefit from more detailed discussions of key parameters constituting the "design" that will be handed-off from the spray coating work to the slot die coating work.
    - Parameters affecting suspension coatability was defined collaboratively by the spray- and slot-die teams and tracked for all batches of suspension that were developed.
  - An industrially relevant PET benchmark should be identified and measured in the lab, instead of relying on literature values.
    - Oriented PET (lowest O2 permeability available) was obtained from a leading manufacturer and measured in the PI's lab as a benchmark.

Responses to Previous Reviewers' Comments

- Highlights from Intermediate (M18) Verification Go/No-Go Review
  - Alterative film thickness measurement method recommented
    - Interferometry instrument identified, budget rearranged to allow its purchase. It is now installed.
  - Explore potential use of alcohol as co-solvent in drying
    - Currently under exploration. Recent literature reviewed on use of alkylated chitosans to improve dispersion in alcohols.
  - Consider a visit to NREL with trial on coating and drying line
    - To be considered when travel restrictions lift.
  - In TEA work be sure to consider side product valuation
    - Protein and mineral side products to be considered in TEA.
  - Focus on lessons learned from drying protocol
    - Deeper study ongoing to evaluate drying variables, water content and O2 permeability response

Publications, Patents, Presentations, Awards, and Commercialization

- Publications
  1. Lang, Y. Ji, A. Dillon, C. Satam, J.C. Meredith, J. Reynolds*, “Photostability of Ambient-Processed, Conjugated-Polymer Electrochromic Devices Encapsulated by Bioderived Barrier Films,” *ACS Sustainable Chemistry and Engineering,* **2021**, in press.
  2. Z. Yu, Y. Ji, V, Bourg, M. Bilgen, J.C. Meredith*, “Chitin- and Cellulose-Based Sustainable Barrier Materials: A Review,” *Emergent Materials*, **2020**, *3*, 919–936 https://doi.org/10.1007/s42247-020-00147-5

- Presentations
  1. AIChE Sustainable Packaging Symposium, July **2020**
  2. Energy and Fuels Renewability Symposium, ACS Spring National Meeting **2020**
  3. University of Florida Dept. of Chemical Engineering Symposium, March 9, **2020**
  4. Frontiers of Green Materials, December 16, **2019**, London.
  5. Workshop on Polymers for a Circular Economy, DOE BETO, Golden, CO, December 11, **2019**
  6. 4th International Symposium on Materials from Renewables, University of Georgia, October 9-10, **2019**, Athens, GA.
  7. Biodegradable Environmental Polymer Society, June 5-7, **2019**, Clemson, SC.
  8. SKC Corporation, May **2019**, Covington, GA.
  9. ACS Bioinspired Polymer Session, April 4, **2019** ACS Spring National Meeting, Orlando, FL.

- Commercialization efforts
  – USDA/US Endowment for Forests P3Nano Proposal submission for commercialization with partner Mars, Inc. (submitted Feb 2, 2021)
  – Tech transfer with a food brand / converter partnership to explore other coating methods