Cellulose-Chitin Composites for Performance Advantaged Barrier Products

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Technology Area Session

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Georgia Tech

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Project Overview

**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
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

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

evaluation of commercially available materials
## 1 – Management

<table>
<thead>
<tr>
<th>Risk</th>
<th>Mitigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compatibility with converters</td>
<td>Focus on scalable coating technology available to converters</td>
</tr>
<tr>
<td>Feedstock availability</td>
<td>cellulose: 137 million tons annual chitin: 3-6 million tons annual</td>
</tr>
<tr>
<td>Process costs</td>
<td>Process design and optimization</td>
</tr>
<tr>
<td>Mechanical properties/durability</td>
<td>Subtask dedicated to optimization and durability testing</td>
</tr>
<tr>
<td>Biodegradability / compostability</td>
<td>Trial with University of Georgia facility</td>
</tr>
</tbody>
</table>
2 – Approach

Biomass sources with potential to exceed oxygen barrier properties of PET

Cellulose Nanocrystals (CNCs)

Exploit synergism between chitin and cellulose-based nanofibers

Chitin Nanofibers (ChNFs)

Produce dense, well-adhered interfaces through layering

Achieve barrier performance, mechanical and optical properties

Crustacean food waste/ Fungi

Wood/Plant
2 – Approach

Develop Roll-to-roll Manufacturing of PABP

PABP Design Concept

- CNC (optional layer)
- ChNF (optional layer)
- CNC (cellulose nanocrystal)
- ChNF (chitin nanofiber)
- CA (cellulose acetate)

Performance Advantage
10% to 500% decrease in O₂ permeability vs. PET

Commercial Applications

Food Packaging

Electrochromic Display Packaging

Roll-to-roll process
Slot Die

Biomass
- woody
- shellfish waste

[Diagram showing the process flow and materials used in the 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
- O₂ 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 m² 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

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

Circular return of CO\textsubscript{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

https://ourworldindata.org/faq-on-plastics
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* 3 919–936 (2020)

2 articles in preparation
*ACS Sustainable Chemistry & Engineering* (IF = 7.6)
*ACS Applied Materials & Interfaces* (IF = 8.76)

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

<table>
<thead>
<tr>
<th>Task</th>
<th>Description</th>
<th>Planned Completion</th>
<th>% Complete</th>
<th>Actual Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial Verification</td>
<td>31-Mar-19</td>
<td>100%</td>
<td>31-Mar-19</td>
</tr>
<tr>
<td>2</td>
<td>PABP Design and Prototyping</td>
<td>30-Jun-20</td>
<td>100%</td>
<td>1-Aug-20</td>
</tr>
<tr>
<td>2.1</td>
<td>Chitin and cellulose stock material production</td>
<td>30-Jun-20</td>
<td>100%</td>
<td>1-Aug-20</td>
</tr>
<tr>
<td>2.2</td>
<td>Optimization of suspensions for single layer slot die</td>
<td>1-Mar-20</td>
<td>100%</td>
<td>1-Mar-20</td>
</tr>
<tr>
<td>2.3</td>
<td>Lab-scale exploration of PABP design and composition</td>
<td>31-Dec-19</td>
<td>100%</td>
<td>31-Dec-19</td>
</tr>
<tr>
<td>2.4</td>
<td>Produce slot-coated PABPs / characterize barrier</td>
<td>30-Jun-20</td>
<td>100%</td>
<td>1-Aug-20</td>
</tr>
<tr>
<td>2.5</td>
<td>Intermediate verification task</td>
<td>30-Jun-20</td>
<td>100%</td>
<td>1-Aug-20</td>
</tr>
<tr>
<td>3</td>
<td>Optimization for food and device packaging</td>
<td>31-Dec-21</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Barrier property optimization</td>
<td>30-Jun-21</td>
<td>30%</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Mechanical property optimization</td>
<td>30-Jun-21</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Optical property optimization</td>
<td>30-Jun-21</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Apply PABP to electrochromic display packaging</td>
<td>31-Dec-21</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>PABP Manufacturability</td>
<td>31-Dec-21</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Implement multilayer slot die processing</td>
<td>31-Dec-21</td>
<td>20%</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Cost estimation for chitin-cellulose PABP production</td>
<td>31-Dec-21</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Final Verification and Reporting</td>
<td>31-Dec-21</td>
<td>0%</td>
<td></td>
</tr>
</tbody>
</table>
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
**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$^{-1}$kPa$^{-1}$ produced, depending on conditions. Exceeds GNG target of 9 cm$^3$µm m$^{-2}$d$^{-1}$kPa$^{-1}$.

The ‘best’ oriented PET on the market is 10 cm$^3$µm m$^{-2}$d$^{-1}$kPa$^{-1}$. 
4 – Progress and Outcomes

**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.

 Photostability

- **Glass**
- ITO
- ECP-EH
- **O₂**
- Glass or Barrier Film
- **CA-ChNF/CNC Barrier film**
- Gel Electrolyte
- **In situ PEDOT**
- PEDOT:PSS
- **Cellulose Acetate**
- PET

![Graph showing photostability over days irradiated.](image-url)
### 4 – Progress and Outcomes

<table>
<thead>
<tr>
<th>Milestone</th>
<th>Description</th>
<th>Planned Completion</th>
<th>% Complete</th>
<th>Actual Completion</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.ML.1</td>
<td>Production of required quantities of ChNF and CNC</td>
<td>30-Jun-19</td>
<td>100%</td>
<td>30-Jun-19</td>
</tr>
<tr>
<td>2.2.ML.1</td>
<td>Measure wetting properties of suspensions from 2.1</td>
<td>3-Jun-19</td>
<td>100%</td>
<td>30-Jun-19</td>
</tr>
<tr>
<td>2.2.ML.2</td>
<td>Measure rheological properties / lower boundary limit</td>
<td>30-Sep-19</td>
<td>100%</td>
<td>30-Sep-19</td>
</tr>
<tr>
<td>2.3.ML.1</td>
<td>Produce spray-dried prototypes and report O2</td>
<td>31-Dec-19</td>
<td>100%</td>
<td>31-Dec-19</td>
</tr>
<tr>
<td>2.4.ML.1</td>
<td>Design multilayer slot die</td>
<td>31-Mar-20</td>
<td>100%</td>
<td>31-Mar-20</td>
</tr>
<tr>
<td>2.5.ML.1</td>
<td>Chitin-cellulose PABP produced with 10% PO2</td>
<td>30-Jun-20</td>
<td>100%</td>
<td>30-Jun-20</td>
</tr>
<tr>
<td>2.5.ML.2</td>
<td>PABP films have at least 10% PO2 improvement</td>
<td>30-Jun-20</td>
<td>100%</td>
<td>17-Aug-20</td>
</tr>
<tr>
<td>3.4.ML.1</td>
<td>Identify gel electrolyte with acceptable performance</td>
<td>30-Sep-20</td>
<td>100%</td>
<td>31-Dec-20</td>
</tr>
<tr>
<td>4.1.ML.1</td>
<td>Fabricate bilayer or multilayer PABP on CA with multilayer</td>
<td>31-Dec-20</td>
<td>100%</td>
<td>31-Dec-20</td>
</tr>
<tr>
<td>3.4.ML.2</td>
<td>Achieve optical performance with PABP coating intact</td>
<td>31-Mar-21</td>
<td>50%</td>
<td>31-Dec-20</td>
</tr>
<tr>
<td>3.2.ML.1</td>
<td>Determine process conditions that optimize mechanical</td>
<td>30-Jun-21</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>3.4.ML.3</td>
<td>Attain increase in bleaching time with PABP</td>
<td>30-Sep-21</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>4.3.ML.1</td>
<td>Verification of final performance for PABP</td>
<td>31-Dec-21</td>
<td>0%</td>
<td></td>
</tr>
</tbody>
</table>
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 O₂ permeability vs. PET -final target 80% reduction in O₂ 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 O₂ 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 O₂ permeability, effects of humidity, mechanical properties, process design and cost analysis.
Quad Chart Overview (Competitive Project)

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

<table>
<thead>
<tr>
<th>FY20 Costed</th>
<th>Total Award</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE Funding</td>
<td>$334,012</td>
</tr>
<tr>
<td>Project Cost Share</td>
<td>$70,614</td>
</tr>
</tbody>
</table>

| DOE Funding       | $1,015,501      |
| Project Cost Share| $285,075        |

**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**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Permeability</td>
<td>2 cm$^3$ μm / (m$^2$ kPa d)</td>
</tr>
<tr>
<td>Water Vapor Transmission Rate</td>
<td>1 g mm/(m$^2$ d)</td>
</tr>
<tr>
<td>Puncture strength</td>
<td>50 Mpa</td>
</tr>
<tr>
<td>Strain % at break</td>
<td>35 %</td>
</tr>
<tr>
<td>Light Transmission</td>
<td>90 %</td>
</tr>
</tbody>
</table>

**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 recommended
    • 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

• 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
  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
  – Tech transfer with a food brand / converter partnership to explore other coating methods