In-Silico Design of Next Generation Cellulose-Derived Packaging Materials

Cooperative Research and Development Final Report

CRADA Number: CRD-21-18015

NREL Technical Contact: Peter Ciesielski

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Technical Report
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Cooperative Research and Development Final Report

Report Date: December 20, 2024

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Futamura USA, Inc

CRADA Number: CRD-21-18015

CRADA Title: In-Silico Design of Next Generation Cellulose-Derived Packaging Materials

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Sponsoring DOE Program Office(s):

Office of Energy Efficiency and Renewable Energy (EERE), Advanced Manufacturing and Materials Technologies Office

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources Government In-Kind
Year 1	$300,000.00
Year 2, Modification #1	$.00
Year 3, Modification #2	$.00
Year 4, Modification #3	$.00
TOTALS	$300,000.00

Executive Summary of CRADA Work:

Developing sustainable solutions for single-use packaging is an important objective to combat the environmental crisis of plastics pollution. Most embodiments of cellulose-based packaging materials, including Cellophane™, are completely biodegradable in both terrestrial and marine environments. However, petroleum-derived alternatives offer some performance advantages for metrics such as moisture barriers and mechanical properties.

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This project leverages molecular dynamics simulation to investigate how molecular modifications to cellulose-based polymer assemblies impact their material properties. An important performance criterion for the modified materials was to retain biodegradability; thus, modifications by naturally occurring, biodegradable additives were the focus of this study.

Specifically, we developed models with xylan and lignin of varying monomeric compositions into the cellulose matrix. The mechanical properties were investigated by performing stress-strain simulations, and the water barrier and hydrophobicity were investigated by simulating the water contact angle.

Our findings indicate that the incorporation of xylan into the cellulose matrix tends to increase the mechanical properties with an optimal loading of ~27 wt%. We also predict that orienting the nanoscale directionality of the xylan chains such that they are perpendicular to the cellulose fibrils will dramatically increase mechanical strength. In contrast, the incorporation of lignin tends to weaken the composite at all loadings investigated.

Simulations of water contact angle predicted that coating polymers on the surface of the cellulose assembly creates a more hydrophobic surface than incorporating them throughout the matrix. Of the coatings investigated, lignin resulted in the most hydrophobic surface, followed by pectin and keratin, which both imparted modest increases in hydrophobicity.

Future experimental work done by Futamura will focus on designing material prototypes to capitalize on the predictions of performance enhancement obtained from molecular modeling. While substantial progress was made by the simulations performed in this project, there still exists a vast parameter space that we were unable to investigate, including branching, functional group decoration, and degree of polymerization of polymer additives. However, the methods developed in this initial investigation will facilitate more rapid evaluation of the impact of molecular characteristics on the performance of biopolymer composite materials and thereby accelerate future materials discovery efforts in this area.

CRADA benefit to DOE, Participant, and U.S. Taxpayer:

- Assists laboratory in achieving programmatic scope, and/or
- Uses the laboratory's core competencies, and/or
- Enhances U.S. competitiveness by utilizing DOE developed intellectual property and/or capabilities.

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Summary of Research Results:

Task 1: Computational Method Verification for Cellophane – Completed four months after start

This task will provide the initial verification that the molecular dynamics (MD) simulations predict accurate properties for base material, cellophane. Specifically, models of molecular assemblies for cellophane will be constructed based on information from Futamura and additional details from the literature as needed. Material properties will be computed and compared to experimental measurements.

Task 2: Property Prediction for Candidate Materials - Completed 9 months after start

Activities: This task will construct in silico models of molecular assemblies of novel cellulose-derived polymers. At least 10 different polymers will be investigated based on input from Futamura regarding which modifications are synthetically achievable and likely to increase performance metrics. Simulations will be performed to calculate the thermal, mechanical, and barrier properties of each novel polymer.

Information flow: Guidance regarding which molecular modifications are synthetically achievable and economically feasible will be provided to NREL from Futamura. Predictions of material performance metrics will be provided by NREL to Futamura.

Task 3: Material Candidate Evaluation and Down-Selection - Completed 12 months after start

Activities: This task will evaluate the required supply chain and potential value proposition of the top performing material candidates as predicted by Task 2. The analysis will be primarily conducted by Futamura but NREL will assist as needed with the Materials Flows Through Industry tool.

CRADA Final Report: Preparation and submission in accordance with Article X.

This report serves to meet the requirement for the CRADA Final Report with preparation and submission in accordance with the agreement's Article X.

Introduction

The world is in an existential situation relative to climate destabilization and land/marine accumulation of single-use packaging. Single-use packaging is predominantly made from mixed materials that are made from fossil-derived plastics, which have no end-of-life other than landfill or, if collected, could be potentially subsidized for repurposing or chemical recycling. Another alternative is to leverage nature's stored energy and sequestered carbon found in plant biomass. Utilization of intact biopolymers for packaging applications is inherently energy and carbon-efficient because the energy of production is contributed by sunlight and the carbon comes directly from CO_2. These elegant, naturally mass-produced materials can be derivatized into new materials that are exceptionally well-suited for single-use packaging. However, accessing these materials to meet constantly evolving societal needs requires rapid innovation in materials design and manufacturing technologies that must be accelerated by high-performance computing.

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To feed a population that is approaching 9 billion people while avoiding catastrophic levels of plastic pollution, it is imperative to develop packaging materials that are 100% compatible with the circular economy. Materials with photosynthetic beginning-of-life and an earth-digestible end-of-life minimize energy inputs throughout the lifecycle because they leverage naturally occurring materials synthesis processes (solar-energy-driven CO_2 sequestration) and do not require energy-intensive collection, sorting, and chemical recycling or repurposing to complete the lifecycle. One category of materials is made from dissolving-grade cellulose pulp called viscose that can be then cast into packaging films. This technology was originally called Cellophane™. Cellophane was the first transparent packaging film used in the world after its invention by DuPont at the turn of the 20th century.

There is a rapidly heating "sustainability" froth amongst brands and retailers. Increasing equally at an alarming rate is the collective demand for earth-digestible/compostable single-use packaging options. These factors have created a manufacturing opportunity that will be transformational in both economic and environmental impact. In fact, the global market of biodegradable plastics is showing a compound annual growth rate of 11.5% and will reach approximately $3.5 billion by 2022.[1] Broadening the application space of cellophane-based packaging can only be achieved by the development of increased properties such as tensile strength, impact resistance, tear resistance, and puncture resistance while maintaining its advantage of being industrial and home compostable as well as soil, anaerobic, and marine-degradable.

Advances in molecular modeling of carbohydrate materials over the last decade will be leveraged to accelerate modernization of cellulose-based material solutions to meet application demands. By modeling the structure-property relationships of accessible cellulose polymer structures, we will identify new materials to serve the heightened market demand more effectively than complicated and time-consuming trial-and-error. The figures of merit, such as bulk mechanical properties, thermal properties, and barrier properties, are emergent properties that arise from mesoscale (or larger) assemblies of many polymer chains. Simulating molecular systems of this size is only achievable with high-performance computing resources. The future of compostable, single use, flexible packaging critically depends on the ability to develop higher-performing materials.

In this project, we systematically investigated new synthetically accessible cellulose derivatives to identify production targets with performance advantages. Molecular models of cellulose derivatives were constructed based on input from Futamura and existing characterization data from the literature. Initially, validation of the force field was performed by computing the viscosity of cellulose and viscose solutions over a range of degree of polymerization (DP) and comparing them to experimental measurements. Following validation, a variety of biopolymer composites containing cellulose, xylan, and lignin at different compositions were constructed. The ultimate tensile strength and elastic modulus of each system were determined using MD simulations of mechanical deformation. Next, the impact of additives and surface coatings on the hydrophobicity of the film was investigated by simulating the water contact angle.

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Results

Force Field Validation

To verify the appropriateness of the Chemistry at Harvard Macromolecular Mechanics (CHARMM) force field for the biopolymer systems in question, we calculated the viscosity of five different systems of molecular assemblies for viscose. The DP of the cellulose xanthate ranges from 10 to 100, resulting in systems between ~44,000–995,000 atoms in size. The compositions of the viscose systems follow the experimental characterizations from Futamura. Specifically, the concentration of cellulose and NaOH is 9% and 6%, respectively. The γ-No is 30, which is defined as the number of xanthate groups per 100 glucose units. For each of the five systems, we have constructed 40 models with the cellulose xanthates randomly placed in the simulation box, as shown in Figure 1. The equilibration run was 10 ns long, and the production run was 4 ns for each model. The viscosity of the systems was calculated using the Green−Kubo relation:

$$\eta = \frac{V}{k_B T} \int_0^\infty \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle \, dt \quad (1)$$

where V is the system volume, k_B is the Boltzmann constant, T is temperature, and $P_{\alpha\beta}$ is the off-diagonal pressure tensor. The calculated viscosity data for the five systems were used to fit the Mark-Houwink equation:

$$[\eta] = k \cdot DP^{\alpha} \quad (2)$$

where η is the viscosity, k and α are the fitted parameters. This equation is then used to predict the viscosity of cellulose xanthate with a large DP. The preliminary results of calculated viscosity are shown in Figure 2A.

The realistic viscose solution is a mixture of cellulose xanthate ranging from ~7-2500, resulting in an average DP of ~430, as shown in Figure 2B. Our results demonstrate good agreement with the expected behavior predicted by the Mark-Houwink relationship and thereby may be extrapolated to provide excellent experimental viscosity measurements for this system. This validation exercise suggests that our force field is appropriate for modeling systems consisting of cellulose and its derivatives.

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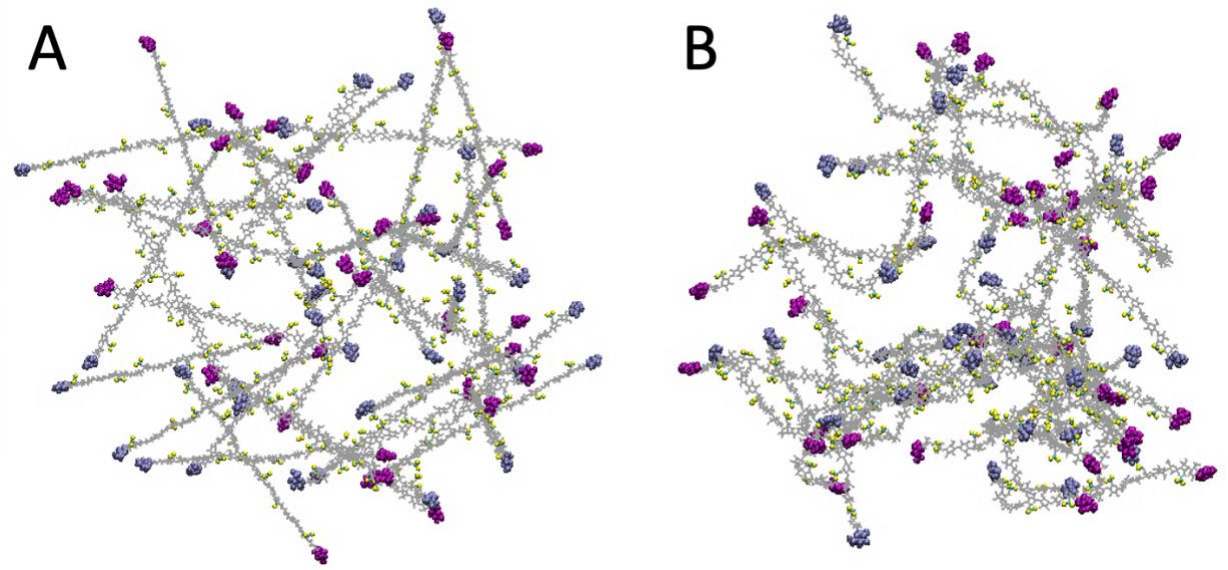

Figure 1. The initial structure of the constructed viscose model with cellulose xanthate randomly placed in the simulation box (A). The structure of the cellulose xanthate at the end of 10 ns MD simulation.

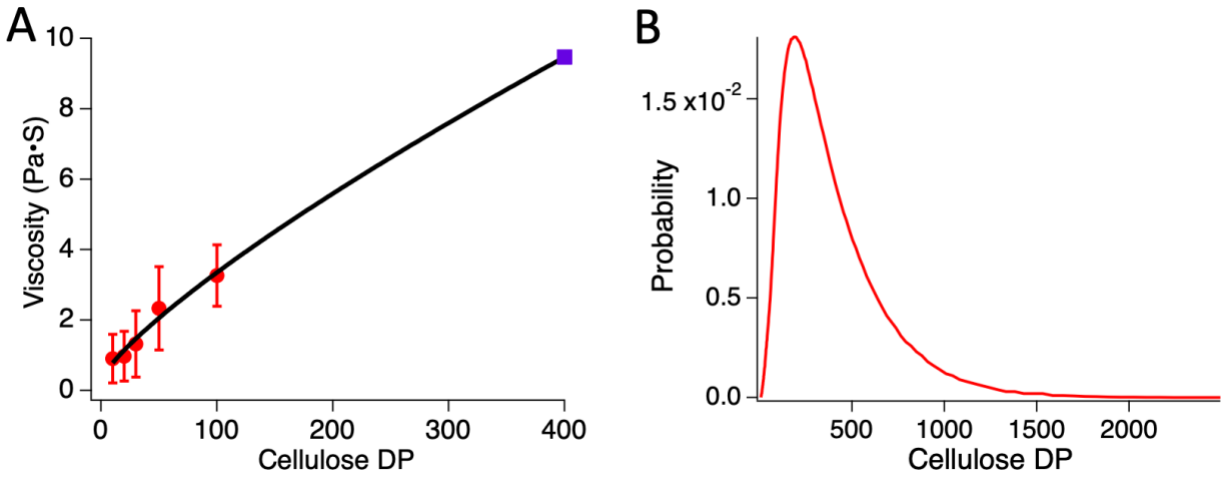

Figure 2. The calculated viscosity at a function of the DP of cellulose xanthate (A). The purple square indicates the predicted viscosity value for DP = 400 using the Mark-Houwink equation. The distribution of cellulose xanthate DP characterized by experiments (B).

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Mechanical Deformation Simulations

Two DP 40 cellulose-II fibrils roughly 50 x 50 x 100 Å were built in CHARMM and modified by adding differing amounts of either xylan or lignin polymers to analyze the effect of xylan or lignin modification on mechanical failure and modulus. A total of fifteen systems were built: One system consisting of two cellulose-II fibrils without any modifications; four systems with varying amounts of xylan placed randomly in a parallel orientation to the axial direction of the cellulose fibrils referred to as x4, x8, x16, and x32; four systems with varying amounts of xylan chains placed randomly perpendicular to the orientation of the axial direction of the cellulose fibrils referred to as xp4, xp8, xp12, and xp16; and six systems with varying amounts of lignin chains placed randomly parallel to the orientation of the cellulose-II fibrils, referred to as l6, l12, l24, and l48. The lignin in each system was built with an S:G ratio of 13:7, and an additional two systems with 24 lignin chains and S:G ratios of 0:1 and 9:1 were built to examine the effect of S:G ratio on the fracture behavior. Each system is shown in figures 3 and 4.

Molecular dynamics simulations were performed on each system in CHARMM to examine fracture behavior by restraining the C1 atoms on one of the two cellulose-II fibrils with a 5 kcal/(mol*Å^2) force constant harmonic restraint and applying a force on the C1 atoms in the other crystal in the x-direction away from the restrained crystal. The lignin or xylan in the system was unrestrained, and no explicit force was applied to them in the simulations. The simulations were run using periodic boundary conditions with a gap in the x-direction to allow the cellulose-II fibrils to separate an ample distance.

The force at failure was estimated for each of the fifteen systems by running a binary search algorithm written in Python consisting of short CHARMM fracture simulations with different forces applied to the unrestrained cellulose-II crystal. At the end of the short dynamics, the algorithm determined if the data of the distance between the two cellulose-II fibrils was indicative of fracture behavior modeled by a second-order polynomial function or non-fracture behavior modeled by a square root function. The algorithm assigned a penalty value for each model, and the force was either increased or decreased depending on the penalty value. The minimum force required to elicit a fracture response from each system was recorded as the force at failure.

After the force at failure for each of the fifteen systems was ascertained, that number was divided by ten to get the force increment, and mechanical stress simulations as described above were run on each system. The simulations were run with an applied force of zero to the force at failure, incrementing the force by the force increment for a total of eleven simulations for each of the fifteen systems. Molecular dynamics simulations were run at each applied force until the separation distance between the cellulose-II fibrils remained constant, which occurred within 1 ns. The applied force and separation distance were averaged over the last 0.1 ns for each simulation run and used to calculate the stress and strain according to Equations 3 and 4, respectively. The stress and strain for each system were plotted, and the slope of the linear region was calculated, giving the modulus for each system.

$$\sigma = \frac{F}{A} \tag{3}$$

$$\varepsilon = \frac{L - L_0}{L_0} \tag{4}$$

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Where F is the total applied force, A is the cross-sectional area perpendicular to the direction of the applied force, L is the separation distance between the two cellulose-II fibrils, and L_0 is the initial separation distance between the two cellulose-II fibrils.

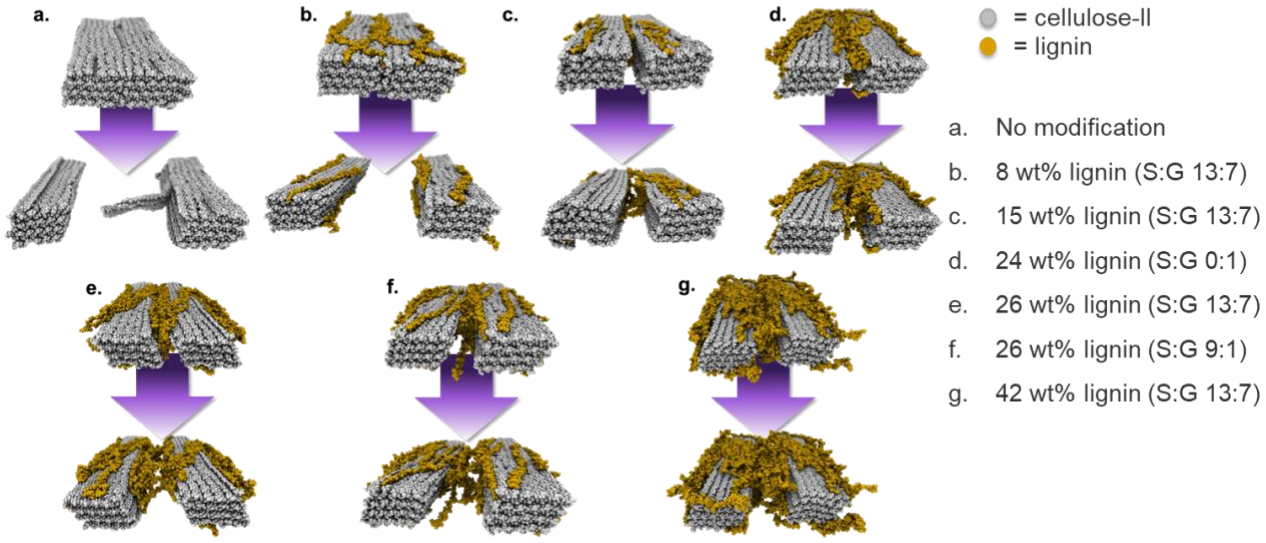

Figure 3. Cellulose-II systems without modification and modified by addition of lignin before and after fracture simulations. Lignin is shown in yellow, and cellulose is shown in grey. Arrows point from the initial system to the final system after simulation. A-D show the cellulose-II systems with no modification, 6 lignin chains with S:G ratio 13:7 added, 12 lignin chains with S:G ratio 13:7 added, and 24 lignin chains with S:G ratio 0:1 added, respectively. E-G show modified cellulose-II systems with 24 lignin chains with S:G ratio 13:7 added, 24 lignin chains with S:G ratio 9:1 added, and 48 lignin chains with S:G ratio 13:7 added.

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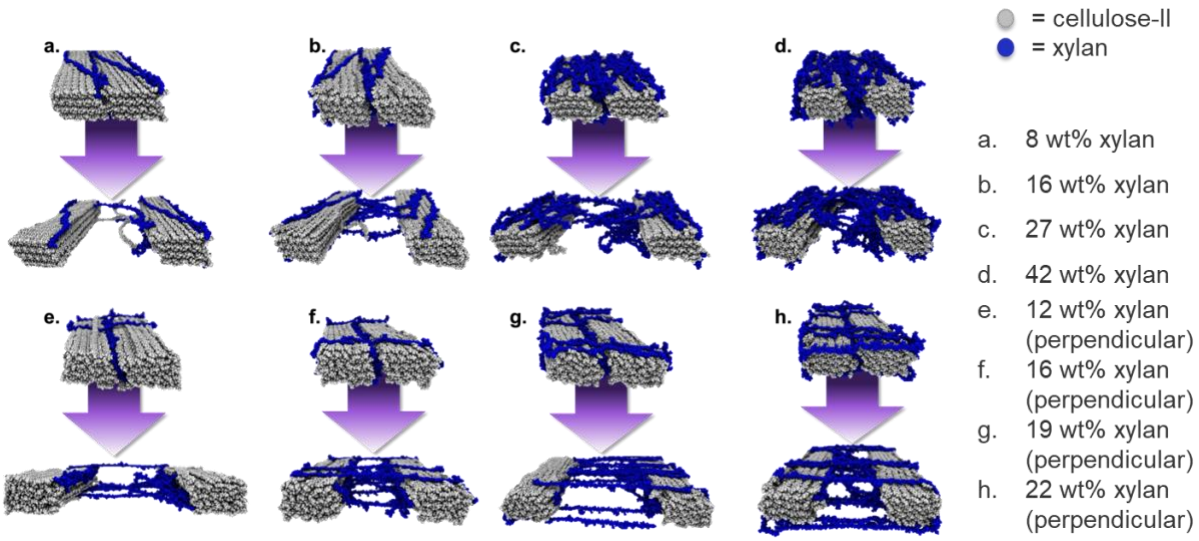

Figure 4. Cellulose-II systems modified by the addition of xylan before and after fracture simulations. Xylan is shown in blue, and cellulose is shown in grey. Arrows point from the initial system to the final system after simulation. A-D shows the modified cellulose-II systems with 4, 8, 16, and 32 xylan chains added parallel to the axial direction of the cellulose, respectively. E-H shows modified cellulose-II systems with 4, 8, 12, and 16 xylan chains added perpendicular to the axial direction of the cellulose, respectively.

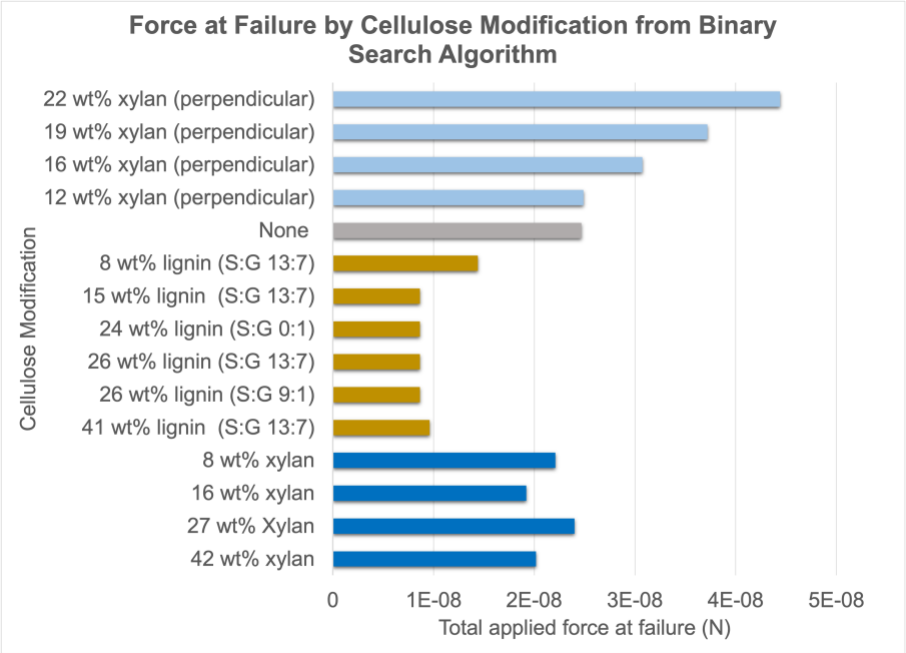

Figure 5. Force at failure from binary search algorithm. Cellulose with no modifications shown in grey, Cellulose with xylan modification shown in dark blue to represent parallel placement of xylan polymers and light blue to represent perpendicular placement. Cellulose with lignin modifications shown in yellow.

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Figures 3 and 4 show all fifteen systems that were built for mechanical stress simulations in their initial and final states. After eleven runs of mechanical stress with incremental force applied, the cellulose-II fibrils separated and fractured. The applied force and separation distance of the cellulose fibrils from each simulation are used to calculate the force at failure and the modulus for each system.

Figure 5 shows the force at failure given by the binary search algorithm. The placement of xylan perpendicular to the cellulose-II axial direction, shown in light blue, results in an increase in the required force to fracture the system as compared to no modifications, shown in grey. As the number of perpendicular xylan chains increases, so too does the force at failure. Adding xylan chains parallel to the axial direction of the cellulose, shown in dark blue, slightly reduces the force at failure without a clear trend with respect to the number of xylan chains. Additionally, adding lignin chains parallel to the axial direction of the cellulose, shown in yellow, lowers the force at failure with a similar lack of direct correlation to the number of lignin chains.

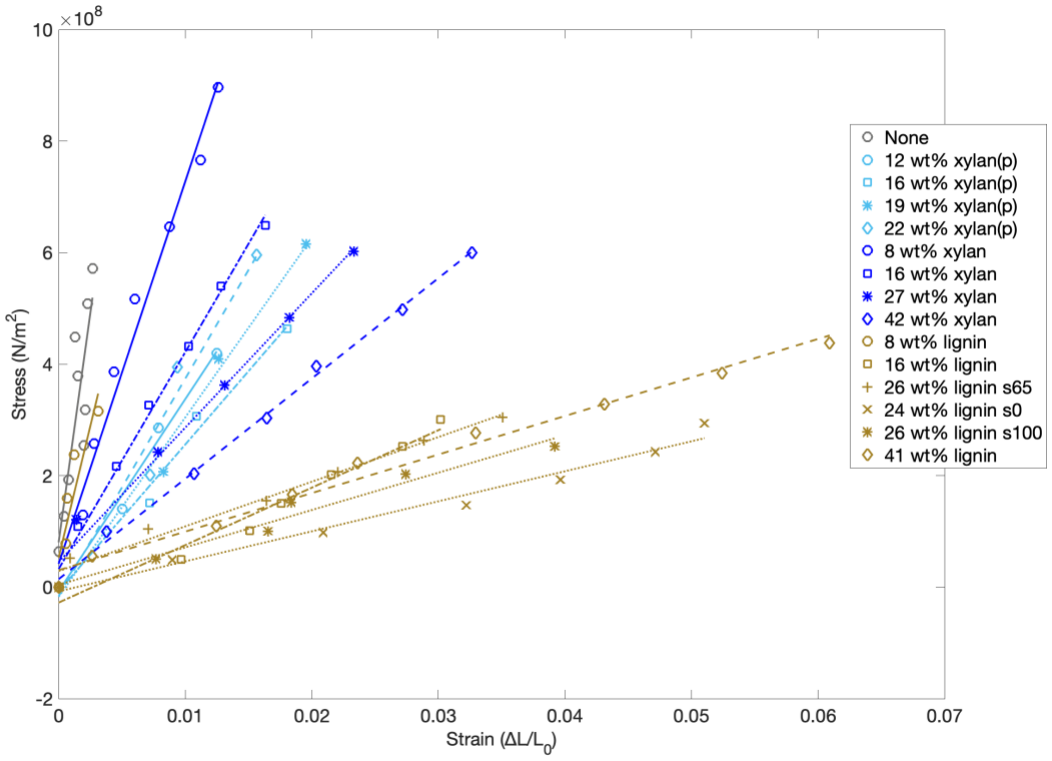

Figure 6. Linear region of stress vs. strain graph for each modified cellulose system. Cellulose with no modifications shown in grey, Cellulose with xylan modification shown in dark blue to represent parallel placement of xylan polymers and light blue to represent perpendicular placement. Cellulose with lignin modifications shown in yellow.

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Table 1.

System	Modulus (GPa)
None	164.2
12 wt% xylan (perpendicular)	34.4
16 wt% xylan (perpendicular)	26.3
19 wt% xylan (perpendicular)	32.2
22 wt% xylan (perpendicular)	39.0
8 wt% xylan	68.5
16 wt% xylan	38.9
27 wt% xylan	24.1
42 wt% xylan	18.0
8 wt% lignin	94.2
16 wt% lignin	10.3
24 wt% lignin (S:G 0:1)	5.4
26 wt% lignin (S:G 13:7)	8.0
26 wt% lignin (S:G 9:1)	6.7
41 wt% lignin	6.9

Figure 6 shows the linear region of the graph of stress vs. strain for each of the modified cellulose-II systems. Table 1 shows the modulus of each system, calculated as the slope of the respective line in Figure 5. The unmodified cellulose-II system has the highest modulus, followed by the systems with the fewest lignin or xylan added. Increasing the number of xylan or lignin chains in parallel orientation corresponds to a lower modulus, with the addition of lignin lowering the modulus significantly more than the addition of xylan. Modifying the lignin S:G ratio while keeping the number of lignin chains constant results in a slightly lower modulus for the S:G 0:1 and S:G 9:1 systems with the 24 S:G 0:1 lignin chain system exhibiting the lowest modulus of all of the systems. The moduli of the perpendicular xylan systems lie in the middle of the parallel xylan data, with less of an effect of the number of chains on modulus values.

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Water Contact Angle Simulations

Water contact angle (WCA) simulations provide an estimate for hydrophobicity, a key surface performance metric for plastics and especially plastic films. The crystal structure of cellulose II was presented by Kolpak and Blackwell (*Macromolecules* **1976**) and further refined by Langan *et al.* (*Biomacromolecules* **2001**). The cellulose II unit cell from Langan *et al.* is shown in Figure 5A. It has been well-established by multiple studies that the predominant exposed crystal faces of cellulose II are the 110, 1-10, and 020 (e.g. Yamane *et al. Polymer J.* **2006**). For clarity, we note that the 020 face is indistinguishable from the 010 (all these faces are annotated in Figure 5A).

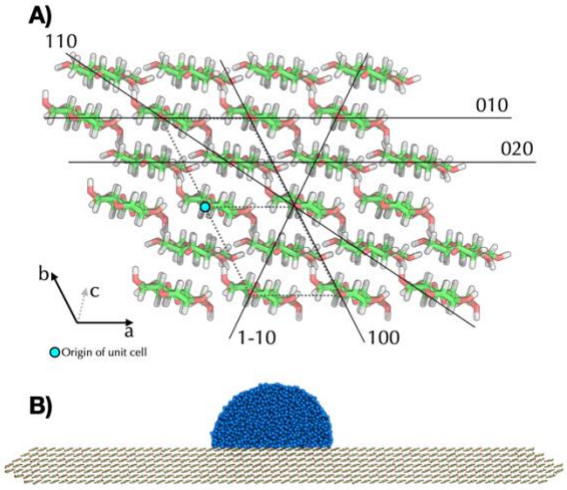

Figure 7. A) the unit cell and major crystallographic faces of cellulose II. B) An example of the starting configuration for water contact angle simulations. Shown in "sticks" representation is a cellulose II crystal with water droplet (blue spheres) on top of the 110 face.

We prepared surfaces *in silico* for each exposed face and computed the WCA via MD simulations. The starting configuration (Figure 1B) has a contact angle of approximately 90° and generally relaxes to the equilibrium WCA after ~15 ns. Experimentally, this number has been reported to range from 12° (Yamane *et al. Polymer J* **2006**) to 60° (Faria-Tischer *et al. Mat Sci Eng C* **2015**). It is generally regarded as a highly hydrophilic film (Yamane *et al. Polymer J* **2006**, Trentin *et al. Biomacromolecules* **2021**), suggesting a low contact angle, but this can be influenced by the roughness of the surface, among other factors. In addition, cellulose II surfaces have been estimated to be ~50-60% crystalline (Aulin *et al. Langmuir* **2009**).

Each surface we build has these common characteristics: DP = 20, 4-6 layers "deep" (~20-30 Å), and 300-400 Å wide. An "infinite" half cylinder of water is placed on top of the surface (axis going in and out of the page in Figure 5B). In each case, 30 ns of MD simulation is sufficient to estimate the equilibrium water contact angle. The results for the three pristine major crystal faces of cellulose II are shown in Figure 6.

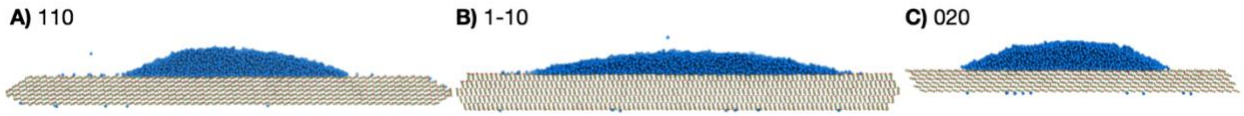

Figure 8. Water contact angle results for the three major exposed crystal faces of cellulose II. These configurations are following 30 ns of molecular dynamics.

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We subsequently explored several natural molecules as coatings to examine their effect on surface hydrophobicity. These include decorating the cellulose II surface with 1) lignin, 2) pectin, and 3) keratin. Figure 7 shows the effect on WCA for three different loadings of lignin.

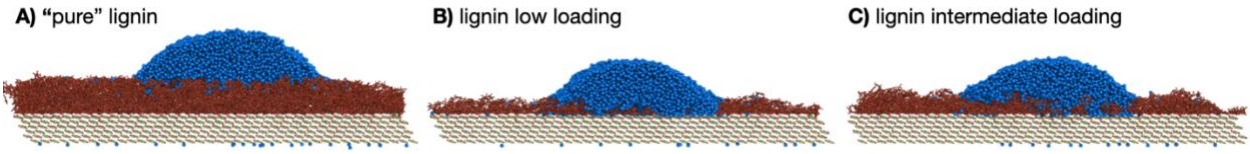

Figure 9. Water contact angle on the 020 face of cellulose II for three different loadings of lignin. A) "pure" lignin denotes that the lignin loading, and configuration prevents water from interacting with the cellulose surface; B) "low loading" comprises 48 chains of lignin (each chain MW: 4,500 g/mol); C) "intermediate loading" comprises 72 chains of lignin.

To further explore cellulose II coatings that are naturally derived and food-safe, we deposited pectin and keratin on 020 surfaces of cellulose II. Pectin is an important structural polysaccharide in plants, mainly composed of galacturonic acid (a galactose-derived sugar acid), and keratin is a structural protein found in myriad vertebrate structures, including hair, scales, nails, feathers, horns, claws, hooves, and skin. Unlike lignin, however, both pectin and keratin demonstrate a hydrophilic character that results in a WCA that is comparable to or lower than the bare cellulose II 020 surface (Figures 8B and 8C).

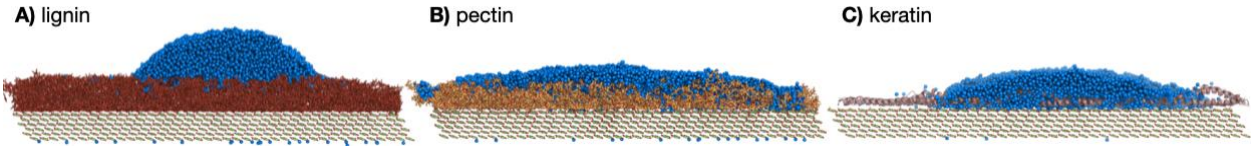

Figure 8. Water contact angle on the 020 face of cellulose II for three different natural coatings. A) lignin (this is the same as Figure 3A and is included here for comparison); B) pectin; C) keratin.

Discussion

Mechanical Property Modification

The lack of clear correlation to the number of polymer chains added in the systems with lignin or xylan placed parallel to the axial direction of the cellulose-II fibrils is likely because the chains are randomly placed, with greater or fewer chains between the cellulose-II fibrils irrespective of the total number of chains added. The strongest interaction in the system is between the two cellulose-II fibrils, so systems with more xylan or lignin in between the cellulose fibrils may require a lower force for fracture. Likewise, systems with less xylan or lignin in between the cellulose fibrils may require a higher force for fracture. This likely explains the high force at fracture for the system with 6 lignin chains added (Lignin x6 on the graph). This behavior was addressed in the perpendicular xylan systems by placing 8 xylan chains in between the cellulose-II fibrils for each system, and then an additional 4, 8, 12, or 16 chains were placed randomly. The trends with increasing xylan chains are much clearer for the perpendicular xylan systems, suggesting that the location of the modification within the cellulose-II matrix has a large impact on the mechanical behavior of the assembly.

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Comparing the perpendicular xylan x4 and perpendicular xylan x16 systems suggests that increasing the number of perpendicular xylan chains increases the modulus; however, the values in between do not follow this trend. This may be due to the 8 chains of xylan that lie between the cellulose fibrils in all the perpendicular xylan systems, perhaps dominating the effect on the modulus in these systems. These results suggest that not only the type of polymer but also the orientation and location of polymers added to the cellulose-II matrix have a large effect on the mechanical properties of the composite material.

In general, the results may be interpreted as follows:

- In general, disruption of cellulose-cellulose interactions weakens the assembly.
- Addition of xylan can improve mechanical strength until ~30 wt %, after which additional hemicellulose begins to weaken the assembly.
- Xylan applied perpendicular to the axis of the cellulose fibrils is particularly effective.
- Lignin weakens the tensile strength but may act as a plasticizer to enhance resilience to compression and bending.

Surface Wettability

From Figure 8, each crystal face of cellulose II is seen to display relatively low hydrophobicity, though none exhibit complete wetting. In a recent computational study of various crystal forms of cellulose, these three faces were all determined to have WCA < 5°, which was determined to be the limit of sensitivity for the method (Trentin *et al. Biomacromolecules* **2021**). We suspect a key difference may be in the choice of water model; whereas Trentin *et al.* utilize the TIP3P water model, we use SPC/E, which has been shown to more closely match the experimental water/air surface tension (Chen and Smith *J. Chem. Phys.* **2007**), which is a key parameter in determining the WCA.

Cellulose-lignin composites have recently been shown experimentally to increase the hydrophobicity of cellulose I (Wang *et al. Small* **2021**). Here, we examine the effect of coating the cellulose II surface with lignin. As shown in Figure 9, a “pure” lignin surface (in which water molecules do not “see” the cellulose surface, but only lignin) increases the hydrophobicity of the cellulose II surface, as do lower loadings of lignin, to a lesser extent.

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Implementation

The workflow was divided into three tasks with the following descriptions and milestones:

Task 1: Computational Method Verification for Cellophane

This task will provide the initial verification that the MD simulations predict accurate properties for base material, cellophane. Specifically, models of molecular assemblies for cellophane will be constructed based on information from Futamura and additional details from the literature as needed. Material properties will be computed and compared to experimental measurements. If property predictions differ from experimental values by greater than 15%, simulation methods, including run time, system size, and macromolecular architecture, will be modified until satisfactory values are obtained.

Task 1 Milestone: Validation of methods by prediction of materials properties for cellophane within 15% of experimental measurements. This milestone was completed by verifying the predictions of viscosity against experimental measurements.

Task 2: Property Prediction for Candidate Materials

This task will construct *in silico* models of molecular assemblies of novel cellulose-derived polymers. At least 10 different polymers will be investigated based on input from Futamura regarding which modifications are synthetically achievable and likely to increase performance metrics. Simulations will be performed to calculate the thermal, mechanical, and barrier properties of each novel polymer. Guidance regarding which molecular modifications are synthetically achievable and economically feasible will be provided to NREL from Futamura. Predictions of material performance metrics will be provided by NREL to Futamura.

Task 2 Milestones: Predict materials properties of at least 10 novel modified cellophane polymers.

This milestone was completed by investigating the mechanical properties of 14 novel polymer systems and 4 variations of novel surface coatings.

Task 3: Material Candidate Evaluation and Down-Selection

This task will evaluate the required supply chain and potential value proposition of the top performing material candidates as predicted by Task 2. The analysis will be primarily conducted by Futamura, but NREL will assist as needed. The top-performing material candidates will be predicted by NREL and provided to Futamura. Futamura will use the results of the evaluation to determine which material candidate(s) will move forward for commercial production.

Task 3 Milestone: Downselect to the top 3 material candidates based on supply chain and TEA. We were not able to complete the TEA analysis required for this milestone within the lifetime of the project due to bandwidth constraints; however, the top-performing formulations were delivered to Futamura, and they will be evaluated in the coming months.

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Issues or Challenges

A major source of uncertainty was the lack of nanostructural characterization of cellophane films. Native cellulose (in plant cell walls, cotton fibers, etc.) exists in bundles ranging from several dozen to hundreds of chains; however, the extent of bundling in regenerated cellulose films is largely unknown. To confront this issue, NREL performed SEM and AFM imaging of cellophane films provided by Futamura. An exemplary SEM image collected at NREL is shown in Figure 9. These preliminary characterizations revealed nanoscale agglomerates of cellulose that appeared to form a layered structure, with each layer consisting of agglomerates of nanoscale bundles. The observations led us to construct models consisting of cellulose bundles roughly 5 nm in diameter such that the inter-bundle adhesive properties could be examined.

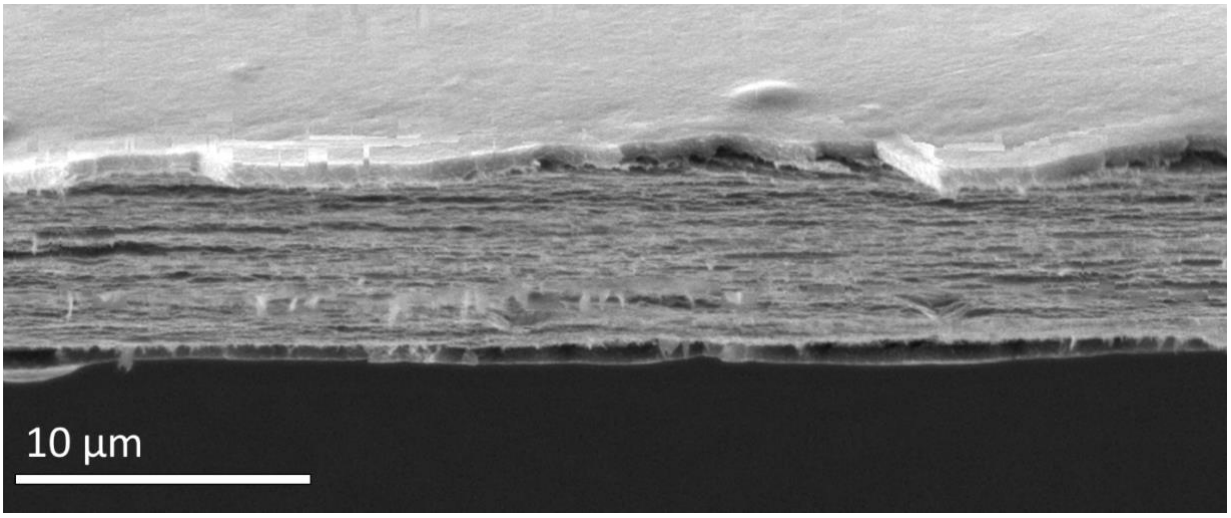

Figure 9. SEM image of a regenerated cellulose film shown in cross-section. These data were used to inform models of the nanostructure of the cellulose agglomerates.

Impact

Company Impact:

The continued development of both the fundamental understanding of our existing process and products and indeed new processes and products is core to Futamura's R&D strategy and forms part of the business's strategic 5-year plan. We actively seek to engage with external partners who can help deliver against this core program. The project with NREL, in our view, has been both valuable and successful in several ways.

1) Being the first (we hope of many) interactions with the team at NREL, we have established a solid working relationship, allowing all parties to gain a greater understanding of the capabilities and knowledge base of each other. While measurable outcomes of a project are primary, it is also of value that this has been a collaborative project that has been enjoyable to work on.

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2) When considering the first target of our collaborative projects, namely "increased fundamental understanding," I believe this project has demonstratively succeeded. Working together, the NREL team has successfully built a model of how the cellulose structure is formed within our film casting process and appears to be able to accurately predict the behavior of our films. Understanding this process provides a platform for modifying the said process. Additionally, the NREL team has successfully produced some of the best SEM microscopy images of the film structure we have ever seen. One interesting facet of this has been the discovery that the different films we produce have a range of structures, whereas we have always believed that one simple structure existed across the film range.

3) When considering the second target of our collaborative projects, namely "developing new processes and products," there is also demonstrative success. The NREL team, using their modeling techniques developed in the first part of the project, was able to begin to model a range of proposed modifications to the filmic structures, mainly focusing on different additives. One key outcome of this was some interesting films modeled using the widely available Xylan as an additive. The key learning gained from this work was the understanding that the conformation of the xylan in the cellulose network was key to deriving these significant differences in mechanical properties in the final film. Whilst this has not yet been converted into a workable real-world process, this work provides a potential springboard for the future development of films with improved mechanical properties. To date, the use of cellulose films is limited to certain markets due to the limit of their mechanical properties. However, the use of such a compostable product would be desirable outside of this limited space. For example, one core product range that may be accessible would-be ready meal tray lidding. Currently, due to the easy tearing nature of cellulose film and the need for high-speed roll-to-roll processing in this sector, cellulose film is not used in this application. However, this sector has been identified around the world as a suitable space for compostable filmic solutions, as plastic films used here cannot be easily recycled due to food contamination. The improvements shown in this modeling work suggest this may be a potential solution to that problem if the structure can be replicated in the real world.

The NREL team has performed some high-level estimates of potential energy savings impact from the development of biodegradable films displacing non-biodegradable alternatives in the circular economy by comparing the energy requirements between two end-of-life scenarios: 1) A generic plastic film is recycled at a material recovery facility (MRF), and 2) an identical quantity of biodegradable film that is industrially composted. This comparison was chosen to isolate the impact from an important attribute of regenerated cellulose films—namely, that it has an end-of-life composting (or, more generally, biodegradation) option that is not available to conventional plastic films. We identified literature estimates of energy requirements (or offsets, in the case of industrial composting) for each of these scenarios, as summarized in the table below:

	Energy required to recycle plastic film (MJ/kg)	**Energy credit from industrial composting (MJ/kg)**
Energy Requirement/Credit	1.49	−1.38
Source	*P. Hou et al.*	*B.G. Hermann et al.*

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The difference between these two values is equal to about 2.9 MJ / kg, which is the estimated energy savings per kilogram of cellulose-based film when comparing these two end-of-life scenarios. We then scale this value up by the assumed production level of 70,000 tonnes, yielding an absolute energy savings estimate of about 200,000 GJ of energy. Much work remains to realize this impact; however, this analysis certainly motivates the effort.

National and International Impact:

During this project, Futamura faced a significant issue in the UK market. The British government were in the process of introducing a "UK Plastics Tax," with a 30% levy placed on all plastic packaging that could not be recycled. However, sadly our compostable, cellulose, and clearly not plastic films was included in the list of taxable products. Futamura was able to lobby the government to address this situation. The NREL team was able to produce a detailed and compelling report in a very short space of time as to why our films are not considered plastic nor modified cellulose. This report played a vital role in what concluded as a successful challenge to the UK government's position, and finally cellulose films were removed from the taxable list. This help was very much appreciated across the business.

Future Work

NREL intends to publish the simulation methods and findings, while Futamura plans to fabricate several of the Xylan-additive films to verify trends predicted by the simulations. Also, although not an intended outcome of this project, the NREL's imaging capabilities proved to be of particular use to Futamura, and collaborations in this area will continue given a suitable funding avenue can be identified.

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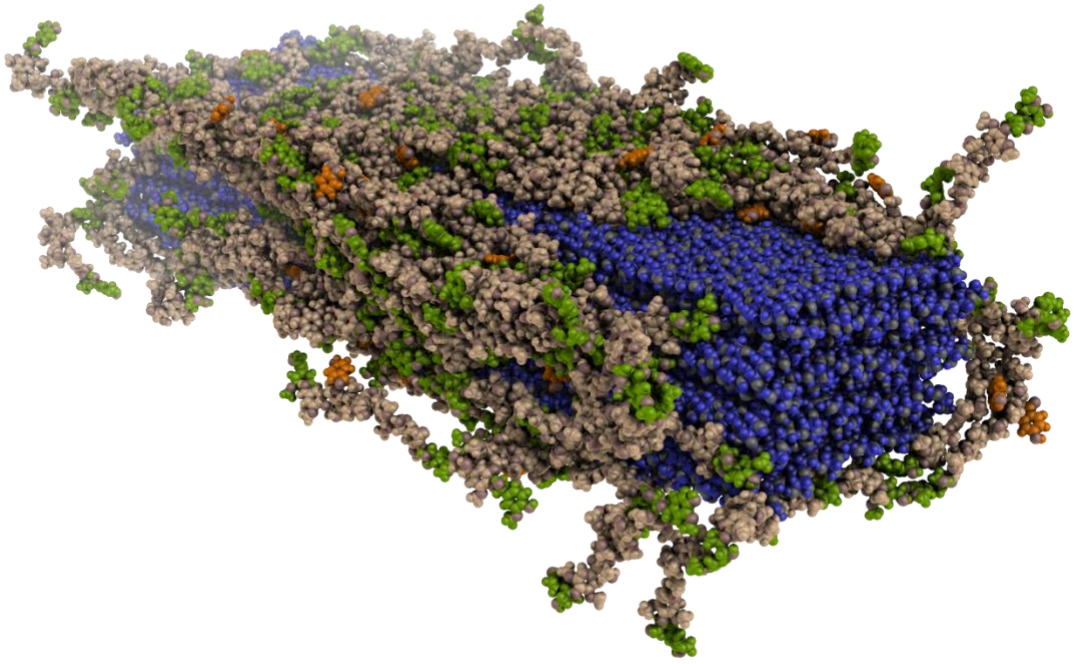
Pictures for Publication:



Caption: Molecular model of a biopolymer assembly used to investigate new sustainable packaging materials. A semi-crystalline cellulose bundle (shown as blue and gray) decorated with lignin containing several variations of monomeric sub-units (shown brown, orange and green) was used to determine how interactions between the polymers impacted the mechanical properties of the material.

Laboratory Principal Investigator (PI) Experience Feedback

(1) Why were you interested in working with the HPC4EI Program?

This opportunity was a perfect fit for our team to apply our unique capabilities in biopolymer simulation to provide direct assistance to an industry partner.

(2) Was your overall experience as part of the HPC4EnergyInnovation Program positive, neutral, or negative? Why?

Extremely positive. It was very rewarding to see how our somewhat fundamental insights provided by molecular modeling were used by Futamura to understand previously confusing experimental results and provide new insights to product design. It was also fortuitous that we were able to help their company avoid the UK plastics tax as described in the international impact section.

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(2) Did your experience as an HPC4EI PI help build your capabilities and expertise? How?

Yes, we developed new capabilities for high-throughput construction and analysis of biopolymer molecular systems. We also hosted an ORISE intern who developed AI algorithms to analyze results and automatically resubmit new simulations based on the results.

(3) How can the HPC4EnergyInnovation program be improved?

The duration of phase 1 should be extended to two years in my opinion, especially in cases where new methods need to be developed. This would allow for a more thorough and comprehensive simulation landscape to be covered.

References:

None

Subject Inventions:

None

ROI#:

None

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