THRUST AREA: BIOBASED PRODUCTS

4.7 — Improving Thermoplastic Properties of Starch for Food and Non-food Packaging Applications

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Site: Iowa State University

Project Objectives. The long-term goal of this study is to develop starch-based packaging materials for a wider range of applications. Native and modified starches with different structures and properties will be selected to understand important factors affecting the application of starch for both food and non-food film usages. The specific objectives are to understand the role of (1) starch sources and their composition (amylose/amylopectin ratio), (2) the degree of branching, (3) the choice of plasticizer, and (4) the choice of blending materials (e.g., nanoclay, fiber) on the properties of the resulting starch-based packaging films. The properties (i.e., strength, barrier properties, hydrophobicity, glass-transition, thermal degradation) and functionality of starch films will be evaluated.

Industrial Relevance, Need, and Appropriateness for the Center. There is increasing interest in using biopolymers from renewable resources for producing materials and products to reduce dependence on petroleum sources, control environmental pollution, and reduce carbon footprint. Starch, the second most abundant biomass in nature, can be used to produce bioplastics, nanoparticles, biomedical products, and carrier material for drug-delivery. Starch-based films are biorenewable, biodegradable, and possess good oxygen barrier properties.

Native starch exists in a semi-crystalline granule and is comprised of two major polysaccharides: amylose and amylopectin. Native starch does not possess the thermoplastic properties needed for polymer-related applications; however, they could be modified to possess these properties with the addition of plasticizers, heat, and shear, usually via extrusion.

Processing factors and starch structure/composition influence starch film properties, thus, their applications. The water-solubility of a film is a very important characteristic in determining its food and non-food applications. Starch films could be made either hydrophilic or hydrophobic based on blends and additives. There is growing market demand for hot-water dissolvable (hydrophilic) packaging materials for pre-mixed food ingredients and pre-packed detergents. Such packages reduce packaging material waste. Hydrophobic starch films could be created to possess properties such as greater mechanical strength, elasticity, flexibility, and surface and barrier properties. The relative proportion of amylose in starch and addition of composite materials affect the barrier and mechanical properties of films. There is a need to understand the structure-property relationship on the thermoplastic properties of starch, targeting a broader range of applications.
Experimental Plan. Selection and modification of starch (source and composition): The ratio of amylose and amylopectin in starch will be varied between 10% to 80% in model starch blends to prepare cast films and property characterization. Natural sources of starch with varying degrees of amylose content (e.g., cassava, 15%; normal yellow dent corn, 24%; waxy rice and corn <2%;) will be used for the preparation of hot-water-dissolvable and water insoluble starch films. Preliminary data obtained in our laboratory showed that film prepared from acid-hydrolyzed waxy corn starch could completely dissolve in boiling water in less than 1.5 min. Partially de-branched or partially acid-hydrolyzed starch will be used to reduce the molecular size of the waxy corn and waxy rice starch to increase the water solubility of the developed starch films while maintaining the tensile properties. High-amylose yellow dent corn, normal yellow dent corn, and normal rice starch will be used alone and in mixtures to prepare films with strong mechanical properties for packaging materials. De-branching reactions will be applied to produce more linear starch molecules to increase the strength of the starch films. Hydroxypropylated, hydroxyethylated, or acetylated starch will be used to prepare starch-based films with improved processability, film clarity, mechanical properties, and stability.

Plasticizers: Water, sorbitol, and glycerol will be evaluated for their plasticizing effects on starch films at various ratios (25-40% w/w, dry starch basis).

Blowing extrusion of films: Cast films will be produced for optimizing amylose content, degree of modification, plasticizer types, and content. For producing proof-of-concept verification at optimal conditions, extruded-blown films will be produced and evaluated. Native or chemically/ enzymatically modified starch will be used to produce starch films using a single-screw extruder. The extrudate will be pelletized and the pellets will be used to produce starch films using a single-screw extruder with a blowing die and tower. To further improve the mechanical properties and water resistance of the starch films, nanoclay (montmorillonite) and fibers will be added at optimal ratios (to be determined experimentally) and the films will be tested for enhanced mechanical and barrier properties.

- Testing of starch or blended starch films: Film samples will be equilibrated in a desiccator with 50% relative humidity for three days prior to testing.
- Mechanical properties: of the starch films: Mechanical properties will be analyzed using an Instron Universal Testing Machine (model 4502, Instron Corporation, Canton, MA) following ASTM protocols. The tensile strength, percentage elongation at break, and Young’s modulus will be determined at a crosshead speed of 5 mm/min. TGA evaluations will be carried out for degradation of films at higher temperatures.
- Water solubility test of starch films: The film will be weighed to the nearest 0.0001 g and placed into a test beaker with 80 mL of deionized water at different temperatures (25, 40, 55, 70, 85, and 100°C) and stirred for 10 min. The remainder of the film after soaking will be recovered and dried at 60°C to a constant weight. The percentage of total soluble matter (% solubility) will be calculated as: % solubility = 100% × (initial dry weight – final dry weight)/initial dry weight.
- Barrier properties: The oxygen transmission rate of the films will be measured using a MOCON OX-TRAN instrument following the ASTM D3985 standard method. There is an oxygen stream on one side of the film and a nitrogen stream on the other side of the film. The outlet of the nitrogen side is equipped with an oxygen detector. The test will be conducted at 23°C and 0% relative humidity, and the rate will be expressed at cc/m2/24 hr. The vapor transmission rate will be related to the amount of water allowed to absorb onto dry beads until saturation per unit time.
- Starch structure: A crystal diffraction refractometer (XDR) will be used to quantify the change in crystallinity in starch molecules. Nuclear magnetic resonance (NMR) will be used to quantify changes in the molecular structure of starch and blend materials in forming complexes.
**Proposed Deliverables.** We will gain a very good understanding of feedstock and processing factors that affect resultant starch film properties and functionality, along with demonstration of two types of thermoplastic starch films as described above.

**Year 1**

1. A variety of starch films will be developed using de-branching and partial acid-hydrolysis. Different starches (e.g., high-amylose and normal yellow dent corn, normal rice), and plasticizers and blend materials will be evaluated. Spectroscopic evaluation of films will be done. Most of the evaluations will be on cast films.

**Year 2**

1. Films will be made using blown extrusion.
2. The mechanical properties, water solubility, and barrier properties will be tested for the blown films.

**Research Facilities.** The Center for Crops Utilization Research at Iowa State University has pilot plant equipment for mixing, compounding, and blowing extrusion of starch films. They include high-speed mixers, a melt flow indexer, single-screw and twin-screw extruders, and Instron Universal Testing Machine. We will use these facilities to prepare films at pilot plant-scale. We will need to identify a MOCON OX-TRAN instrument for oxygen-transmission rate test.

**Timeline and Budget.** The project will be a two-year project. A postdoctoral research associate will be hired to conduct the project. The estimated budget is:

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<th>Year</th>
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