Plastic Films from Soybean Derivatives for Food Packaging

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Objectives of the research

The primary goal of this work is to advance plant protein-based film preparation and demonstrate feasibility of incorporating soybean derivatives, specifically soy protein from soybean and plant (soy) oil-based vinyl monomer (POBM, developed at NDSU, *U.S. Patent, 10,315,95, June11th 2019*), in the formation of (bio)plastic films targeted toward food packaging applications. In an effort to enhance the toughness and barrier properties of unmodified soy protein films, natural additives and POBM-based latexes have been incorporated into the films. These additions act to improve surface hydrophobicity and mechanical properties of the protein-based (bio)plastics. By modifying soy protein-based films and incorporating high oleic soybean oil-based latex polymers we can achieve homogeneous, strong, and flexible films, which demonstrate notable promise in terms of water barrier performance.

Materials and Methods

Synthesis of POBM

High oleic soybean monomer (HOSBM), was synthesized via a one-step transesterification reaction of each oil with *N*-hydroxyethyl acrylamide in the presence of 1.5wt% KOH as catalyst. The resulting monomer mixture was then purified with a 5wt% brine solution and dried under magnesium sulfate with continuous stirring. Rotary evaporation was performed to remove excess solvent. A detailed description of the procedure can be found in *U.S. Patent, 10,315.95, June, 11th 2019.*

Synthesis of Plant Oil-Based Latexes

The prepared monomer (HOSBM) was polymerized in order to form biobased latex using a miniemulsion approach. Latexes of 20% solids content were prepared by mixing 8g of HOSBM with AIBN (1.5wt% of oil phase) as initiator. The aqueous phase was prepared by dissolving certain amounts of surfactant (SDS, 4-8wt% of oil phase) and 0.02g NaCl in miliQ water under constant stirring. After adding the oil phase to the aqueous phase, the pre-emulsion was sonicated for 4min and then the stable miniemulsions allowed to polymerize at 75ºC for 12h under continuous stirring.

Unmodified Soy Protein Film Preparation (SP-based film)

Soy films were prepared as follows. A 10wt% solution of soy protein dispersion (SPD) in miliQ water was prepared and the pH adjusted to 10.5 with NaOH (5N). The dispersion was allowed to stir at 75ºC for 45 min, sonicated for 30sec, and then stored in a refrigerator. The casting solution was prepared by incorporating 50wt% (w/w protein) glycerol and certain amount of the HOSBM-latex into 5g of the SPD and allowed to mix at room temperature for 1h so as to completely homogenize the solution. These solutions were then cast onto glass using a draw down bar and set to dry at room temperature overnight.

Modified Soy Protein Film Preparation (modified SP-based film)

A 10wt% solution of SPD in miliQ water was prepared and the pH adjusted to 10.5 with NaOH (5N). The dispersion was allowed to stir at 75ºC for 45 min, sonicated for 30sec, and then stored in a refrigerator. The casting solution was prepared by incorporating 50wt% (w/w protein) glycerol and certain amounts of the POBM-latexes into 5g of the SPD and allowed to mix at room temperature for 1h so as to completely homogenize the solution. These solutions were then cast onto glass using a draw down bar and set to dry at room temperature overnight.

Film Characterization

Water contact angle of the modified SP-based film films was measured using a drop shape analyzer (DSA 100, KRÜSS, Hamburg, Germany). Reported values are and average of 5 droplets on each side of the modified SP film, for a total of 10 measurements per film.

The mechanical properties of the modified SP-based bioplastics were measured on an Instron model 5542. Tested films had a rectangular shape with constant width of 5mm. A strain rate of 5mm/min was used, and tensile stress at break, elongation at break, and Young's modulus were calculated. Reported values are an average of 4 samples.

Water Vapor Transmission

Water vapor transmission of modified SP-based films was measured gravimetrically according to ASTM E96. Film samples were mounted onto polystyrene dishes filled with water and placed in a desiccator. The film area was constant at 2.55×10^{-3} m^2 and conditions were maintained at 25ºC (±1ºC) and 50%RH.

Results and Discussion

Unmodified SP-based films result in very low tensile stress but demonstrate impressive flexibility. While flexibility is desirable in bioplastic film formation, increased toughness is required for adequate utilization in food packaging technologies.

With food packaging as the target application for this work, we aim to further enhance the toughness and barrier properties of the SP-based films. As shown in **Figure 1**, natural modification to the soy protein films significantly improves tensile strength. Further incorporating poly(HOSBM) into the modified material increases the tensile strain of the film allowing for much greater flexibility. This is expected as the latex provides a soft material which further improves tensile strain. However, sense the plant oil-based latex is hydrophobic, there is no decrease in moisture resistance, thus making poly(HOSBM) an attractive additive in bioplastic film formation.

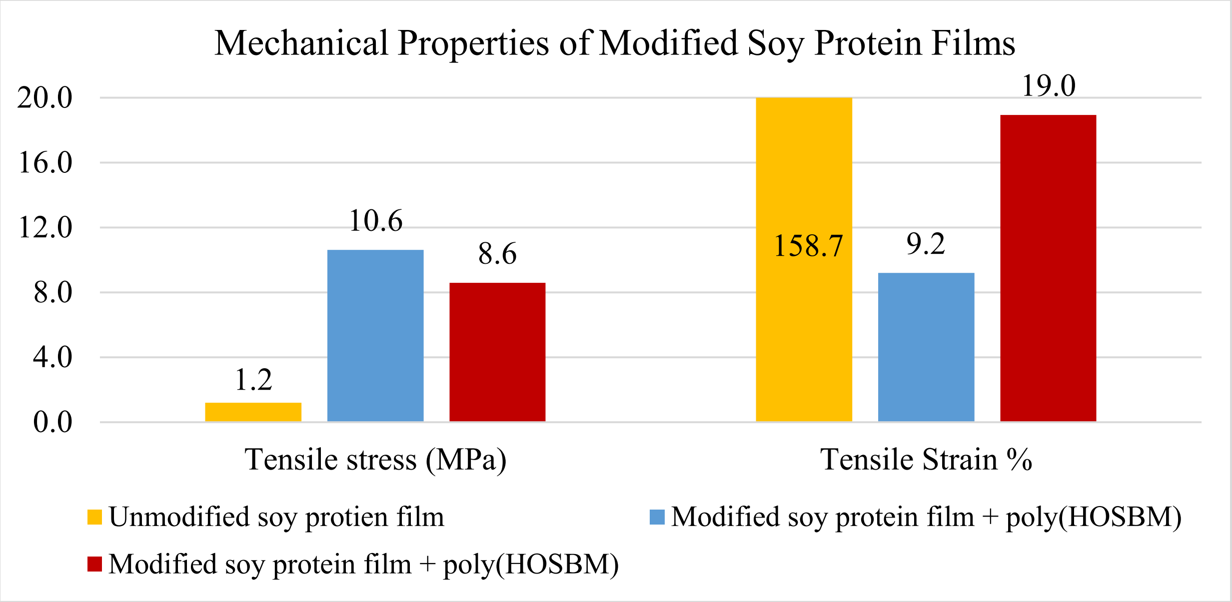

Figure 1. Mechanical properties and performance of modified soy protein films.

Modified soy protein films maintain good transparent appearance with smooth and homogeneous surface.

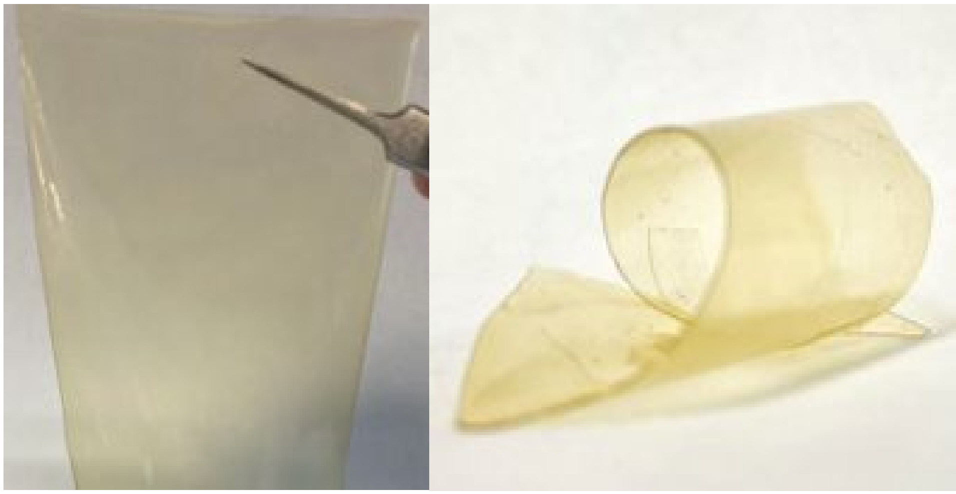

Figure 2. Modified soy protein films.

Once it was determined that poly(HOSBM) incorporation was feasible, we observed the effect that particle size of the latex has on the mechanical properties and appearance of the modified soy protein films. The feasibility of latex incorporation was determined with latexes of 100 ± 31nm. To observe the effect of particle size, poly(HOSBM) was again prepared but with a particle size of 50 ± 25nm (**Table 1**).

Table 1. High oleic soybean-based latex characterizations

Latex Type	Solids %	Conversion %	Particle Size (nm)	Molecular Weight (g/mol)
HOSBM 100	20	60	100 ± 31	~20,000
HOSBM 50	20	60	50 ± 25	~19,500

Upon reducing the particle size, the mechanical properties of the resulting films were measured, and it is illustrated that the smaller particle size latex results in improved film flexibility and slight improvement to the surface hydrophobicity (**Table 2**).

Table 2. Mechanical properties of modified soy protein films with poly(HOSBM) of differing particle size.

Modified Soy Protein Films with Latex	Latex particle size (nm)	Water Contact Angle (º)	Tensile Stress (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
No latex	-	51 ± 4	10.63 ± 1.35	9.2 ± 3.3	627 ± 43
Poly(HOSBM)	50	55 ± 2	8.65 ± 1.20	18.9 ± 3.1	451 ± 58
Poly(HOSBM)	100	51 ± 5	8.09 ± 0.93	16.8 ± 2.3	423 ± 64

The effect of particle size was explained by viewing scanning electron microscopy (SEM) images of the bioplastic films. When the particle size of the latex is decreased, the distribution throughout the modified soy protein film improves. A more uniform distribution allows for better interaction between the proteins and the latex. As interaction is enhanced, the synergy between the materials is optimized. The SEM images clearly illustrate how decrease in particle size enhances latex distribution throughout the modified soy protein film.

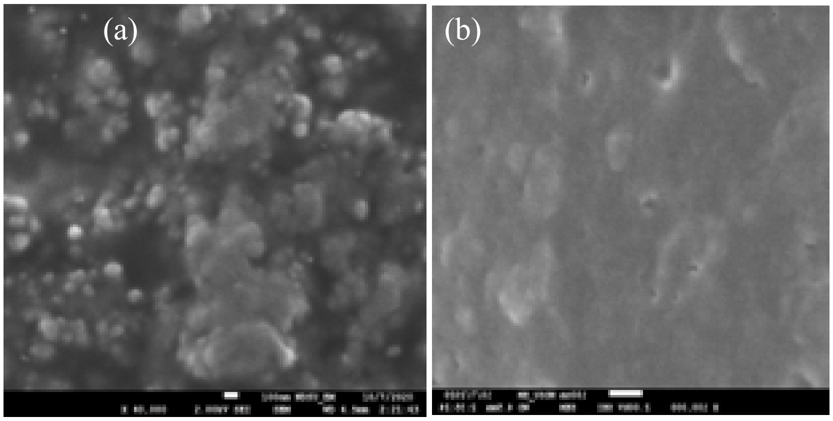

Figure 3. SEM images of modified soy protein film with poly(HOSBM) with particle size (a) 100 ± 30nm and (b) 50 ±25nm.

After determining the mechanical benefits of modifying SP-based films as well as the impact poly(HOSBM) has on mechanical properties and performance, we measured the water vapor permeability of the current optimal films. (**Table 3**). As seen in **Table 3**, the naturally modified soy protein-based films exhibit a significant improvement on water barrier performance. Upon incorporation of the poly(HOSBM), there is a negligible increase in WVT, thus affirming that although the latex is a soft material, it does not compromise water resistance of the film.

Table 3. WVT values of plant protein-based bioplastic films.

Sample	**WVT (g/m^2•s)**
Unmodified Soy Protein Film	0.01649
Modified Soy Protein Film	0.00217
Modified Soy Protein Film + poly(HOSBM)	0.00256

Ongoing work

Currently, we are continuing to investigate the barrier properties of modified SP-based films by determining oxygen vapor transmission. Furthermore, we aim to study the biodegradability of the modified soy protein films and determine the effect of high oleic soybean-based latex on biodegradation of the material.

Conclusions

In conclusion, we determined that modified SP-based films enhanced with poly(HOSBM) result in bioplastic films with increased toughness and good water barrier performance. These materials are attractive alternatives to petrochemical alternatives due to their impressive mechanical and barrier properties. Furthermore, it was demonstrated that utilization of soybean-based materials (i.e. soy protein and high oleic soybean oil) can be mutually incorporated into bioplastic films alongside natural film forming additives.