All-Soy-One-Component Bioplastics for Food Packaging

PI: Andriy Voronov, Professor, Coatings and Polymeric Materials, NDSU, Dep.2760, PO Box 6050, Fargo, ND 58108, phone 701 231 9563, andriy.voronov@ndsu.edu

Objectives of the research

Recently, we combined soy protein (SP) with latex polymers from soybean oil-based vinyl monomer (SBM, developed at NDSU U.S. Patent, 10,315,095 B2, June,11th 2019, U.S. Patent, 10,584,094B2 March,10th 2020) and demonstrated their performance-based feasibility to be applied as bioplastics but, at the same time, observed that compatibility between SP and SBM-based latex polymers limits extent of latex incorporation into the films, and its effect on films properties and performance.

In the current work, we engineered *all-soy-one-component material* for bioplastics films formation by grafting (covalent attachment) of SBM polymer chains to the SP and rendering SP-SBM copolymers with targeted physico-chemical and film-forming properties, as well as mechanical performance promising for in making (bio)plastic films for food packaging applications.

Synthesis of SBM

Soybean oil-based monomer (SBM), 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 SP-SBM copolymers

The synthesis of SP-SBM copolymers was performed using free radical grafting polymerization in emulsion. For synthesis of SP-SBM, first SP was dissolved in water by stirring at 750 rpm under N_2 for 1 h Dissolved in 2 g H_2O initiator (APS, 4-7 wt%) was added into SP solution and kept 10 min at 60^{o}C. After reducing T to 50^{o}C, SBM was slowly added (at various SP:SBM ratios), at 70^{o}C at stirring. After 3 h of grafting polymerization, the resulting material was separated and applied from solution for SP-SBM film preparation (described below). For the

separation, final reaction mixture was centrifuged, washed with water and acetone to separate precipitated SP-SBM, and dried overnight. A series of materials from SP and SBM was prepared at total concentration 20 wt.% at various ratios. The SP-SBM copolymers were characterized in terms of conversion, copolymer composition using ^{1}H NMR spectroscopy, average molecular weight using Gel Permeation Chromatography. Glass transition temperature of the resulting copolymer was determined via modulus TGA using a TA Instruments Q1000 calorimeter.

SP-SBM film (modified) formation

A 10 wt.% solution of SP-SBM 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 50 wt% (w/w protein) glycerol and certain amounts of the Olive Stone Powder (OSP) and Cellulose nanocrystals (CNC) 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.

SP-SBM 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.

SP film (unmodified) preparation

Soy protein unmodified films were prepared as follows. A 10 wt.% 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.

Results

Specific objectives we addressed during this project included i. grafting of SBM polymer chains to SP to yield new SP-SBM copolymers; ii. formation of films from SP-SBM copolymers and their further characterization to demonstrate feasibility as bioplastics.

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

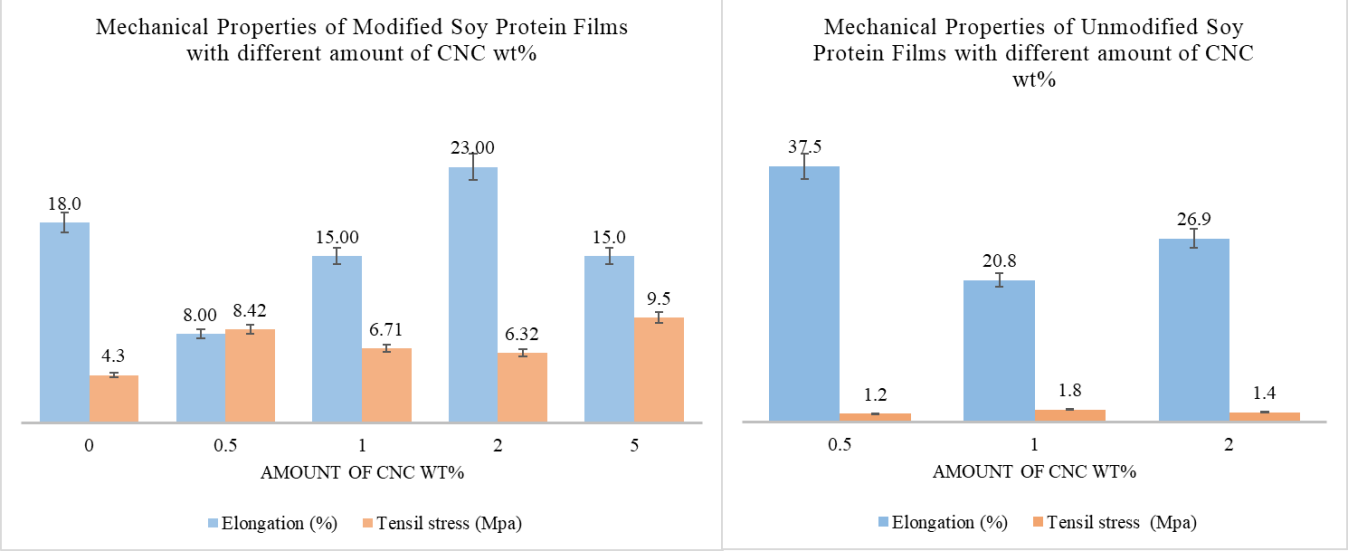

Figure 1. Mechanical properties and performance of unmodified and modified SP films with incorporated different amount of CNC (wt.%).

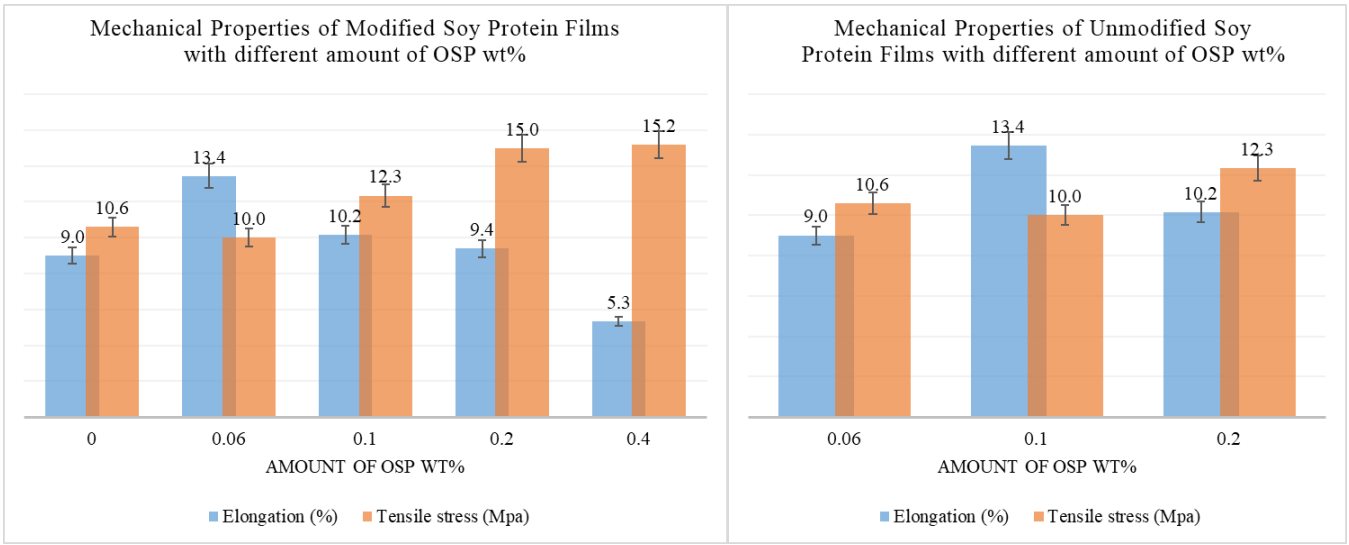

Figure 2. Mechanical properties and performance of unmodified and modified SP films with incorporated different amount of OSP (wt.%).

With food packaging as the target application, we aimed to further enhance the toughness and barrier properties of the SP-based films. As shown in **Figure 1 and 2**, modification of the SP films improves tensile strength. Further incorporating of natural ingredients, olive stone powder (OSP) and cellulose nanocrystals (CNC) into the both unmodified and modified material increases the tensile strain of the film allowing for greater flexibility.

Modified SP films maintain better elongation and tensile stress if compared to unmodified, also films are transparent, smooth with homogeneous surface.

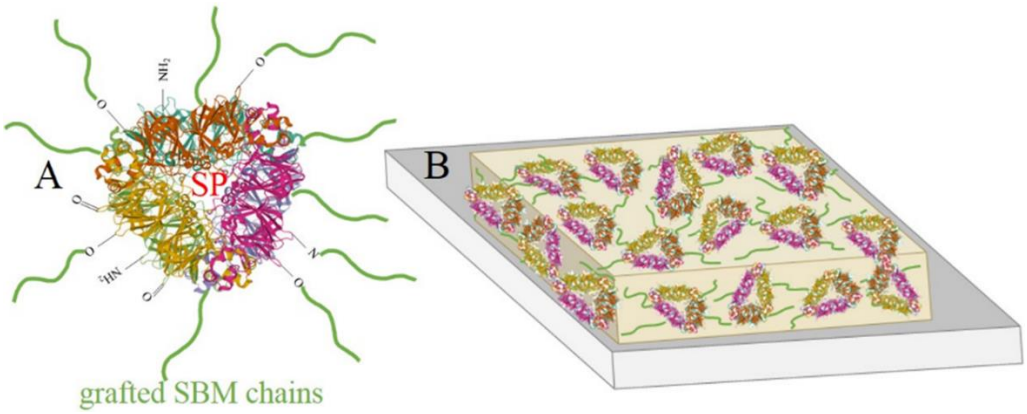

Figure 3. Schematics of SP-SBM copolymer (**A**), SP-SBM film (**B**)

In fact, by incorporating two different additives into the modified SP films, significant improvement of properties is achieved. Results show that the incorporation of CNC increases elongation of modified SP film, with best formulation of 2 wt.% of incorporated CNC. By incorporation OSP, tensile strength increases, thus stronger films are obtained.

Motivated by already observed encouraging improvements in SP-based film properties, basic concept of this project was to engineer *one-component material* via grafting (attachment) of HOSBM polymer chains to the SPI. The goal is to render new materials (SP-SBM copolymers) with targeted physico-chemical, mechanical and film-forming properties (**Figure 3**).

Conversion and grafting content was determined and it shows good result that process was successful (**Table 1**). The higher content was with lower amount of monomer to SPI, there is no point to add more monomer if the same amount of HOSBM can be grafted on the soy protein surface.

Table 1. Formulation and grafting characteristics of SP-SBM

Name of the sample	Ratio (SBM:SP)	Conversion, %	Conversion based on monomer, %	Grafting content, %
TS-020-01	40:60	69.6	23	75
TS-017-01	50:50	69.3	37	64
TS-034-02	70:30	67.1	53	59
TS-037-01	80:20	62.4	53	37
TS-022-04	90:10	64.3	60	32

FTIR-spectra confirm grafting of SBM to SP by presence of peaks at 2930 cm^{-1}, corresponding to CH_2 groups in fatty acid fragments, 1745 cm^{-1} corresponding to ester group and 1154 cm^{-1} corresponding to O=CO-O in SBM structure.

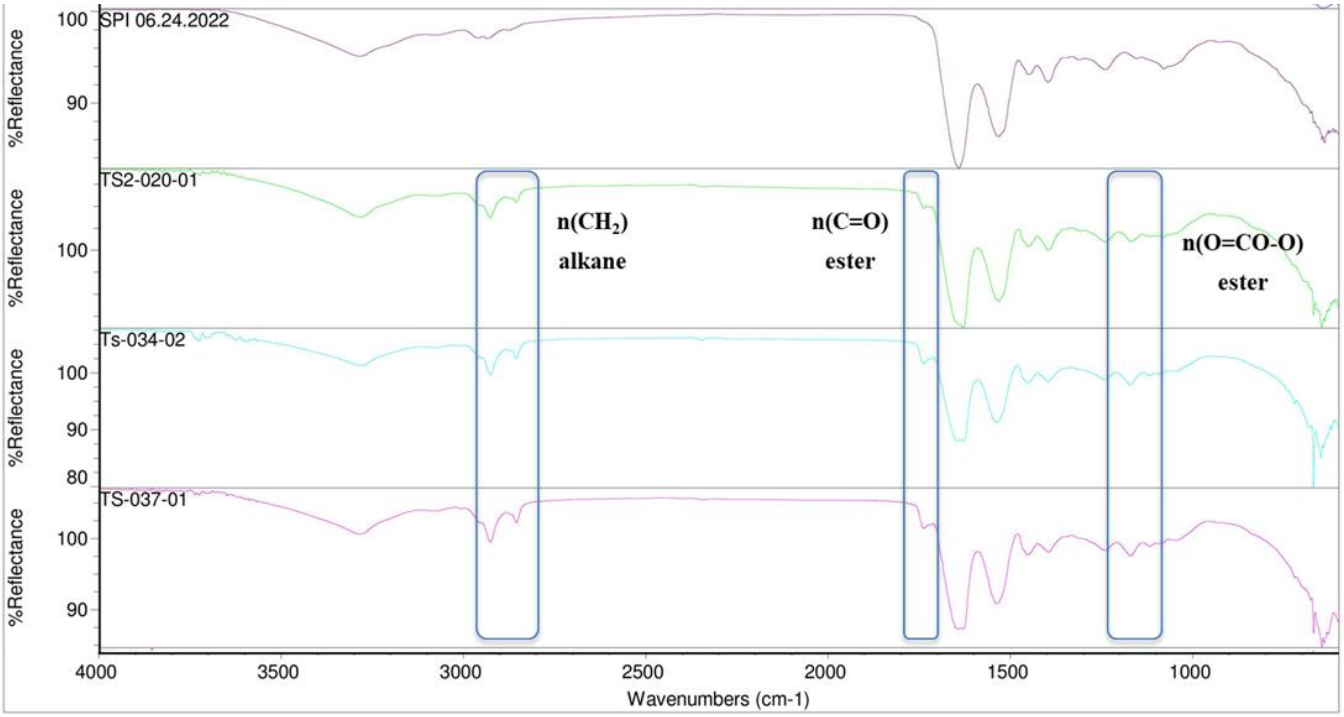

Figure 4. FTIR spectra for SP and SP-SBM copolymer.

Ongoing work

Currently, we continue to investigate barrier properties of modified SP-based films by determining water vapor transmission rate. 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.

Summary

In summary, we demonstrate that grafted SP-SBM copolymers are film forming materials with decent mechanical performance. They can be considered as attractive alternatives to petrochemical counterparts. Furthermore, we show that that utilization of soybean-based materials (i.e. soy protein and high oleic soybean oil) can be mutually incorporated into bioplastic films alongside with other natural film forming additives.