Soy–Based Biodegradable Super-Absorbents for Personal Care and Agricultural Products.

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Objectives of the research

In this project, we are developing a new soy-based super-absorbent polymer (SAP) from soybean oil and soy protein/soy meal. The new bio-based and biodegradable hybrid materials will have the ability to absorb large quantities of water and will find a wide application in personal care, animal care, and agricultural products. The new soy-based SAP will compete with existing polyacrylic acid-based SAPs and, being biodegradable, will sufficiently lower the negative environmental impact.

Completed work:

- Synthesis of soybean oil (SBO) – based emulsions
- Synthesis of SBO-based suspensions containing cellulose and/or soy protein isolate (SPI)
- Synthesis of SBO-based suspensions containing soy meal powder (SMP)
- Preparation of soy-based solid absorbents by air drying and freeze-drying methods
- Water uptake study of different synthesized soy polymers

Progress of Work and Results to Date

In the reporting period, aqueous emulsions were synthesized from modified soybean oil (SBO), α-cellulose, and acrylic acid. SBO was initially reacted with maleic anhydride and then the product, maleinated soybean oil (SOMA), was used in further reactions to synthesize the latexes. First, SOMA was reacted with dried α-cellulose or soy protein isolate (SPI). The weight ratio for SOMA/α-cellulose and SOMA/SPI varied from 4:1 to 3:1. During this reaction, anhydride groups of SOMA were reacted with OH-groups of α-cellulose or SPI. α-Cellulose or SPI pre-reacted with SOMA were dispersed in water with added 2% of surfactant. Polymer latexes were synthesized by suspension polymerization of acrylic acid with pre-reacted SOMA/α-cellulose or SOMA/SPI mixtures in the presence of a water-soluble initiator. The synthesized products are viscous latexes containing copolymers of acrylic acid and SOMA grafted to α-cellulose or SPI. The materials extracted from this latex are soy-based polymer composites containing up to 80 wt.% of soy products.

Since both cellulose and SPI work well in dispersion polymerization with modified SBO, a new polymer dispersion was synthesized with powdered soy meal which contains approximately 45% of protein and 35% of carbohydrates, including cellulose. The toasted soy meal was obtained from Owensboro Grain Company (Owensboro, KY). It was dried in the oven to constant mass, ground in a laboratory grinder, and sifted through a 140 mesh sieve. The resulting product is a fine soy meal powder (SMP) with a particle size <105 micrometers (μm). SMP-based polymer dispersions were synthesized in the same way as SPI-containing dispersion. For some synthesis, dry solvents (ethyl acetate or methyl ethyl ketone) were used in the reaction of SOMA with SMP, to reduce viscosity. The solvents were evaporated after suspension polymerization was complete. The final product is a light brown viscous suspension.

The composition of some of the synthesized suspensions of soy polymers is given in Table 1.

Table 1. Composition of soy-based polymer latexes.

Sample ID	724-AC	724-SPI	728-AC	731-SPI	725-SMP	803-SMP
SOMA, g	6	7	8	8	9	28
Solids (α-Cellulose, or SPI, or SMP)	α-Cel.	SPI	α-Cel.	SPI	SMP	SMP
Solids, g	2	2	2	2	7	14
Water, g	18	20	20	25	32	80
Acrylic Acid, g	2.5	3	2.5	2.5	4	7
Emulsifier SDS, g	0.36	0.4	0.40	0.50	0.65	2.4
Initiator PSA, g	0.21	0.22	0.25	0.25	0.40	1.00
Solvent (ethyl acetate), g	0	0	0	0	12*	24*
Total solids content, %	37	38	38	33	38	38
Soy content in dry polymer, ** %	57	75	64	80	80	85.7

*Solvent was evaporated from latex

**Sum of SOMA and SPI or SMP

The synthesized latexes were viscous and stable for more than 4 weeks. Figure 1 presents the appearance of latexes synthesized by suspension polymerization with cellulose (left) and SPI (right).

The latexes were applied on Teflon-covered glass panels and air dried. The films formed from latexes were brittle and SMP-containing polymers were the most brittle. The samples of latexes were also freeze-dried using a laboratory vacuum freeze-drying system. The material obtained by freeze-drying of SMP-containing suspension is porous and crumby. Both air-dried (AD) and freeze-dried (FD) soy polymers were cured at 120°C for 1 hour for cross-linking and then tested for water uptake. For the water uptake test, the samples were immersed in distilled water for 2h., then swollen samples were weighed, dried, and weighed again. The water uptake was calculated in grams of water absorbed by 1g of dry sample. Since synthesized samples are poly acids, the pH of distilled water drops to the values between 3 and 4, after immersing the samples. For the same samples, the pH of water was increased to 9 by the addition of KOH solution, and the water uptake was re-measured. Table 2 gives the results of water uptake for some air-dried soy polymers measured after immersing in water for 2 hours at different pH values. The results show that neutralizing of the polyacid with potassium hydroxide sufficiently increases the water uptake by soy-based absorbents. The higher water uptake value for the cellulose-containing sample 724-AC can be explained by the higher acid content for this sample, however, cellulose itself may contribute to higher water absorption.

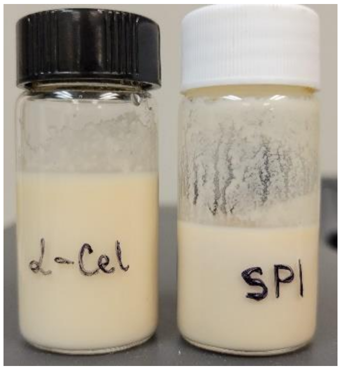

Fig. 1. Latexes synthesized from modified SBO, acrylic acid, and cellulose (left) or soy protein isolate (right).

Table 2. Water uptake for some dried SPIs, tested after 2h immersing in water at different pH.

Sample ID	Acid content in dry polymer	pH	Water uptake, g/g $_{polymer}$
724-AC	23.8%	4	1.7
724-AC	23.8%	9	8.8
724-SPI	20.0%	4	1.5
724-SPI	20.0%	9	4.8
725-SMP	20.0%	4	1.1
725-SMP	20.0%	9	4.5

The sample containing soy meal (725-SMP) shows the lowest water absorption for the air-dried sample. In the next experiment, the water absorption for air-dried and freeze-dried samples was studied. The freeze-dried sample has much higher porosity compared to air-dried ones and is expected to absorb water faster. In Figure 2, the left plot shows the water uptake for air-dried SMP-containing samples at different pH levels. At the basic pH=9, the water uptake at 6 hours exceeds 5 g per gram of polymer, or 500%, while at acidic pH=4, the water uptake is only 200%. The same sample was freeze-dried and tested in neutralized water solution of KOH, at pH=7 and pH=9. The maximum water absorption for the freeze-dried sample is about the same as for the air-dried one, but the freeze-dried sample absorbs water much faster than the air-dried sample, reaching a value of almost 400% in the first hour. Lyophilization or freeze-drying of polymer latex allows the formation of high-porous solid material and the porosity helps to absorb liquids at a high rate, which is very important for the sorbents for personal care products. The photographs of the sample of latex 804-SMP and freeze-dried material obtained from the same latex are presented in Figure 3.

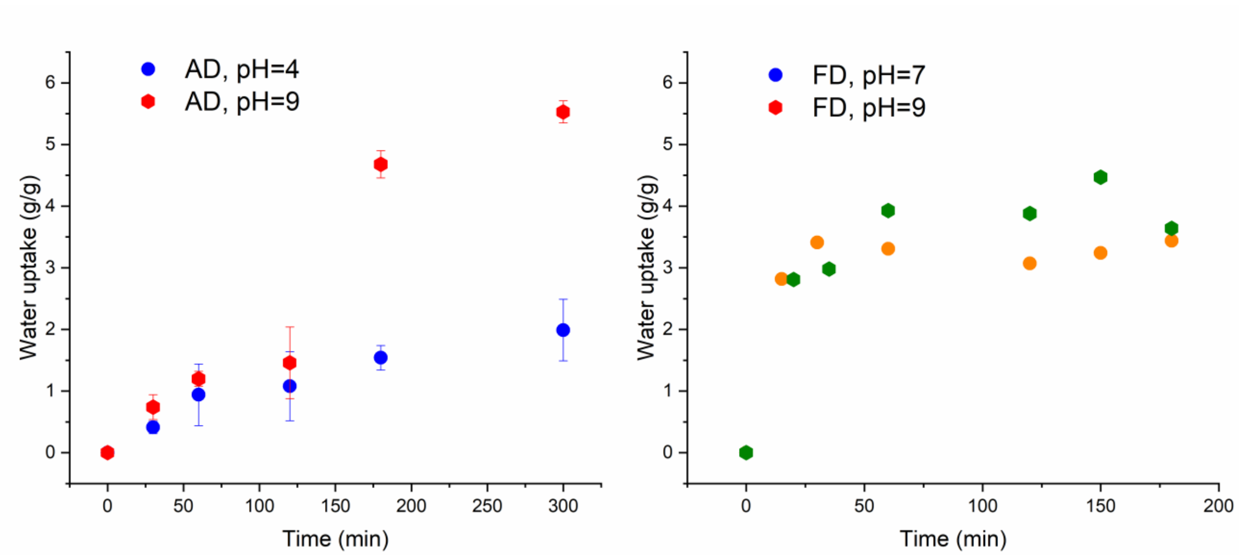

Figure 2. Water absorption kinetic for the polymer sample 803-SMP containing 57% of modified soy oil (SOMA), 29% of soy meal powder (SMP), and 14% of acrylic acid. Left plot – the sample was air-dried, right plot – the sample was freeze-dried.

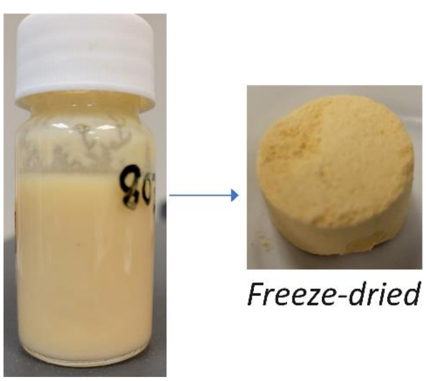

Fig. 3. Latexes synthesized from modified SBO, soy meal powder, and acrylic acid (left) and porous material obtained by freeze-drying of the same latex (right).

Work to be completed:

Optimization of composition of SMP-containing latexes

Water absorption testing at different pH and presence of different cations (Na^+, K^+, Ca^+, Mg^+)

Biodegradability testing

Identification of target composition and target application

Other relevant information: potential barriers to achieving objectives, risk mitigation strategies, or breakthroughs.

N/A

Summary

Stable polymer suspensions containing up to 80 wt.% of soy products, both soy oil and soy meal were synthesized. The product obtained from the suspension after drying is a bio-based composite material that has the ability to absorb up to 500 wt% of water at increased pH. The formation of a porous material by the freeze-drying method allows accelerated water absorption by new soy absorbent. More work needs to be completed to achieve the optimum composition and pH of SMP-containing suspension and to optimize the water absorption capacity of new material.