Soy-Based Biodegradable Agriculture Mulching Materials Final Project Report. 11.30. 2022 Olena Shafranska and Dean Webster Department of Coatings and Polymeric Materials North Dakota State University

Objectives of the research

In this project, we proposed to develop a new soy-based composite material that will be used as a biodegradable mulching material. We planned to explore soybean oil-based polymers that can work as the matrix polymer for cellulose-filled composite or as a coating for paper mulch.

Completed work

- o Chemical modification of soybean oil with maleic anhydride
- o Synthesis of aqueous emulsions from modified soybean oil and vinyl monomers
 - Emulsion of modified soybean oil with acrylic acid
 - Emulsion of modified soybean oil with acrylic acid and vinyl acetate
- Optimizing of formulation for paper coating
- o Coating of agriculture paper and kraft paper with soy-based formulation
- Testing of coated paper in the field
- Aerobic biodegradation of cured soy polymer film

In this project, we developed a new soy-based polymer that can be used as a biodegradable mulching material. We developed a new scalable synthetic route to obtain a soy-based polymer in the form of an aqueous emulsion. The aqueous formulation of soy polymer was optimized to produce a flexible heat-curable coating for the mulching paper. The coated mulching paper was tested for biodegradation in the field and the polymer film obtained from soy polymer emulsion was tested for aerobic biodegradation in the lab.

<u>Results</u>

Soybean oil (SO) was modified with maleic anhydride (MA) to introduce the functional anhydride groups.

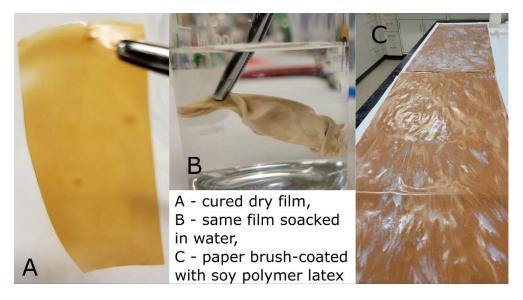
Water/polymer emulsions of maleinated SO (SOMA), acrylic acid (AA), and vinyl acetate (VA) were synthesized via emulsion radical polymerization using ammonia persulphate as an initiator. The polymers obtained in emulsion polymerization were investigated for film-forming properties and for their ability to crosslink while the latexes were tested for viscosity, presence of gel, and

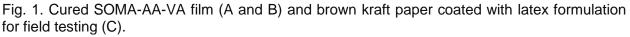
stability. The latexes with a solids content in water of >40 wt.% show high stability against phase separation but at the same time are fast gelling. The latex with 36% solids and SOMA:AA:VA ratio as of 4:2:1 was synthesized for biodegradability testing. This latex sample was free of gel and showed stability over 30 days and high conversion of monomer. The components for formulations for biodegradation in the field and for polymer film biodegradability tests in the lab are listed in Table 1. For the latex for biodegradation in the field, 3 parts of a-cellulose were mixed with 60 parts of SOMA, prior to polymerization, to increase the latex viscosity. The latex for polymer film biodegradability was synthesized without cellulose to ensure no other material will contribute to the biodegradation of soy-based polymer. Since the polymer film from SOMA-AA-VA is brittle, 5% of glycerol as a plasticizer was added to the latex formulation for field testing. This formulation was brush-applied on the brown kraft butcher paper (BKP) from Bryco and commercial weed barrier paper (WBP) from SimplyGro LLC. The paper samples were allowed to dry at room temperature, then rolled, and the paper rolls were thermally cured in the oven for 2 hours at 120°C. The heat curing results in crosslinking of soy polymer preventing washing off the paper. The uncured polymer film can easily be re-dispersed in water; however, the crosslinked film is nondispersible and insoluble in water and most of the organic solvents. The polymer film for the biodegradability test was cured at 120°C for 1 h. Fig.1 shows the appearance of cured dry SOMA:AA:VA film (A), the same film soaked in water (B), and the sample of BKP coated with soybased latex formulation. The water uptake for cured films was tested for different SOMA:AA:VA and SOMA: AA polymers and was between 460-500%.

Components	Formulation for field biodegradation test		Latex for polymer biodegradation test	
	parts	g	parts	g
Water	190	1900	196	196
SOMA	60	600	60	60
AA	30	300	30	30
VA	15	150	15	15
a-Cellulose	3	30		
Glycerol	15	150		
Solids, wt.%	34.5		34.9	
SOMA in polymer, wt.%	57.1		57.1	

 Table 1. Latex formulation for biodegradation tests

<u>Field biodegradation test</u>. The samples of coated papers were placed on the ground (dirt) for environmental decomposition testing. Uncoated paper samples are also used for testing as references. Samples were inspected bi-weekly and tested for weight loss. Both references, BKP and WBP started to biodegrade after the first 4 weeks while coated papers showed no visible degradation. Fig. 2 shows how the weight of different papers decreased over time. The images of the samples of the coated BKP (Soy-BKP) and coated WBP (Soy-WBP) after 8 weeks on the field are presented in the insert of Fig. 2, images A and B, respectively. The image C in the insert shows the remaining fragment of the uncoated WBP sample after 8 weeks of degradation. After 14 weeks, no fragments were found for the reference samples BKP and WBP indicating their complete degradation. The coated samples show some degradation on the edges, but the middle parts of each sample were in place.





An aerobic biodegradability test was conducted in the lab following ASTM D5988. The soil used for this test is sandy loam, with medium nitrogen content and low potassium and phosphorus content. The moisture level is maintained at 100% of the average moisture equivalent (AME) for the tested soil and AME was determined following the procedure in ASTM D2980. All samples and blank reference materials were tested at the temperature of 21±1°C. The reference testing material is corn starch. Biodegradability was determined as the percentage of conversion of the carbon contained in the polymer sample to CO₂. The release of CO₂ for each sample was corrected by subtraction of the amount of CO₂ released by the same amount of soil with no

sample. The biodegradability test for starch was conducted in the same way and the results are used as a positive reference.

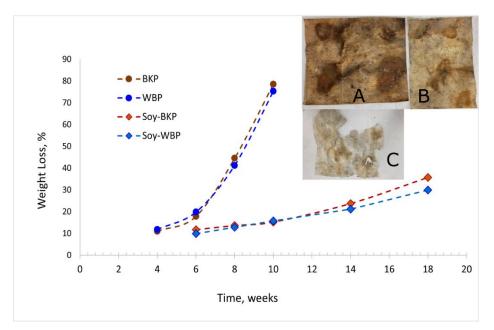


Fig. 2. Degradation of uncoated and coated with soy polymer paper on the field. Images on the insert: A -Soy-BKB, B-Soy-WBP, C- uncoated WBP after 8 weeks degradation on the field

Fig. 3 demonstrates that the degradation rate for the soy polymer is lower than for starch control showing only 4.5±0.4 % in 35 days, compared to 10.5±1.0 % for starch. This explains the slower degradation of soy polymer-coated paper in the field. Nevertheless, soy polymer does undergo degradation, and the low degradation rate will extend the lifetime of the cellulose mulching material.

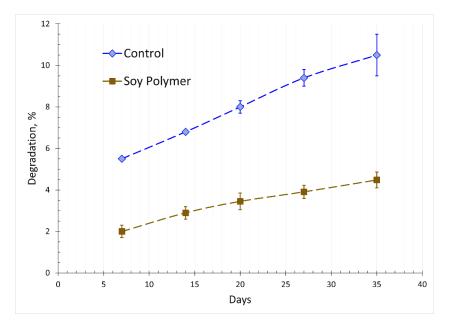


Fig. 3. Aerobic degradation of soy polymer and starch in the soil at 21±1°C.

Conclusions

A soy-based latex formulation was developed using soybean oil modified with maleic anhydride, acrylic acid, and vinyl acetate. The content of soybean oil in the latex formulation and in the polymer is 19.2% and 57.1%, respectively. The latex formulation was used as a polymer coating for the paper, cured, and the coated paper was tested as a biodegradable mulching film. The field tests show slow decomposition of the coated papers compared to the uncoated counterparts. The uncoated paper was completely degraded after 3 months on the field, while the paper coated with soy polymer started to degrade only by the end of the season. The aerobic biodegradability test in the lab shows slow degradation of soy polymer confirming that this material is biodegradable. In this project, we successfully demonstrated the concept of the use of polymer from soybean oil for biodegradable mulching material. However, additional study is needed to develop a commercial product. This study will include the scale-up process of latex formulation and optimization of coating application and curing. Further variations of the composition of the polymer can tune the degradation rate giving the mulching film different lifetimes when in use. The biodegradability testing is continuing, and we plan to continue it for one more month as this test is sufficient for material development.