Soy-Based Biodegradable Agriculture Mulching Materials

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Olena Shafranska and Dean C. Webster

Department of Coatings and Polymeric Materials, North Dakota State University

Objectives of the research

In this project, we are aiming to develop a new soy-based composite material that will be used as a biodegradable mulching material. We are exploring soybean oil-based polymers that can work as the matrix polymer in composite materials filled with cellulose and/or lignin.

Completed work

- Chemical modification of soybean oil with maleic anhydride (MA)
- Crosslinking of MA-modified soybean oil (MA-SO) with various cross-linkers, including bio-based cross-linkers
  - Crosslinking of MA-SO with different amines
  - Crosslinking of MA-SO with epoxidized soybean oil (ESO)
  - Crosslinking of MA-SO with bio-based compounds containing OH-groups
- Characterization of MA-SO-based cross-linked polymers with differential scanning calorimetry (DSC)

Preliminary results

Soybean oil (SBO) was modified with maleic anhydride (MA) in order to introduce the functional anhydride groups for further crosslinking of MA-SO and the formation of the cross-linked polymer. Another modified SBO studied in this project was commercially available epoxidized SBO (ESO).

Synthesis of MA-SO was carried out at elevated temperature (200°C-220°C) and the structure of the product was confirmed by FTIR spectroscopy and DSC analysis. Fig. 1 shows FTIR spectra for SBO, MA-SO, and ESO. The grafting of maleic anhydride to SBO is confirmed by characteristic bands at 1856cm^{-1} and 1780cm^{-1} in MA-SO which correspond to the C=O stretching in the anhydride group.

Curing with amines

The first group of reactions includes the crosslinking of MA-SO by reaction of anhydride functionalities with different amines. The reaction with amines occurs at room temperature, is very fast (click reaction), and the resulting soy-based polymers are hard amber-like solids, however, the properties are different for different amine cross-linkers. Table 1 lists the different amines that were tested, their amine hydrogen equivalent weight (AHEW), and the gel content of soy-based polymers determined by the solvent extraction method.

The polymer obtained from MA-SO and J400 appears to be a good candidate for cellulose-filled composites as a matrix polymer. The disadvantage of the cure MASO with J400 is too fast cure reaction giving not enough time for mixing and formation of the composite. We will evaluate methods to reduce the curing speed.

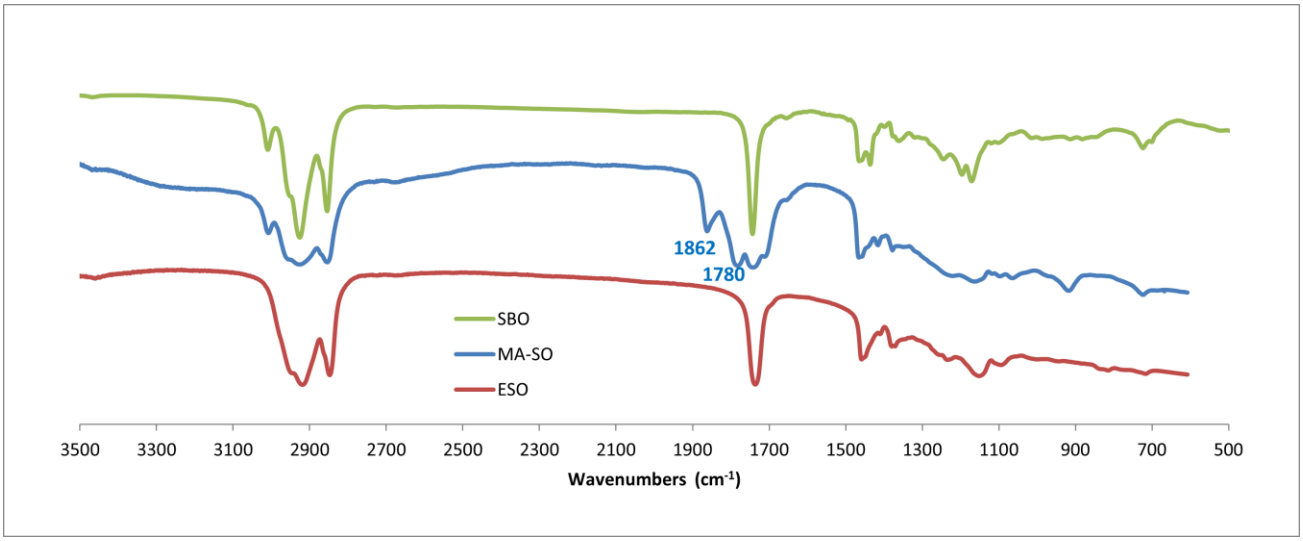

Fig. 1 FTIR spectra of SBO, MA-SO, and ESO

Table 1. Curing MA-SO with amines

Amine	AHEW	Anhydride/ AHEW ratio	MASO/Amine ratio (weight)	Gel content, (wt.%)	Polymer appearance
Hexamethylene diamine (HMDA)	29	1/2	2g/0.21g	48%	Amber-like solid, but fragile
Diethylenetriamine (DETA)	20.6	1/2	2.5g/0.1g	58%	More solid than HMDA gel, fragile
Jeffamine 400 (J400)	115	1/1.5	2g/0.62g	62%	Soft solid
Priamine 1074	135	1/1.5	2g/0.72g	74%	Hard solid

Curing with ESO

The second group of curing reactions includes the reactions of anhydride groups of MA-SO with the epoxy groups of ESO. The reaction of MASO with ESO results in the formation of a 100%-soy-based polymer as both components are derived from SBO. The reaction of anhydride groups with epoxy groups requires elevated temperature and the addition of *tert*-amine catalysts. Different *tert*-amines were studied for curing MA-SO with ESO, including diethyl-aniline (DEA), dimethyl–p-toluidine (DMPT), dimethyl-stearyl-amine (DMSA), and 2-methyl-imidazole (2MI). The mixtures of equivalent amounts of MA-SO and ESO

with the addition of 1wt.% of amine were cured at 150°C for 2 hours. The only catalyst provided the complete cure is 2MI, however, the cure with DMSA resulted in semi-cured soft gel.

Curing with OH-groups

MA-SO was cured by reaction of maleic anhydride with OH groups of α-cellulose and tannic acid. Both, α-cellulose and tannic acid are inexpensive bio-based materials. The curing reaction was performed at 150°C for 2 hours and 2MI was added as a catalyst in the amount of 1 wt.%. The cured polymers were analyzed in DSC. Fig. 2 shows DSC thermograms for uncured MA-SO and some cured MA-SO polymers. The endothermic peaks with the minimum at -6°C to 10°C on each DSC thermogram correspond to the melting transition of MA-SO which contains fatty acid chains. The more cross-linked the MA-SO oil is, the lesser is the heat of fusion which can be estimated from the integrated area of the endothermic peak. The values of endothermic energy are calculated for each thermogram and presented in the insert of Fig.2. The lowest value shows MA-SO cross-linked with α-cellulose and the highest shows MA-SO cross-linked with ESO, however, this polymer is formulated from two modified SBOs and uncross-linked fatty acid chains of both oils contribute to greater heat of fusion

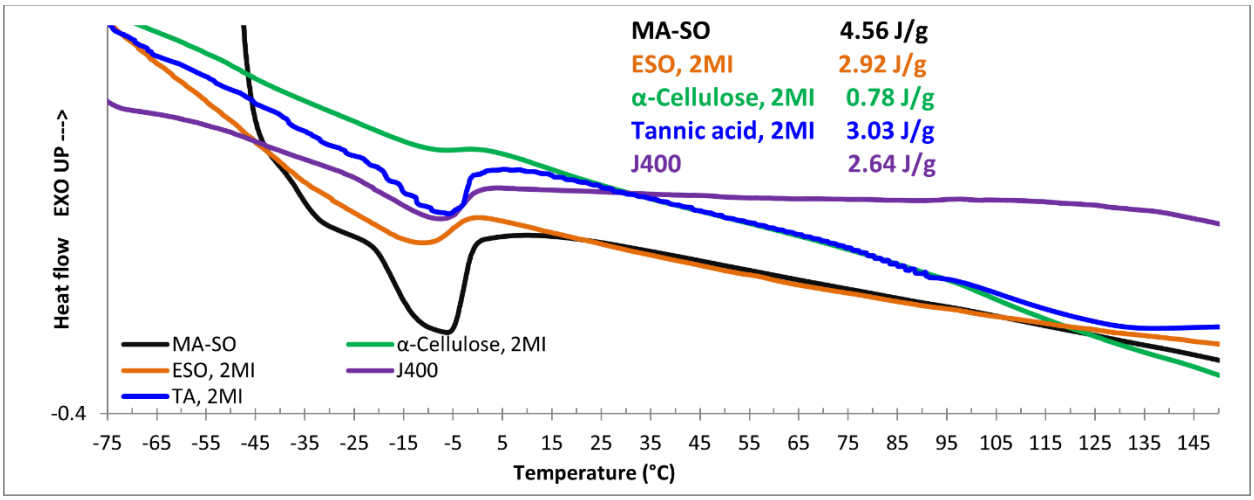

Fig. 2 DSC thermograms for MA-SO and some MA-SO polymers cured with different curing agents. The insert tab gives the calculated heat of fusion for each compound.

Conclusion

Soybean oil modified with maleic anhydride is able to form solid polymer for the use as a matrix in cellulose-filled composites. The possibility to cure the maleinated soybean oil with cellulose is promising for the formation of soy-cellulose composite material. The epoxidized soybean oil is another good candidate for soy-based materials. More work needs to be completed to achieve the optimum composition of modified oils and curing agents.

Work to be completed

We plan to optimize the curing MA-SO and ESO with cellulose and form soy polymer/cellulose composite materials that will be used as a mulching material. Before spring, the first composites must be formulated, and a bio-degradation study for the new composites will start.