Highly Soy-Based Pressure-Sensitive Polymer Adhesives

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Main goal of this project is to develop new highly soy-based pressure-sensitive adhesives (PSAs) using polymers derived from soy components - soybean oil-based vinyl monomer (SBM) and soybean oil-based polymer surfactant (SBPS) (both materials are invented at NDSU) for applications in food packaging and/or medical industries. **Specific aims** include synthesis of SBM and SBPS, formulation of PSAs thereof, and evaluation of properties/performance of highly soy-based PSAs.

Preliminary results. As we previously demonstrated, the presence of SBM fragments in PSAs provides the needed multiple bonding/debonding, required for these materials to function properly. We are capable of synthesizing in our lab up to two liter batches of SBM (as well as high oleic soybean oil-based monomer, HOSBM) and use this material for synthesis of PSAs (with up to 50 wt% of soy-based fragments). Such formulations possess a range of controlled properties including adhesive capabilities determined by the synthesized soy-based polymers structure and composition. At the same time, we demonstrated the feasibility of both, SBM and HOSBM to be copolymerized with other counterparts. This work targets new copolymers to act as soy-based polymeric surfactants (SBPS) which will facilitate controllable physicochemical characteristics of PSAs, enhance soy content in the final material, as well as adhesion properties

Completed work. In this project, we have employed one-step transesterification reaction of the soybean oil (high oleic soybean oil) and acrylamide alcohol, N-hydroxyethyl-acrylamide, using a method developed by the NDSU team to synthesize SBM and HOSBM (**Objective 1**). The reaction yields 95+% conversion of respective oil into SBM or HISBM. FTIR, NMR spectrscopies, and high-resolution MS spectrometry was used to confirm the purity and structure of the resulted monomers. Both synthesized SBM and HOSBM were then used for **Objective 2** which is synthesizing new soybean oil-based polymer surfactant (SBPS) and applying the resulted SBPS for synthesis of PSAs also containing SBM fragments. The SBPS (alternating copolymer poly(MA-*co*-HOSBM/SBM) was synthesized in chain copolymerization using the procedure developed during initial stage of this project. Hence, 2.7 g of maleic anhydride (MA) and 0.2 g of initiator AIBN were loaded to the reactor and dissolved under continuous magnetic stirring in 10 g of 1,4-dioxane. 10.4 g of SBM/HOSBM was dissolved in 41 g of 1,4-dioxane and added dropwise into the reactor. The reaction mixture was stirred under an argon blanket at 70^{o}C for 6 h. 1,4-Dioxane was distilled off and the resulting SBPS was precipitated three times with methanol from 1,4-dioxane solution, dried under nitrogen blanket before further characterization. The

chemical structure and molecular weight of SBPS confirmed by gel permeation chromatography, ^{1}H NMR and FTIR spectroscopy, respectively.

To demonstrate that we can move into **Objective 3**, surface activity of SBPS was confirmed by measuring critical micelle concentration (CMC) using pyrene solubilization and surface tension techniques. Due to the migration of pyrene probe molecules between hydrophilic and hydrophobic domains of polymeric micelles, a red shift of the adsorption band is observed with an enhanced excitation intensity determined by the micellar environment of pyrene. In this study, intensity signal of pyrene was monitored in the wavelength range of 300 - 360 nm (**Figure 1A** inset). Based on pyrene excitation spectra, the intensity ratios $I_{336.5}/I_{332.5}$ were plotted versus HOSBM-MA concentration (**Figure 1A**). CMC of HOSBM-MA corresponds to the rapid increase in the intensity ratio. The data indicate that HOSBM-MA copolymer is surface active, macromolecules self-assemble into the micelles at 1.7 x 10^{-7} mol/L (1.9 mg/L) concentration.

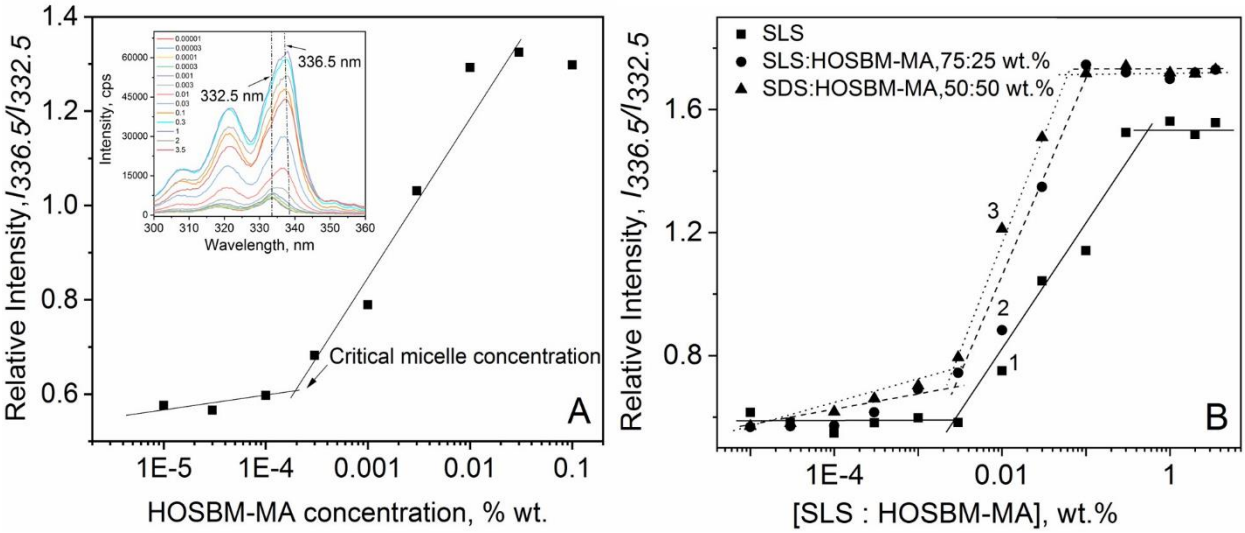

Figure 1. Intensity ratio $I_{336.5}/I_{332.5}$ of excitation spectra of pyrene in SBPS solutions versus HOSBM-MA concentration (**A**), in mixtures SLS/HOSBM-MA (**B**)

In the next experiment, an ability of SBPS in aqueous solution to solubilize poorly water-soluble hydrophobic materials was demonstrated. Being insoluble in water, a highly lipohilic dye Nile red (7-diethylamino-3,4-benzophenoxazine-2-one) shows no absorption in optical spectroscopy. In the presence of a micellar solution of SBPS the dye conversely is immediately solubilized and incorporated into the polymeric micelles which is demonstrated by increasing adsorption intensity of the selected wavelength at 547 nm with an increasing HOSBM-MA concentration (**Figure 2A** inset). The appearance of HOSBM-MA aqueous solutions containing various concentrations of the solubilized Nile red dye is shown in the same Figure. The obtained result shows that polymeric micelles provide a microenvironment capable of incorporating highly hydrophobic molecules in water.

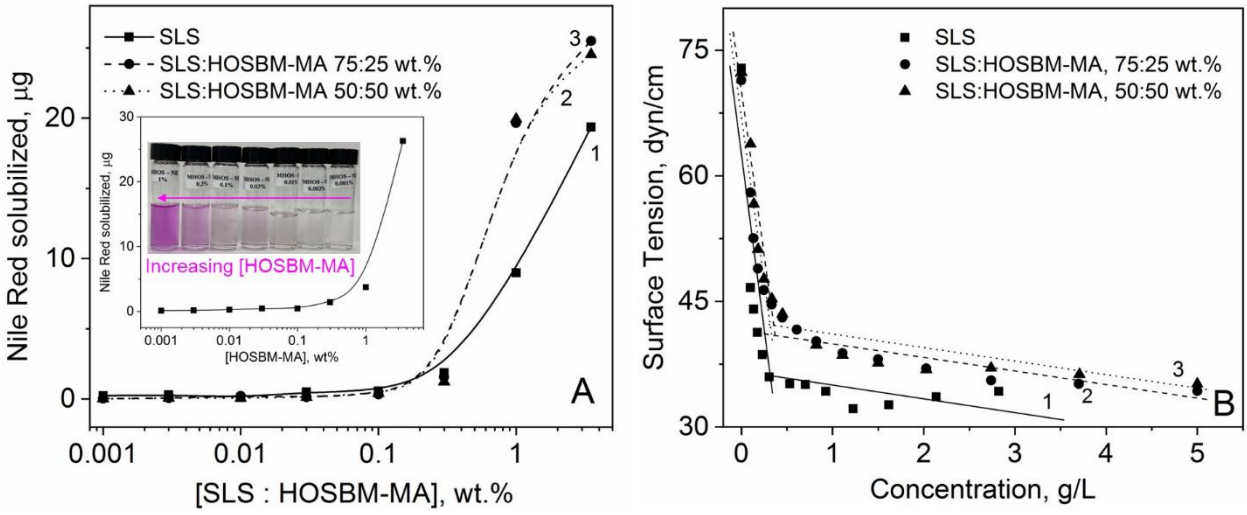

Figure 2. Solubilization of insoluble dye by SBPS macromolecules and mixtures with SLS in aqueous solutions (**A**). Surface tension measurements of SLS/SBPS mixture in aqueous solutions **(B).**

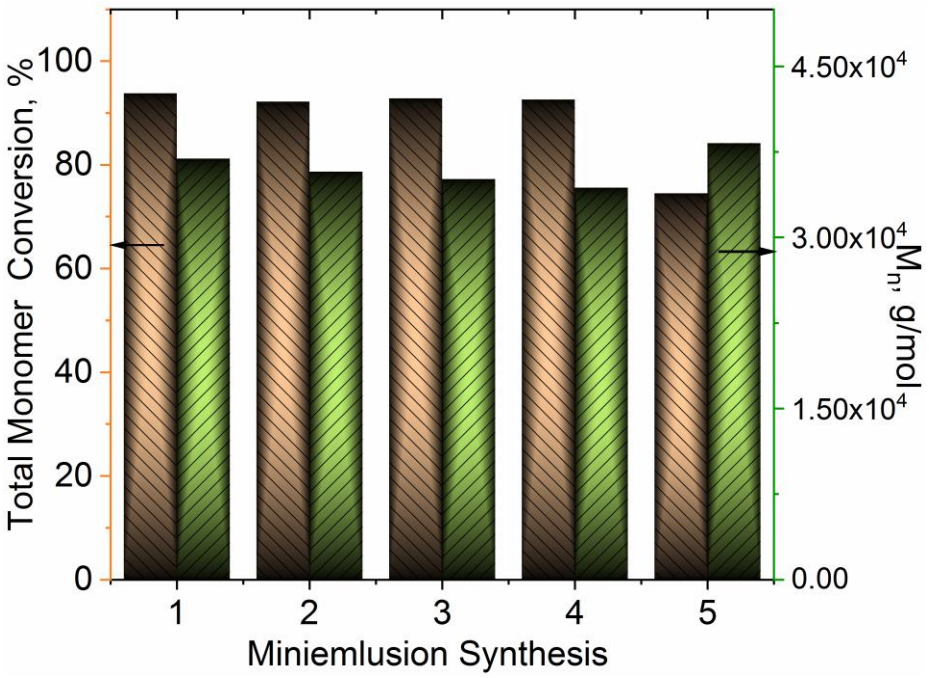

Figure 3. Total monomer conversion and number average molecular weight of emulsion copolymers from styrene and HOSBM synthesized in the presence of HOSBM-MA/SLS mixtures (1-SLS, St), 2-SLS/HOSBM-MA, 75/25wt.%, St), 3-SLS/HOSBM-MA (SLS, St/HOSBM, 90:10wt.%), 4-SLS/HOSBM-MA (75/25wt%, St/HOSBM, 90:10wt.%), 5-SLS/HOSBM-MA (50/50 wt%, St).

The possible synergy between HOSBM-MA and low molecular weight anionic surfactant SLS, as well as a potential for soy-based surfactant to substitute the SLS was investigated next. For this purpose, surface activity of SBPS/SLS mixtures was determined by measuring CMC with both surface tension and pyrene solubilizations. The obtained data (**Figure 1B** and 2**B**) show that adding two different amounts of HOSBM-MA (25 and 50 wt.%) results in a shift of CMC towards the lower (in comparison

to pure SLS) values, while almost no changes in CMC value is observed in surface tension measurements. Remarkably, both mixtures demonstrate higher capacity in terms of Nile red dye solubilization as the data presented in **Figure 2A** show.

To ensure applicability of the SBPS as polymeric surfactants/emulsifiers, synthesis and characterization of emulsion polymers (latexes) was conducted next. This study was carried out for both single SLS formulation (as a reference), as well as SBPS/SLS surfactant mixtures, at the same ratios as applied for surface activity and dye solubilization experiments.To distinguish the feasibility of latex formation in the presence of HOSBM-MA/SLS mixtures, the total monomer conversion, final latex particles' size, molecular weight were determined for emulsion polymers synthesized from styrene (St) and styrene - HOSBM (90 -10 wt.%) monomer feed at 4% of either SLS or SLS/HOSBM-MA mixtures in miniemulsion polymerization. Synthesized latexes with an average particle size of 40–50 nm exhibit high stability at room temperature within several months. The characteristics of the resulting latex copolymers are shown in **Figure 3**. The obtained data clearly show that the synthesized SBPS are feasible to act as emulsifiers and can be moved into next step of **Objective 2** (synthesis and formulation of highly soy-based PSAs) and **Objective 3** (testing of highly soy-based PSAs).

Work to be completed. By the introduction of up to 50 wt.% of SBPS in place of sodium lauryl sulfate (SLS) during emulsion/miniemulsion polymerization, we expect to not only preserve the stability of the obtained latex but also promote interactions of the polymeric surfactant SBPS with the adhesive copolymer, which contains soy-based monomer as a primary component (part of **Objective 2**). Enhanced compatibility is assumed to prevent phase separation and migration of surfactant to the substrate surface. To achieve our goal, we will examine the most common pressure-sensitive adhesive metrics (peel strength, tack, and shear strength) on glass and steel substrates (**Objective 3**). The results for the latexes with a combination of SBPS and SLS will be compared with a control containing only SDS as well as commercial benchmark tapes, such as office and packaging tape.

Summary. Latex pressure-sensitive adhesives gain increased attention with hot-melt adhesives over solvent-borne systems due to further restrictions on volatile organic compounds. Latex adhesives are synthesized via emulsion or mini-emulsion polymerization using amphiphilic surfactants to stabilize polymer particles in a water medium. While surfactants are essential for preserving latex stability, they can negatively affect the final adhesive properties, such as water resistance, substrate wetting, and adhesion to certain substrates (surfactant partially blocks the surface of the substrate and reduces interaction with the adhesive). To overcome these challenges, we partially substitute conventional anionic surfactant with the soy-based polymeric surfactants developed in our group (SBPS).