

Soy-Based Biodegradable Pressure-Sensitive Adhesives

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Main goal of this project is to develop biodegradable PSAs based on polymers from soy derivatives, high oleic soybean oil- and soybean oil-based vinyl monomers (HOSBM and SBM, developed at NDSU) for applications in food packaging and/or medical industries. **Specific aims** include synthesis of SBM- and HOSBM-based polymers range, formulation of PSAs thereof, evaluation of properties/performance of soy-based PSAs (including biodegradability).

Preliminary results. We are capable of synthesizing (in lab) 2 liter batches of novel soy-based monomers for free radical polymerization from soybean oil and high oleic soybean oil and use them interchangeably for synthesis of soy-based polymers (including water-based polymers, currently, 1 liter lab batches per experiment). Feasibility of synthesizing copolymers which are ingredients for PSAs formulations, with up to 50 wt% of soy-based fragments has been demonstrated during our preliminary study. Resulted candidates for PSAs show wide range of controlled properties (glass transition temperature, film forming, moisture resistance, toughness), including adhesive capabilities determined by the synthesized soy-based polymers structure and composition.

Completed work

In this project, we have employed semi-batch free-radical emulsion polymerization with different mechanisms of initiation – thermal and redox initiation. Changing the initiation mechanism allows for variation in the reaction temperature and thus tuning the final adhesive properties and performance. To synthesize pressure-sensitive adhesives in this research, commercial acrylic monomer 2-Ethylhexyl acrylate (2-EHA), styrene (St), and high-oleic soybean oil-based monomers HOSBM) have been used at this point of time. Despite the extremely high hydrophobicity of HOSBM, we have previously shown that it can be homo- and copolymerized using the emulsion polymerization process. The weight ratio between monomers was fixed as follows HOSBM 40 wt.%, 2-EHA 45 wt.% and St 15 wt.%. Thermally initiated polymerization was conducted at 80°C using an ammonium persulphate (APS) initiator. For the redox system, we have used a tert-butyl hydroperoxide initiator, ascorbic acid reducing agent, and FeSO₄. Reaction temperature varied from 20-50°C with a step of 10°C. The solid content of all latexes was kept at 30 wt.%.

As can be seen, in all systems, high total monomer conversion (up to 86-89 %) can be achieved. At the same time, by decreasing the polymerization temperature, latex particles of smaller sizes are obtained. The final copolymer composition was measured and calculated using ¹H NMR spectroscopy. As the data show, copolymer compositions are slightly enriched by 2-EHA and St content compared to the monomer

feed (**Table 1**). The molecular weight and thermo-mechanical properties of the synthesized copolymers were evaluated using gel-permeation chromatography (GPC), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) (**Table 2**).

Table 1. Physico-chemical characteristics of synthesized HOSBM-based copolymers.

Sample	Solid content, %	Conversion, %	Number average particle size, nm	PSD	Polymer composition, wt.% of monomers (HOSBM-2-EHA-St)
HES-9 (80°C)	28.3	88.8	592.5	0.670	42.1-47.9-10.0
HES-3 (50°C)	28.8	87.0	119.3	0.259	-
HES-4 (40°C)	30.2	89.5	47.9	0.301	40.2-47.1-12.7
HES-7 (30°C)	27.0	86.1	102.7	0.354	39.5-46.5-14.0
HES-8 (20°C)	30.0	87.2	64.8	0.447	44.8-43.2-12.0

Table 2. Physico-chemical characteristics of synthesized HOSBM-based copolymers.

Sample	Mn	Mw	PDI	Tg measured by DSC, °C	Tg measured by DMA, °C	Storage modulus, MPA	Loss modulus, MPa
HES-9 (80°C)	13 100	82 500	6.3	-57.0	-35.0	9.5	0.1
HES-3 (50°C)	19 700	113 400	5.7	-54.5	-29.0	12.5	0.24
HES-4 (40°C)	30 200	155 700	5.1	-	-	-	-
HES-7 (30°C)	35 500	278 300	7.8	-	-	-	-
HES-8 (20°C)	28 300	174 500	6.2	-56.5	-20.0	18.1	0.41

Based on the obtained data, it is clear that with the switch to a redox system and decrease in reaction temperature, molecular weight increases dramatically with almost no change of polydispersity (PDI). Thermal analysis shows that glass transition temperature (Tg) remains unchanged regardless of reaction conditions (**Table 2**).

DMA was performed to assess how the viscoelastic behavior of pressure-sensitive adhesives changes depending on synthetic conditions. A significant increase in storage modulus can be observed in the material with higher molecular weight that potentially may impact the cohesive strength of the adhesive (**Figure 1**).

The adhesive performance of all synthesized polymers was tested using a 90-degree T-peel test widely used for pressure-sensitive adhesives characterization. For this purpose, the adhesive was applied to Mylar (polyester) primary substrate from a toluene solution to form the pressure-sensitive tape.

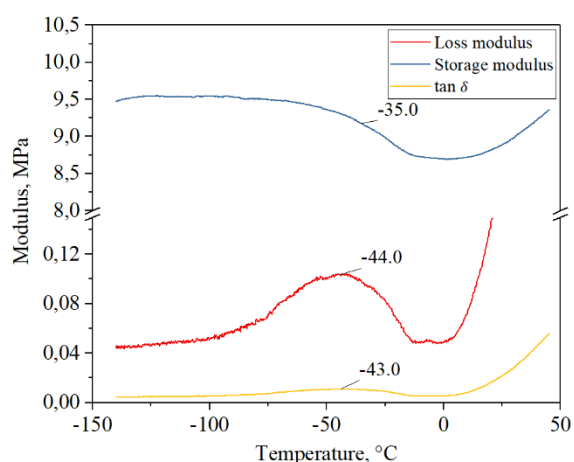


Figure 1. DMA of selected HOSBM-based copolymer.

Then this tape was attached to another Mylar substrate or paperboard. Important to note that the paperboard is one side covered with a mineral clay layer according to the manufacturer.

The obtained results show that HOSBM-based copolymers synthesized by redox emulsion polymerization demonstrate enhanced peel strength on all substrates compared to counterparts synthesized using thermally initiated emulsion polymerization. Important to note that on the paperboard substrate, different modes of bonding failure occur. In substrate failure, one of the substrates become damaged, while in adhesive failure mode, both substrates keep their integrity with a break of the adhesive layer. **(Figure 2)** With all mentioned above, we can point out that substrate failure (indicating excellent adhesive performance) is more characteristic of polymers HES-3, HES-4, HES-7, and HES-8. Moreover, sample HES-4 can be fully removed from both sides of the paperboard without residual material, while HES-9 on all substrates leaves parts of the material after the peel-strength test.

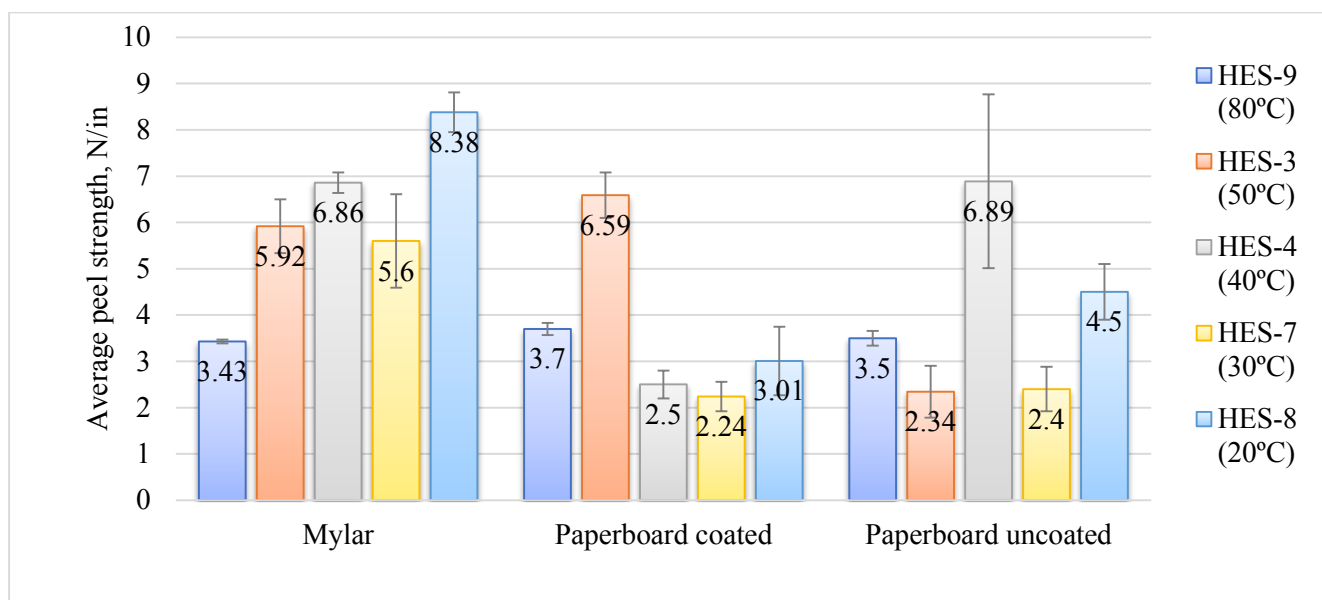


Figure 2. Adhesive performance of HOSBM-based pressure-sensitive adhesives.

Work to be completed

Adhesive materials fail by one of two modes of failure – cohesive failure with a loss of substrate material integrity and adhesive failure with full delamination of substrate material. The molecular weight of the polymer adhesive is one of the crucial parameters affecting the type of failure. With the increase of polymer adhesive molecular weight, cohesive strength increases due to higher intermolecular interactions (macromolecular entanglements). The latter allows to avoid the break of the substrate materials. On the other hand, too high molecular weight may drastically impact adhesion. Combination of the proper cohesive strength to ensure material integrity and adhesion to provide adhesion performance must be balanced. Polymers with bimodal molecular weight distribution (MWD) may

satisfy both conditions necessary to obtain optimal pressure-sensitive adhesive. Employing redox emulsion polymerization rather than thermal emulsion polymerization is targeted to achieve bimodal MWD.

Low molecular weight polymer itself has an excellent adhesion performance. Another way to increase its cohesive strength is to introduce a cross-linking stage to form network structure. Permanent cross-linking is meant to provide a similar increase in macromolecular interactions as physical entanglements of high molecular weight macromolecules. In this project, HOSBM is used, which has allyl double bonds that can be cross-linked via autoxidation. By varying cross-linking degree or HOSBM content cohesion strength can be tuned.

The same effect can be obtained by replacing HOSBM with soybean oil-based monomer (SBM) which is more unsaturated and facilitates formation of polymer network with higher cross-linking density. The work with SBM is planned to be done in this project as well.