

## **Soy-Based Biodegradable Pressure-Sensitive Adhesives**

PI: Andriy Voronov, Professor, Coatings and Polymeric Materials, NDSU, Dep.2760, PO Box 6050, Fargo, ND 58108, phone 701 231 9563, andriy.voronov@ndsu.edu

*Dates of Project: July 1<sup>st</sup>, 2022 – June 30<sup>th</sup>, 2023*

### **Background Information**

Acrylic pressure-sensitive adhesives (PSAs) have been known for decades and are valued by the customers because of their high water resistance, weatherability (UV-resistance), and intrinsic pressure-sensitivity, which allows their usage without additives, which increase tackiness. They are used in many areas, such as packaging, automotive, medical, electronics, building and construction, etc. However, most of the adhesives are formulated using petroleum-based monomers - acrylic and methacrylic acid derivatives. Nowadays bio-based acrylic and methacrylic acid can be readily obtained. Nevertheless, the most used monomers in PSAs butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA) have low biobased carbon content of 37 and 27 % respectively even being synthesized from bio-based acrylic acid. That is why synthesis of monomers with high biobased carbon content is of particular importance. Acrylic monomers synthesized using soybean oil and high oleic soybean oil allow to increase hydrophobicity, bring effect of plasticization and carry functional groups available for post polymerization reactions. Such a set of properties make them good candidates to serve as a replacement for petroleum-based BA and 2-EHA in PSAs for various applications. Combination of environmentally friendly polymerization process (emulsion polymerization) with the use of soy-based raw materials allows increase sustainability of the end-product, while the maintaining desired properties or even outperforming current adhesives on market.

### **Research Objectives**

In this project, we have focused on the development of a competitive copolymer synthesis to incorporate soybean oil-based (SBM) or high-oleic soybean oil-based (HOSBM) monomers as an alternative to commercially available soft counterpart 2-EHA and evaluate the feasibility of obtained polymers as PSAs.

To find the optimal type and conditions of polymerization, which yields polymer with the most prominent adhesion properties, we varied initiating systems for semi-batch emulsion polymerization. Obtained polymer after emulsion polymerization is called latex and consists of polymer particles dispersed in water media and stabilized with the surfactant. The use of semi-batch process instead of batch allows to decrease the particle size of latex via changing of the feeding time in the process, which in turn increases the stability of polymer system. One of the initiation systems that was used in free-radical polymerization utilizes thermal decomposition of initiator, which has weak bonds in the structure. However, relatively high temperature (70-80°C) is used for initiator decomposition and generation of free-radicals, which increases the rate of chain termination reactions, leads to formation of lower molecular weight polymer and increases the rate of side reactions (chain transfer). In contrary, initiation with redox systems utilizes electron transfer reactions to generate free radicals instead of thermal decomposition of initiator, decreasing the amount of heat to be applied, allowing to decrease polymerization temperature, suppress the rate of chain termination and side reactions affecting polymer

molecular weight. It was assumed that change in reaction temperature would allow to control molecular weight and molecular weight distribution of resulting polymer.

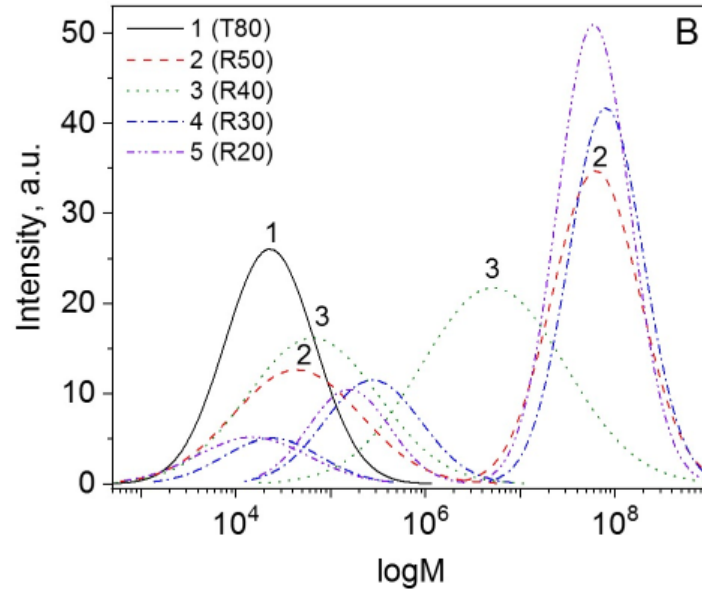
Adhesion performance of the soy-based PSAs obtained with different initiation systems and reaction conditions (reaction temperature) have been evaluated by measuring tack, peel strength and shear strength on substrates with different surface energy and roughness. Correlation of PSAs properties, mainly molecular weight and adhesion performance was performed to discover optimal synthetic conditions and the most prospective polymer compositions, which can compete with some of the existing PSAs available on the market.

### Research Findings

To evaluate the effect of polymer molecular weight on adhesion performance we have developed a model polymer composition, which would satisfy the requirements to PSAs: low  $T_g$  in a range -60 to -40 °C, ability to obtain high molecular weight or cross-linked structure for increased cohesion of the system, presence of units that increase tackiness and adhesion of the system. This polymer contains 40 wt.% of SBM or HOSBM and 44 wt.% of 2-EHA as soft counterpart with 15 wt.% of styrene as rigid counterpart (1 wt.% of methacrylic acid was used as functional monomer). In **Table 1** we present characteristics of latexes obtained with thermal initiated polymerization at 80°C (T80) and redox initiated polymerization at 50-20°C (R50-R20). While solid content for all systems is close to theoretical (30 wt.%) and high conversion is achieved (86-90 %), copolymer composition measured with <sup>1</sup>H NMR shifts to slightly higher incorporation of SBM or HOSBM when reaction temperature is decreased. The enormous effect of initiation system on polymer molecular weight and its modality was observed (**Figure 1**). With decrease of reaction temperature 2 or 3 molecular weight distributions appear with very high molecular weight fraction of polymer. These fractions are assigned to the 1. linear ( $10^4 - 10^5$  g/mol), 2. short-chain branched ( $10^6 - 10^7$  g/mol) and 3. long-chain branched ( $10^8 - 10^9$  g/mol) polymer configurations.

**Table 1. Characteristics of synthesized latexes**

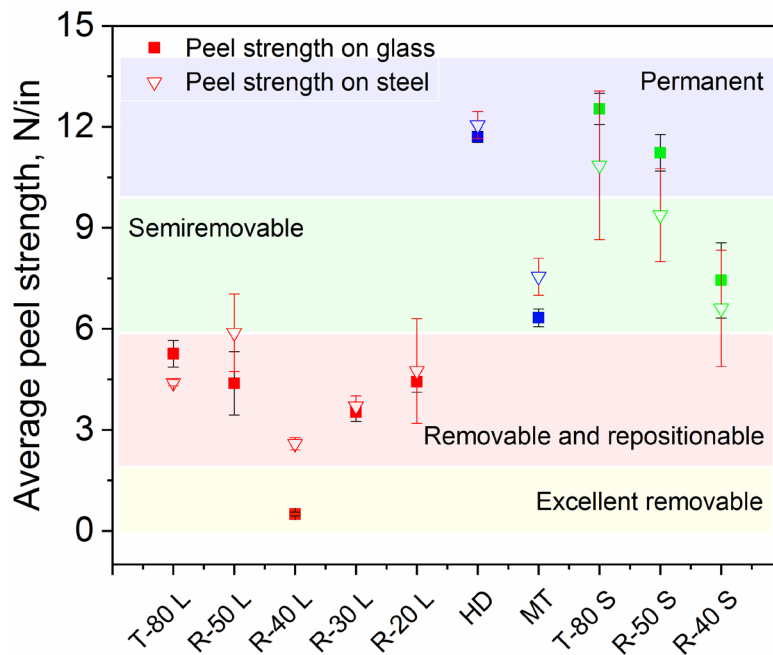
	Solid content, %	Conversion, %	Copolymer composition, wt.%
<b>T80</b>	28.3	89	38 - 52 - 10
<b>R50</b>	28.8	87	37 - 51 - 12
<b>R40</b>	30.2	90	37 - 54 - 9
<b>R30</b>	27.0	86	41 - 48 - 11
<b>R20</b>	30.0	87	42 - 46 - 12



**Figure 1.** Deconvoluted gel permeation chromatography (GPC) plot for molecular weight distributions (MWDs) of the soy-based latexes

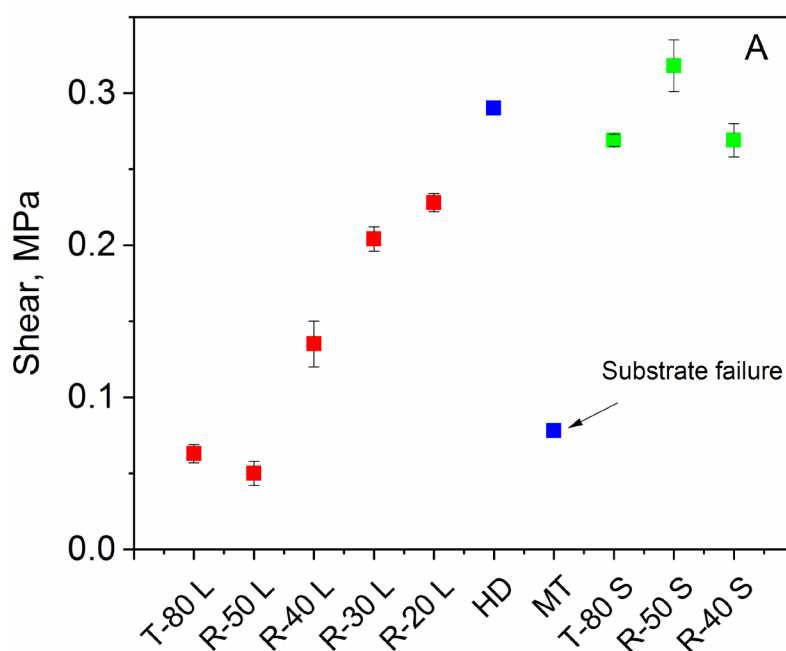
Since the glass transition temperature of all polymers measured by differential scanning calorimetry falls in a range of  $-54$  to  $-57^{\circ}\text{C}$  and copolymers have similar chemical composition, the change in adhesion performance was attributed to the variations in molecular weight and molecular weight distributions, depending on the experimental conditions.

Adhesion performance of soy-based PSAs applied directly from latex, precipitated and applied from solution and commercial tapes (manufactured by 3M) was compared on glass and steel substrates in peel (**Figure 2**), tack and shear (**Figure 3**) tests.



**Figure 2.** Peel strength results for PSAs (L – latexes adhesives, S – adhesives applied from solution), HD and MT – commercial tapes from 3M) on glass and steel substrates.

Preliminary results on paperboard substrates showed substrate failure, meaning that adhesive bonding was stronger than paperboard substrate. Soy-based adhesives applied from solution (green labels) demonstrated remarkable peel and shear strength, comparable to commercial samples (blue labels), with slightly lower tack than of latex adhesives. Meanwhile, soy-based latex adhesives showed lower value of peel strength, higher tack and increase in shear strength with increase in molecular weight of the polymer. Important to emphasize that high molecular weight fractions often compromise adhesion performance, weakening tack and peel, but it was not observed for the synthesized polymers. Some of the compositions, such as R20 applied from latex and T80/R50 applied from solution can maintain all of the adhesion properties at high level to be applied as pressure-sensitive adhesives comparable to existing products on the PSA market.



**Figure 3.** Shear strength (A) for PSAs (L - latexes, S - copolymers applied from solution, HD – commercial product).

### Benefits to Soybean ND farmers and industry

The developed technology targets to demonstrate feasibility of using soybeans produced in the state of North Dakota for high value and high profit polymeric materials for PSAs industry. Using soybean oil and high oleic soybean oil for making new biobased PSAs has the ability to add more value to the crop, thereby make it more profitable for farmers.

Ability to produce soy-based biodegradable PSAs from soy oils from crop grown in state of North Dakota is a key benefit of the developed materials. Obtained results demonstrate that the developed PSAs may diversify soy-based polymeric products market with increased demand for soy oils and thus benefit North Dakota soybean farmers. In particular, the developed PSAs may succeed at the market of food packaging and/or medical applications. The latter helps the state of North Dakota economy to involve investors and other soy processing industries.