

BIORENEWABLE PRESSURE-SENSITIVE ADHESIVES VIA MINIEMULSION

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Abstract

Currently, there is a considerable interest in the development of sustainable solutions for consumer goods, including adhesives and coating. Efforts to utilize renewable mass in pressure-sensitive adhesive (PSA) products have focused mostly on chemicals derived from starch, sugars and vegetable oils. These components are usually not directly compatible with free radical polymerization used to generate water-borne PSA and need to be chemically modified to introduce functional groups. Research discussed here describes an approach to incorporate significant amounts of renewable macromonomers in water-based acrylic polymerization by addressing the macromonomer miscibility of renewable macromonomers in miniemulsion polymerization systems. The effectiveness of this approach is demonstrated through the direct substitution of *n*-butyl acrylate (*n*-BA) with renewable monomers in a commercial PSA containing an equal mass blend of monomers *n*-BA and 2-ethylhexyl acrylate (EHA), while retaining similar performance properties.

1. Introduction

Fossil fuels are the primary source of synthetic chemicals used to produce polymeric consumer goods such as plastics, adhesives, coatings and foams. Most petroleum-based polymers are non-recyclable and non-compostable and complete their life cycles as waste. (Plastics and other petroleum-derived materials constitute 20% of municipal solid waste).¹ Concerns over the environmental impact of these products as well as diminishing oil reserves have driven the pursuit of more sustainable options for our modern needs. Currently, there is considerable interest in biomass derived from woody, herbaceous, and aquatic plants and grasses as a replacement for petroleum-derived feedstocks. Use of biomass for this purpose may lead to the generation of products with closed life cycles. Furthermore, utilization of non-food energy crops can generate employment, restore fallow lands, and replace agricultural intensive crops with less intensive crops, resulting in a reduced need for fertilizers and pesticides.² National security concerns, specifically the need to reduce our dependency on foreign sources for energy and raw materials, offers further incentive for utilizing biomass in energy and chemical feedstock production. (In 2009 the United States imported nearly 60% of its petroleum demand.³)

In this presentation, our efforts to develop PSA containing high levels of biomass will be discussed. Pressure-sensitive (PS) products have become ubiquitous in our homes and offices. Most of these products contain water-based acrylic PSA, which is produced mainly from petroleum-based raw materials. More than 300 million dry pounds of acrylic adhesive was sold in the United States in 2006.⁴ A significant portion of this PSA ends its life cycle as landfilled recycling mill sludge. The introduction of biomass as a substitute for petroleum-based raw materials will make a significant contribution in the development of sustainable products, particularly when these materials can be made biodegradable.

Past efforts to utilize renewable mass in PSA have focused mostly on chemicals derived from starch, sugars and vegetable oils. These components are usually not directly compatible with free radical polymerization used to generate water-borne PSA and need to be chemically modified to introduce functional groups. Copolymers of acrylate monomers and sugar-derived moieties have been prepared by reacting alkyl polyglycosides with maleic acid anhydride, to introduce two functional double bonds that participate in free radical polymerization.⁵ These biosynthetic hybrid sugar-acrylate copolymers have been marketed as biomass-based PSAs that are easily removed during paper recycling. Although plant-based fatty acids are unsaturated, the double bonds are not reactive enough to directly participate in radical polymerization. Macromonomers from acrylated or hydroperoxidized fatty acids and triglyceride derivatives have been used in miniemulsion polymerizations to prepare waterborne resin coatings. Similarly, acrylated oleate derived from sunflower oil triglycerides were copolymerized with methyl methacrylate and EHA. These copolymer materials demonstrated comparable tack, shear, and elasticity compared to commercial available PSAs, although peel values were lower, due to the molar mass of the polymers being close to the critical molar mass for physical entanglements.⁶

Research discussed here involves the attachment of lactic acid macromonomers onto the backbones of representative acrylic PSA polymers. Although conventional emulsion polymerization is the standard approach used to generate water-based PSA, slow diffusion of high molecular weight (renewable) macromonomers makes them incompatible with conventional emulsion polymerization. Instead, PSA polymers were generated via miniemulsion polymerization in which the propagation step and chain growth occur in sub-micrometer monomer droplets formed prior to reaction initiation by high shear forces. The absence of mass transport results in faster reaction rates and allows the use of high molar mass components. Monomer droplet stability is achieved through the use of surfactants, but the miscibility of the macromonomer with the other components is critical as well for producing stable miniemulsion precursors and coagulant free latexes.^{7,8} Miniemulsions are formed via ultrasonication, which is popular for small laboratory scale, but a number of mechanical methods are possible for larger scale production.

2. Preparation of Lactide-Containing Macromonomers

Similar to plant oil and sugar derivatives, lactide cannot directly participate in the free radical polymerization used in the preparation of water-borne PSA polymers. Chemical modification of lactide can be achieved by choosing an appropriate initiator for the ring-opening polymerization (ROP). Acrylated PLA has been prepared by ROP of 2-hydroxyethyl methacrylate (HEMA).⁹⁻¹² This method has been used to prepare copolymers of acrylated PLA macromonomers with *n*-butyl methacrylate (BMA) in a miniemulsion process that contained up to 34 wt% biomass.¹⁰ Higher biomass incorporation was not possible in this case, due to the immiscibility of macromonomers with higher molar mass.

Adopting the approach described by Ishimoto *et al.*, we prepared acrylated PLA macromonomers (MMs) with the aim of developing biorenewable PSA polymers by copolymerization of biomass MMs with suitable acrylate monomers. The addition of a few repeat units of lactic acid in the MM (from 6 to 12 repeat units) caused a significant increase in the glass transition temperature (T_g) and a change from a viscous liquid to a waxy solid for 12 repeat units (see Figure 1). Although L6¹ was miscible with BMA,

ⁱ The notation used to identify the macromonomers consists of a letter to indicate the monomer, followed by the number of repeat units *n*. For example, L6 denotes a HEMA-functionalized poly(lactic acid) MM with 6 repeating units of lactic acid (L), whereas L8C4 indicates a statistical copolymer MM consisting of 8 L and 4 ϵ -caprolactone (C) moieties.

a homogeneous mixture of L8 and BMA could only be obtained upon moderate heating and sonication. L12 could not be mixed with BMA or other acrylate monomers and, therefore, could not be used in miniemulsion polymerization. The poor miscibility of the MMs with more than 8 repeat units strongly limits the amount of biomass that can be incorporated in the final PSA product and makes processing on larger scales difficult.

Poly(ϵ -caprolactone) is a liquid polymer at room temperature with a T_g of $-60\text{ }^\circ\text{C}$. Therefore, a copolymer of repeating units of both ϵ -caprolactone monomer and semi-crystalline L-lactic acid was expected to have a low T_g , due to the flexibility of the aliphatic ϵ -caprolactone chain, and the suppression of the crystallization of the lactic acid by the statistical incorporation of another monomer. Recently, a process to obtain ϵ -caprolactone from starch has been described, adding ϵ -caprolactone to the list of renewable building blocks.^{13, 14} Thus, for our purpose of developing low- T_g biomass-based functional macromonomers, ϵ -caprolactone is particularly suitable. As expected, the copolymer MM of lactide and ϵ -caprolactone are viscous liquids with T_g 's from -20 to $-52\text{ }^\circ\text{C}$ and are fully miscible with acrylate monomers. Utilizing this copolymer strategy, high molar mass MMs and acrylate monomers could be copolymerized, increasing the amount of biomass in the final PSA product to near 60 wt%.

Table 1 lists the composition of a set of MMs and their glass transition temperatures. The composition and molar mass of the macromonomers were determined from $^1\text{H-NMR}$, based on the ratio between the peaks at 4.3 ppm (HEMA, $-\text{O}-(\text{CH}_2)_2-\text{O}-$), 5.1 ppm (lactic acid, $-\text{COO}-\text{C}(\text{H})\text{CH}_3-$), and 2.3 and 4.0 ppm (ϵ -caprolactone, $-\text{CH}_2-\text{CH}_2-\text{C}=\text{O}$ and $-\text{O}-\text{CH}_2-\text{CH}_2-$). The compositions calculated based on the NMR spectra were consistent with the feeding ratio of lactide and ϵ -caprolactone to HEMA, indicating that the reaction proceeded to near completion.

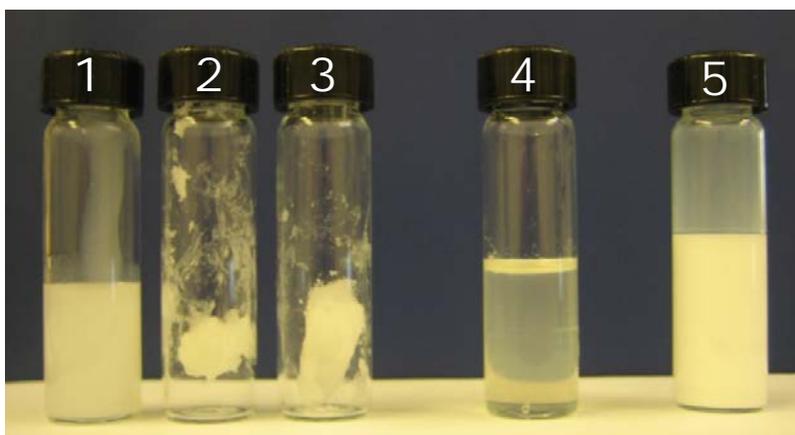


Figure 1: With increasing molar mass, the lactide-based macromonomers go from a viscous liquid to a waxy solid at room temperature. Shown are samples L6 (1), L8 (2), and L12 (3). Macromonomers containing both lactide and ϵ -caprolactone were viscous at room temperature, even for higher molar mass, as for macromonomer L8C4 (4), and formed stable miniemulsions. Shown here is the miniemulsion of L8C4 with *n*-butyl methacrylate (5) one week after formation.

Table 1: Biomass Macromonomers

Macromonomer	MW (g/mol)	Biomass (%)	T_g (°C)
L6	562	77	-26
L8	706	82	-20
L12	994	87	-8
L8C4	1162	89 ^a	-38

^a ϵ -Caprolactone can be derived from lactide.^{13, 14} Therefore, both L and C are included in the biomass contents calculation.

3. Preparation of Lactide-Based Biomass PSAs via Miniemulsion

The macromonomers L6, L8, and L8C4 were copolymerized with BMA and EHA in a miniemulsion polymerization process. The compositions of the final latexes are listed in Table 2. Conventional methods for monitoring the conversion of monomer, such as gravimetry, which rely on evaporation of the unreacted species, are not suitable for miniemulsion polymerizations, due to the presence of the volatile acrylate monomers and the non-volatile MMs.

Table 2: Latexes with biomass macromonomers

Latex	MM	comonomer	wt/wt	Biomass content (%)
L8-co-BMA	L8	BMA	1:1	41
L8-co-EHA	L8	EHA	1:1	41
L8-co-EHA	L8	EHA	2:1	55
L8C4-co-BMA	L8C4	BMA	1:1	45
L8C4-co-EHA	L8C4	EHA	1:1	45

We used confocal Raman microscopy (CRM) to determine the fraction of a given functional group quantitatively by comparing its characteristic peak with a reference peak, as previously described by us.¹⁵ The conversion of the miniemulsion polymerizations were followed by analyzing aliquots of the initial emulsion and during the reaction. Spectra of the MMs listed in Table 1 are shown in Figure 2A. The conversion of the miniemulsion reactions were followed by monitoring the disappearance of the C=C peak at 1642 cm^{-1} , using the peak intensities of the carbonyl groups at 1724 cm^{-1} (HEMA) and 1768 cm^{-1} (L and C) as reference peaks. The reaction conversions determined by this method are shown in Figure 2B for the free radical copolymerization of L8 (circles) and L8C4 (squares) with BMA. The polymerizations were fast, as is typical for miniemulsions, and the reactions proceeded to 90% conversion within the first hour, approaching full conversion after 2 hours. The solids contents of the latexes were 30 wt%, which is a typical value for macromonomer emulsions without additional

polymeric co-surfactants.¹⁶ The latex particles were characterized with dynamic light scattering (DLS) and transmission electron microscopy (TEM), as shown in Figures 3 and 4. The particles were spherical with diameters of 50-500 nm, which are common values for miniemulsion latex particles.^{17, 18}

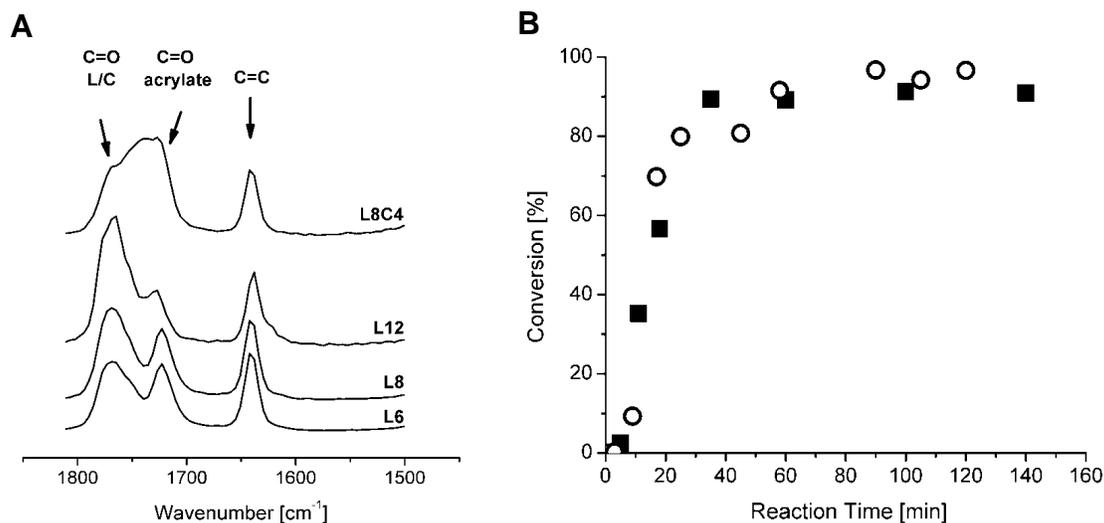


Figure 2: Raman spectra of Sample L6, L8, L12, and L8C4 (A). The conversion of the acrylate-macromonomer copolymerization in the miniemulsion can be monitored by the disappearance of the double carbon-carbon bond peak at 1640 cm⁻¹, present in both the HEMA-functionalized biomass macromonomers and acrylate monomers (B).

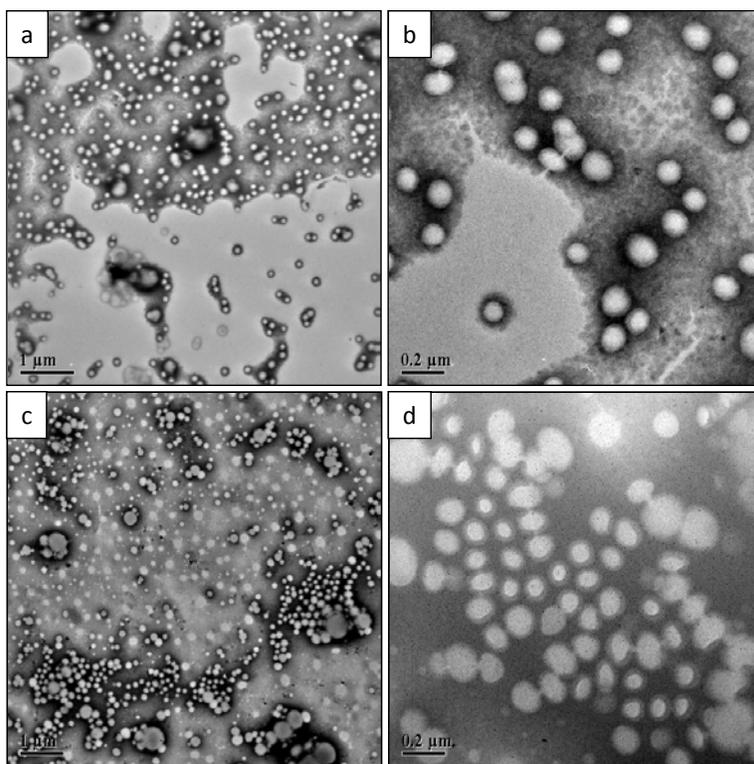


Figure 3: Transmission electron microscopy (TEM) images of 1:1 wt/wt L8-co-BMA (a and b) and 1:1 wt/wt L8C4-co-BMA (c and d) latex particles.

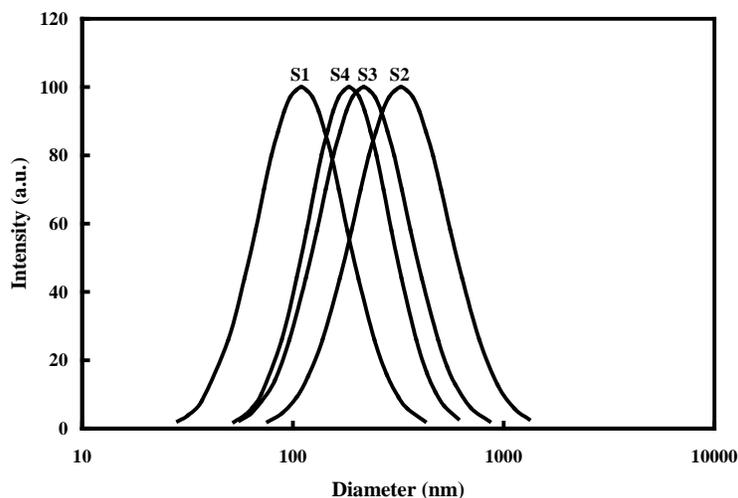


Figure 4: Dynamic light scattering (DLS) was used to determine the average particle size in latexes of 1:1 wt/wt L8-co-BMA (1), 1:1 wt/wt L8-co-EHA (2), 2:1 wt/wt L8-co-EHA (3), and 1:1 wt/wt L8C4-co-BMA (4).

4. *Properties of Lactide-Based Biomass PSAs*

Dynamic mechanical analysis temperature sweeps carried out at 10 rad./s were used to determine the temperature dependence of the storage (G') and loss modules (G'') for films cast from the latexes shown in Table 2 as well as a commercial PSA (see Figure 5). The adhesive properties, such as glass transition, storage modulus, and tack of the copolymer latex of L8C4-co-EHA compared well to a commercially available, removable PSA, which contains approximately 1:1 wt/wt EHA and *n*-BA. In comparing our biomass copolymer to the commercial PSA, we effectively replaced 50 wt% of non-renewable *n*-BA with biomass-derived macromonomer, while retaining the adhesive properties. The storage modulus for films of L8C4-co-EHA copolymers was well below 10^5 Pa at room temperature, which is a good indication of pressure-sensitive behavior according to the Dahlquist criterion,¹⁹ while the T_g was determined to be -45 °C. In Figure 6, the maximum tack load measured by probe tack of the biomass PSA and a commercial PSA are compared.

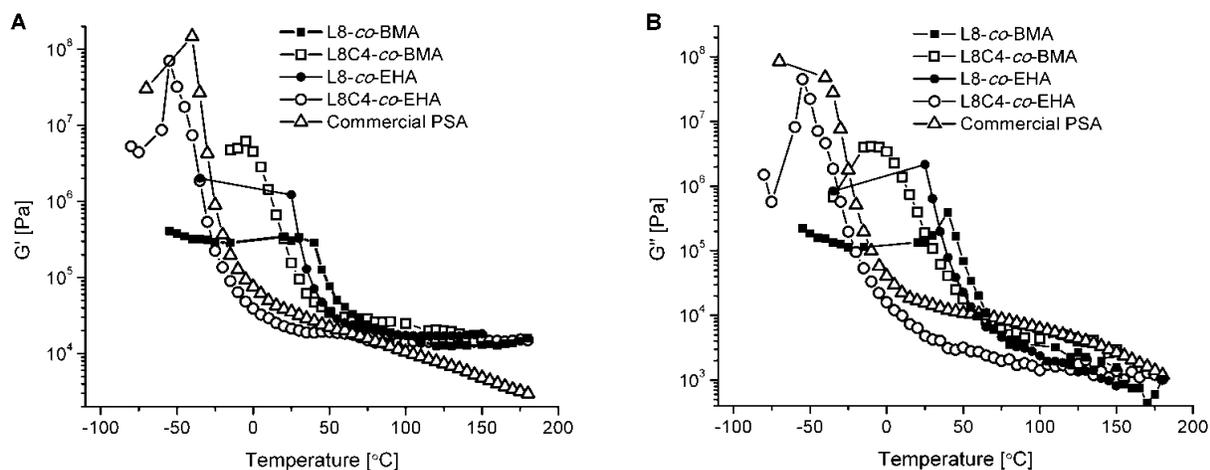


Figure 5: Dynamic mechanical analysis (DMA) of films prepared from biomass-based latexes composed of 1:1 wt/wt copolymers of L8 or L8C4 macromonomer with BMA and EHA monomer. For comparison, a commercial removable adhesive is shown as well.

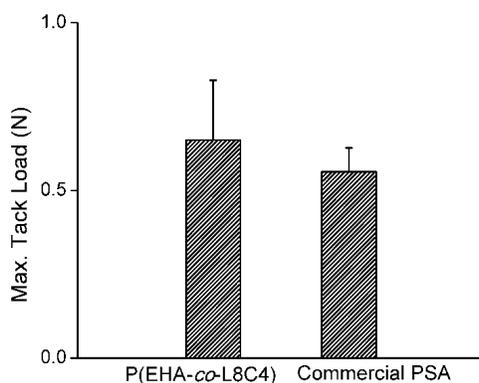


Figure 6: Comparison of probe tack of a biomass-based and a commercial removable adhesive.

5. Summary and Future Work

An approach was described to incorporate significant amounts of renewable macromonomers in water-based acrylic polymerization by addressing the macromonomer miscibility of renewable macromonomers in miniemulsion polymerization systems. The effectiveness of this approach is demonstrated through the direct substitution of renewable monomers for *n*-BA in a commercial PSA containing an equal mass blend of monomers *n*-BA and EHA, while retaining similar performance properties. Future work will include an investigation of the effect of copolymer composition on adhesive performance for a large number of lactide-based macromonomers, and an extension of the hybrid copolymer approach to include other renewable materials. In addition, semi-synthetic copolymers based on renewable monomers are being developed that will have long life times and are recycling compatible and fully biodegradable. Our first results indicate that with the hybrid copolymer approach the means for producing both recycling compatible and compostable, commercially-feasible biomass-based products will be available.

6. Literature Citations

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7. Acknowledgements

This research was partially funded by a grant from the United States Postal Service, Stamp Acquisition and Distribution, and by IREE grant Sustainable Polymers: Tomorrow's Advanced Materials (RL-0009-09). Parts of this work were carried out in the College of Science and Engineering Characterization Facility, University of Minnesota, which receives partial support from NSF through the MRSEC program.