Polyacrylates with High Biomass Contents for Pressure-Sensitive Adhesives Prepared via Mini-emulsion Polymerization

Gang Pu, Matthew R. Dubay, Jiguang Zhang, and Steven J. Severtson*

Department of Bioproducts and Biosystems Engineering, University of Minnesota, 2004 Folwell Avenue, St. Paul, Minnesota 55108, United States

Carl J. Houtman

USDA, Forest Products Laboratory, One Gifford Pinchot Drive, Madison, Wisconsin 53726, United States

ABSTRACT: *n*-Butyl acrylate and other acrylic monomers were copolymerized with an acrylated macromonomer to produce polymers for pressure-sensitive adhesive (PSA) applications. Macromonomers were generated through the ring-opening copolymerization of L-lactide and ε-caprolactone with 2-hydroxyethyl methacrylate (HEMA) at an average molar composition of 5:4:1, respectively. Conversion in the mini-emulsion polymerization was followed using Raman spectroscopy and was nearly complete within 2 h. Testing of these adhesive polymers indicates that performance properties meet or exceed those of commercial water-based acrylic PSAs.

■ INTRODUCTION

In recent years, sharply rising oil prices, an unstable supply, and potential shortages have greatly raised the interest in replacing petrochemicals with renewables. Pressure-sensitive adhesive (PSA) materials are just one type of commercial product which are ready to be replaced by renewable options. Most of the chemical components found in PSAs today are petroleum-based and not biodegradable, but movement toward using renewable materials is restricted by higher raw material costs and reduced performance.

Renewable raw materials that could feasibly be developed for replacing traditional monomers in PSA production are fatty acids, triglycerides, and polyols (derived from vegetable and/or animal fats and oils) along with lactides and lactones (derived from carbohydrates).[1,2] Recent examples of adhesive polymers generated entirely from such sources include polylactide/poly(menthide), ABA triblock copolymers,[3−5] and ether-linked expoxide soy oils.[6] These and other examples demonstrate that progress is being made on the generation of PSAs based solely on biomass, but these materials have cost and/or performance issues preventing them from being commercially viable in the near future.

An alternative to a completely renewable PSA is a hybrid structure, one that takes advantage of current technology, in particular acrylic monomers, but combines it with significant amounts of renewable materials. However, a major barrier to this approach is that biobased monomers extracted from plants cannot participate directly in free-radical polymerization reactions unless modified to introduce reactive double bonds. Latex resin coatings have been prepared via mini-emulsion polymerizations of biomass macromonomers composed of acrylated or hydroperoxidized fatty acids and triglyceride derivatives.[7,8] Copolymers of acrylated oleates (from soybean oil) and the conventional acrylate monomers (methyl methacrylate and 2-ethylhexyl acrylate) have showed perform-ance properties similar to some existing PSA materials.[9] More recently, Canada has funded an initiative by the company EcoSynthetics Inc. for the development of macromonomers that can react with standard acrylics to produce paints, coatings, inks, surfactants, and PSAs.[10] These approaches are promising and may be part of future technologies.

Here we report on a technology that could conceivably be commercialized relatively quickly. The research reported here advances the previous investigations of ring-opening polymerization (ROP) of L-lactide initiated with 2-hydroxyethyl methacrylate (HEMA) to prepare acrylated poly(lactic acid) (PLA) macromonomers[11−14] for use in the free-radical copolymerization of practical polymers. This general approach was introduced by Ishimoto et al.[12] to prepare copolymers consisting of acrylated PLA macromonomers and *n*-butyl methacrylate in a mini-emulsion process, yielding polyacrylates with 34 wt % biomass contents. These polymers do not have the properties of a PSA, but we have shown that they can be adapted to successfully produce such materials. The synthesis of both the macromonomers and PSA copolymer are described, and data from their characterization is presented. Also discussed are the performance properties of films cast from formulated latexes of the adhesive polymer, which are compared against films cast from commercial removable- and permanent-grade, water-based PSA formulations.

■ EXPERIMENTAL SECTION

Materials. L-Lactide was kindly donated by PURAC America, Inc. (Lincolnshire, IL) and recrystallized twice from ethyl acetate prior to use. Monomers ε-caprolactone, 2-
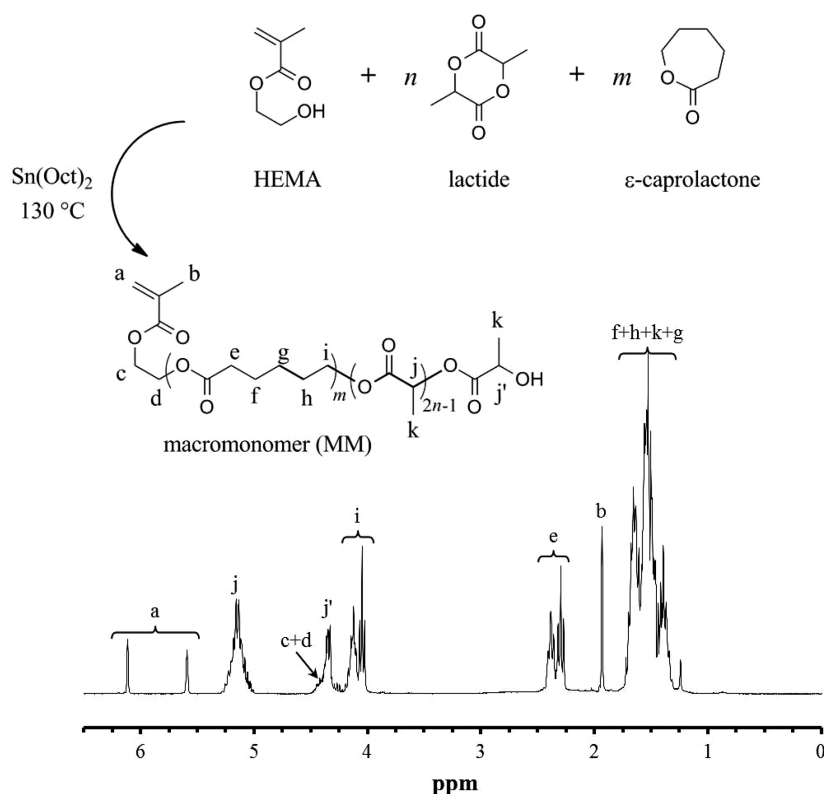
Figure 1. ROP synthesis scheme and ^{1}H NMR spectra of the resulting MM.

hydroxyethyl methacrylate (HEMA), *n*-butyl acrylate (BA), vinyl acetate (VAc), methacrylic acid (MAA), stannous octoate $(Sn(Oct)_2)$, and potassium peroxodisulfate (KPS) were purchased from Sigma-Aldrich Inc. (St. Louis, MO) and used as received. The anionic (M_n = 905 g/mol) and nonionic (M_n = 598 g/mol) nonylphenol ethoxylate (NPE) surfactants were provided by Franklin International (Columbus, OH). The tackifier, Aquatac 6085, was obtained from Arizona Chemical (Jacksonville, FL), and used as received.

Synthesis of Macromonomer. Macromonomer (MM) was synthesized using molar ratios of HEMA/lactide/*ε*-caprolactone/$Sn(Oct)_2$ consistently at 1:5:4:0.1 in ring-opening polymerization (ROP) reactions of 100 g total. All of the reactants except for the stannous octoate catalyst were added to a round-bottom flask (RBF) fitted with a condenser, heated to 130 °C, and stirred continuously. Catalyst was added via needle and syringe once the RBF and its contents stabilized at 130 °C. The contents of the RBF were initially purged with N_2 gas and maintained under N_2 during the entire 4 h reaction time. The product was then cooled and the MM product was washed at least twice with a 3:1 *n*-pentane/ethanol solution. After the final decanting of the wash solution, the final product was then dried overnight under a 25 in Hg vacuum and 50 °C. The acrylated poly(lactic acid-*co*-*ε*-caprolactone) macromonomers produced were viscous, opaque, and considered to be 90% biomass ($^{wt}/_{wt}$) after NMR analysis concluded complete conversion. Reaction yields were typically above 90%.

Miniemulsion Polymerization. The generated macromonomers were copolymerized with BA mixtures in a mini-emulsion polymerization process. In a typical procedure, acrylated poly(lactic acid-*co*-*ε*-caprolactone) MM (5 g) was combined with 4.05 g of BA, 0.27 g VAc, and 0.4 g MAA in a beaker and stirred for 10 min to form a homogeneous liquid.

Anionic (0.7 g) and nonionic (0.1 g) nonylphenol ethoxylate (NPE) surfactants, $NaHCO_3$ (0.05 g), KPS (0.03 g) with distilled, deionized 18 MΩ water (16 g) were then added into the acrylate mixture under stirring, and a coarse emulsion was formed. The mixture was subjected to sonication for 1 min using a Cole-Parmer CPX-750 ultrasonic generator (Vernon Hills, IL), resulting in a milky mini-emulsion. Once formed, these mini-emulsions were stable for at least two weeks before phase separation occurred. The mini-emulsion was transferred into a 100 mL three-neck flask and immersed in an oil bath preheated to 80 °C. The flask was equipped with a nitrogen inlet and a condenser. The reaction flask was purged for 10 min with N_2 while stirring and then allowed to react for 3 h before cooling and storing. To follow the reaction kinetics, aliquots of the reaction mixture were removed at various time intervals and quenched in cold water for further characterization.

Film Preparation and Mechanical Testing. Adhesive films were prepared by casting solutions of the latex dispersions onto a 2 mil thick poly(ethylene terephthalate) (PET) film with an average size of about 10 in. × 12 in. The films were dried at 90 °C for 5 min, followed by storage in a 50% relative humidity conditioned room overnight prior to testing. Latex solutions were diluted in order to produce cast films with consistent coating weights of 28 ± 2.8 g/m^2 (approximately 1 mil). Performance properties of adhesive films cast from formed latexes were measured using ASTM standard methods.[15−17]

Polymer Characterization. ^{1}H NMR spectra were recorded in $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA) solvent using a Varian (Palo Alto, CA) Unity 300 spectrometer (with a Varian Inova console). Differential scanning calorimetry (Discovery series, TA Instruments) was performed under N_2 at a heating rate of 20 K/min after erasure of thermal history. The kinetics of the mini-emulsion
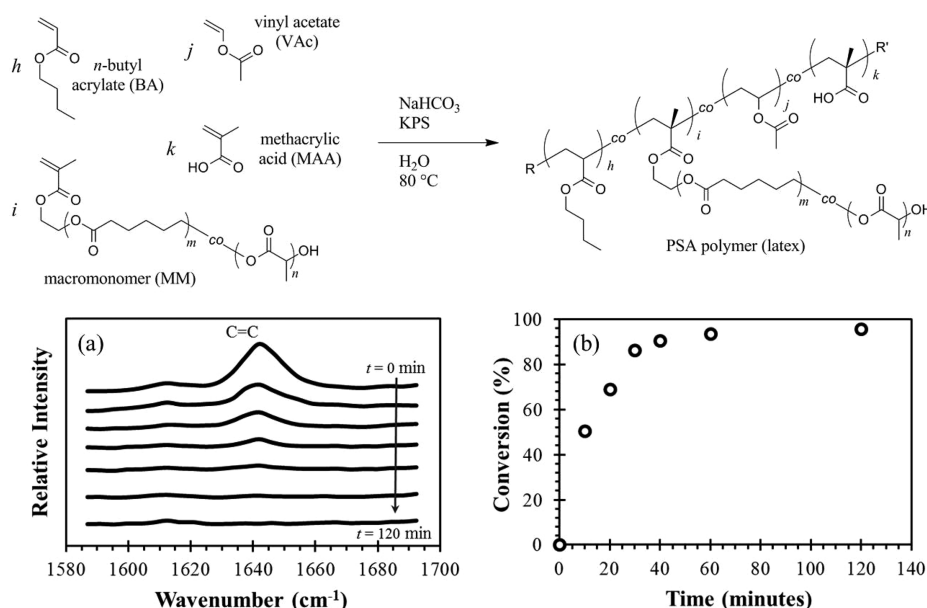
Figure 2. Scheme for synthesis of adhesive polymer via mini-emulsion polymerization (top), CRM spectra showing acrylate alkene peaks centered at 1642 cm^{-1} (a), and monomer conversion as determined from integration of CRM peaks (b).

polymerization was monitored using confocal Raman microscopy (CRM), and the composition of the final dried latex was characterized by the same method.[18−20] CRM was performed with a 300R confocal Raman microscope equipped with a UHTS200 spectrometer and a DV401 CCD detector from WITec (Ulm, Germany).

■ RESULTS AND DISCUSSION

Properties of Macromonomers. Figure 1 shows the synthesis scheme used to generate the acrylated biomass macromonomer. Gravimetric yields for this reaction are typically >90%, and the generated macromonomer is a viscous liquid at room temperature, which is soluble in n-butyl acrylate. The combination of lactide and ε-caprolactone provides for a glass transition temperature (T_g) of the MM which is low enough to act as a suitable substitute for n-butyl acrylate monomer (T_g, −32.1 °C via DSC). Given that poly(ε-caprolactone) has a T_g of about −60 °C, the role of ε-caprolactone can be considered that of a modifier, which offsets the high T_g of poly(lactic acid). In addition, ε-caprolactone also has the advantage of being biodegradable.[22,23] Although, ε-caprolactone is currently derived commercially from petroleum, it can be synthesized from renewable resources.[1]

Analysis of the ^{1}H NMR spectra of the macromonomer as exemplified in Figure 1 revealed four useful pieces of information. First, the reaction was found to have gone to completion due to the absence of ε-caprolactone and lactide peaks. Second, the number-average molecular weight (M_n) was found to be 1280 ± 108 g/mol after peak integration, and the monomer residual composition was found to closely resemble the feed ratio (9.3 lactic acid and 4.1 ε-caprolactone residuals per MM). Third, it was noticed through the lack of peaks at 3.65 ppm, that no significant amounts of MM were terminated with an ε-caprolactone residual. Lastly, it was determined that the statistical arrangement of the MM co-mers were fairly random due to the nearly equal amounts of caprolactone−lactide, carprolactone−caprolactone, and lactide−caprolactone dyads.

Properties of Biomass-Containing Polymers. The generated macromonomers were copolymerized with BA, VAc, and MAA via a mini-emulsion polymerization process. This reaction scheme is shown in Figure 2. Conventional methods for monitoring the conversion of monomer, such as gravimetry, rely on evaporation of the unreacted species, and are therefore not applicable to mini-emulsion polymerizations due to the presence of both volatile (acrylate) and nonvolatile (macro)monomers. In previous work, the use of confocal Raman microscopy (CRM) to quantitatively determine the composition of a polymer film was reported.[18−20] This setup was used to follow the conversion of the present mini-emulsion polymerizations by analyzing aliquots of the emulsion initially and during the reaction. The conversion of the mini-emulsion reactions were followed by monitoring the disappearance of the acrylate C═C stretching band at 1642 cm^{-1}, as shown in Figure 2a,[21] and conversion as a function of time is shown in Figure 2b. The reaction proceeded quickly, reaching nearly 90% conversion within the first hour.

The initial mini-emulsion, containing monomers and surfactant and generated via sonication, had a particle size of 179 ± 2 nm, which changed little as a result of the polymerization process (187 ± 2 nm via DLS). The slight broadening of the distribution and its shift to larger particles is consistent with Ostwald ripening, which appears to have only a minor impact on particle size here. The generated latex was stable and possessed a solids level of around 38 wt %. The T_g of the adhesive polymer as measured by DSC was −18.6 °C.

Determination of the molecular weight for the acrylated biomass adhesive polymer proved challenging. The main problem was that the polymer would not dissolve in any commonly used organic solvents including tetrahydrofuran (THF), chloroform, dimethyl sulfoxide, pH 9 buffered water, methanol, acetone, etc. For THF, nearly 60 wt % of the sample formed a gel, which was removed via a 0.45 μm filter before SEC analysis. The mass that did dissolve gave peaks in the oligomer range and one around 100 000 g/mol relative to polystyrene standards. However, the recovery off the column was poor, at about 50%. The observed values are not reported

here since they are not of great significance, but it is of interest that the PSA biomass copolymer appears to resemble a highly cross-linked network. This possibility will be explored in future work through modifications to the macromonomer structure and focused characterization of their impact on mechanical properties.

Performance Properties of Adhesive Films. Films of the biomass-containing latex were handled in the same fashion as the commercial latexes generated via emulsion polymerization. Adhesive films cast on PET films were clear and homogeneous, two criteria which are necessary for a variety of PSA applications.

Figure 3 shows the comparison of the biomass containing PSA with 2 commercial products from a major international
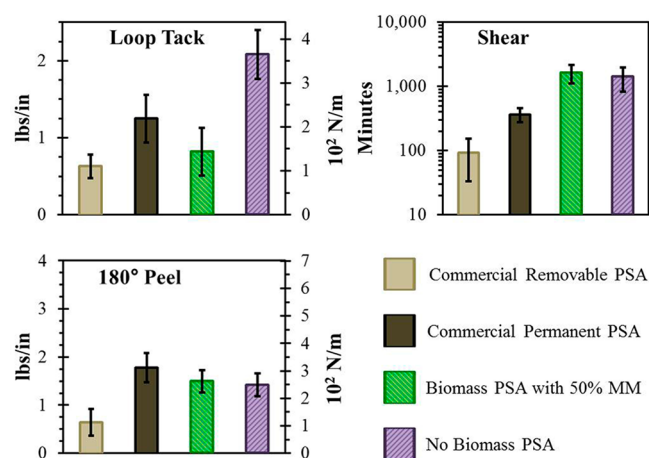

Figure 3. A comparison of results from performance testing for the new hybrid PSA containing 50 wt % MM and nonhybrid PSA with commercial removable and permanent PSAs.

adhesive producer as well as a PSA produced without the biomass. In other words, the biomass was replaced with *n*-butyl acrylate. It can be seen that the biomass containing PSA matches up well against the commercial formulations, which includes an ultraremovable and a general purpose permanent grade used in a wide variety of tape and label applications. Thus, prior to any attempt to engineer its structure or composition, it appears the new PSA possesses performance properties that are comparable with those of formulations currently used in the marketplace. Specifically, the biomass-containing PSA provides similar loop tack and peel performance and greatly outperforms these formulations in shear. The comparison of the PSA containing only *n*-butyl acrylate as the "soft monomer" with that for the biomass containing polymer in which over half of the *n*-butyl acrylate has been replaced with the macromonomer indicates that the introduction of the biomass may increase cohesive strength, which is not surprising given its higher T_g.

The high shear values provide room for specific tailoring of future formulations since increased tack and peel typically come at the expense of shear strength. Figure 4 shows the trends of peel strength, loop tack, and shear strength as a function of tackifier dispersion concentration (product basis), which was added to the biomass latex prior to casting test films. It can be seen that the addition of this particular tackifier has only a modest impact on loop tack but significantly increases peel values. A wide variety of tackifying dispersions are available for formulating PSAs. This particular product is known to provide
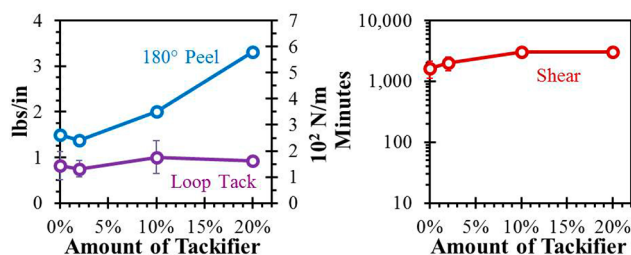

Figure 4. Effects of a tackifying dispersion on the performance properties of the hybrid PSA containing 50 wt % MM.

modest improvements in tack and peel properties but with a limited impact on shear, which is consistent with our data. The results demonstrate that the new biomass-containing PSA can be engineered with such additives as is common practice in the industry. The addition of the tackifying dispersion has the added benefit of raising the biomass content of the PSA, given that the tackifier used was a rosin ester derived from crude tall oil, a renewable resource.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: sever018@umn.edu. Tel.: (612) 625-5265. Fax: (612) 625-6286.

Notes
The authors declare no competing financial interest.

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