

# RENEWABLE TRIBLOCK COPOLYMERS IN SUSTAINABLE PSAs

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## Abstract

New pressure-sensitive adhesive (PSA) systems were studied through two complementary projects. The first project focused on the synthesis of renewable ABA triblock copolymers as thermoplastic elastomers for PSA formulations. Polylactide-polymenthide-polylactide (PLA-PM-PLA) triblock copolymers were prepared using plant-based monomers by sequential ring-opening polymerization. The polymers were characterized by NMR spectroscopy and size exclusion chromatography and exhibited narrow molar mass distributions. Transesterification was minimized during polymerization of lactide from a polymenthide macroinitiator, as shown by small-angle X-ray scattering and differential scanning calorimetry. The second project explored the formulation of the aforementioned elastomers with a renewable tackifier, with subsequent evaluation of the green PSA system using probe tack, peel adhesion, and shear strength tests.

## Introduction

Polymers are essential to myriad technologies we encounter every day. Over the past century an immense and highly integrated knowledge base has evolved that guides the manipulation of petroleum feedstocks, the design of polymerization catalysts, and the development of structure/property relationships in a small set of relatively simple homopolymers. Yet the production and disposal of these products presents inescapable environmental challenges that are costly to correct at a minimum and unsustainable in the long term. In response to a global mandate for sustainability, the development of alternatives based on renewable and more complex feedstocks such as carbohydrates, plant oils, and terpenes is of central importance. In addition to the environmental benefit offered by sustainable polymer technologies, there is tremendous opportunity to tap the structural diversity provided by Nature to develop the materials of tomorrow; one can envision an enticing array of structures arising by contemporary (catalytic) functional group transformations of natural compounds/products. Realizing the tremendous potential for bio-based materials hinges on the creation of a new, chemistry-based foundation. In this talk, I will discuss recent progress in the sustainable pressure sensitive adhesives arena being carried out at the University of Minnesota's Center for Sustainable Polymers.

Increased emphasis on polymeric materials obtained from natural products such as various plants is due to their biocompatibility, biodegradability, eco-friendly, and renewable characteristics.<sup>1</sup> Currently, such polymers are used for biomedical applications, food packing, and disposable daily commodities. However, the limited property profiles of the polymers block their widespread applications, compared to oil-derived materials.<sup>2</sup> In order for replacement of these materials to be realized, it is essential to produce renewable polymers with properties that are useful for diverse industrial applications including elastomers, plastics, fibers, films, coating, ink materials, and adhesives.<sup>3</sup>

Pressure-sensitive adhesives (PSAs) are materials that adhere to various substrates upon applied slight pressure, which are used in a variety of products such as tapes, labels, stamps, and sticky notes. The distinctive characteristic of PSAs is that they do not solidify, but remain viscous and shape-persistent

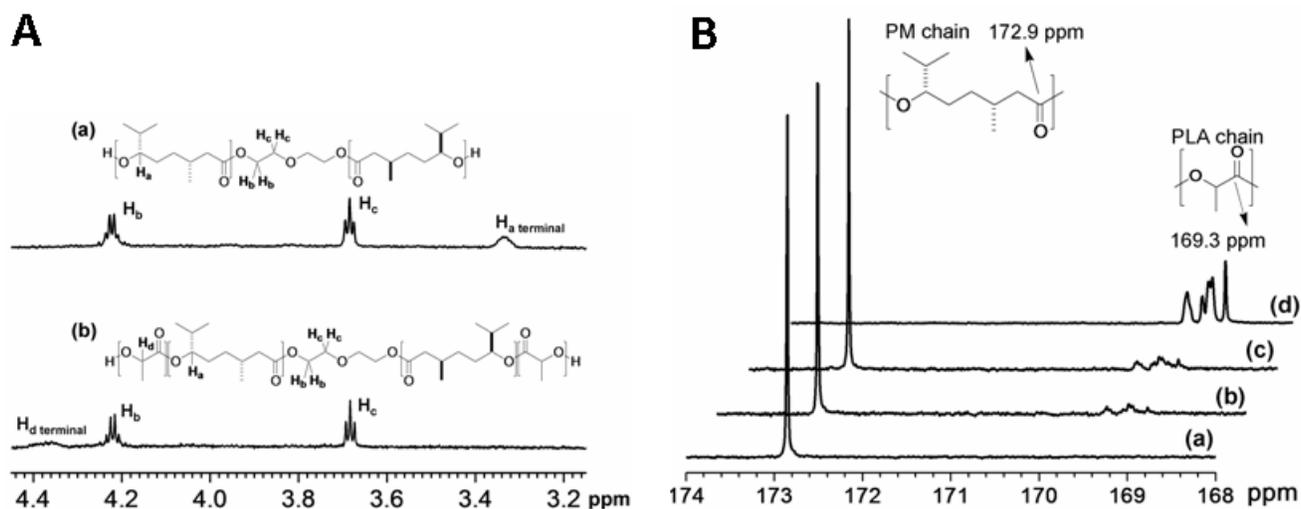
under ambient conditions.<sup>4</sup> Their viscoelastic properties give them permanent tackiness and the ability to wet surfaces on contact. There are a few elastomers used in PSA applications, such as polyacrylates, natural rubber, silicone, and styrenic block copolymers (SBCs). Since the 1970s, SBCs such as SIS (polystyrene-polyisoprene-polystyrene) and SBS (polystyrene-polybutadiene-polystyrene), which are petroleum-derived, have been an important class of ABA triblock thermoplastic elastomers (TPEs).<sup>5</sup> The general concept of TPEs, based on ABA triblocks, involves enhancement of the incompatibility of the A and B blocks to drive microphase separation within the copolymer structure. In addition, the B mid-blocks are meant to be flexible at ambient conditions while the A end-blocks have to be sufficiently hard to facilitate physical crosslinking (i.e., have a high glass transition temperature).<sup>6</sup>

In this report, we describe the development of a green chemistry-based PSA system composed of PLA-PM-PLA triblock copolymers from corn and mint, and a rosin ester as a tackifier. The polymer/tackifier blends were formulated with different ratios to investigate and optimize the PSA properties. Peel adhesion, probe tack, and shear strength tests were used to evaluate the adhesive performance of the PSA systems. The work described in this presentation is based in part on a recent publication.<sup>7</sup>

### Preparation of PLA-PM-PLA Triblock Copolymers

Menthide (**M**), the monomer used to prepare the polymenthide (**PM**) midblock of our ABA triblock copolymer, was obtained from (-)-menthone on a multigram scale using Oxone<sup>®</sup> (potassium peroxymonosulfate) in aqueous solution as an alternative to *m*CPBA in a Bayer-Villiger oxidation.<sup>8</sup>  $\alpha,\omega$ -Hydroxy terminated **PM** was synthesized through tin-catalyzed ring-opening polymerization (ROP) of **M** from a difunctionalized initiator. <sup>1</sup>H NMR spectroscopy suggested that the monomer conversion was almost quantitative. Conversion of the initiator hydroxy group into the corresponding ester of **PM** induced a shift of both methylene resonances downfield. The methine proton resonance at the **PM** chain end was observed at  $\delta$  3.33 ppm (Figure 1. A(a)).<sup>9</sup> We targeted synthesis of triblock copolymers having a **PM** segment long enough to induce microphase-separation with a minimum Polylactide (**PLA**) content by analogy to the commercially available styrenic triblock systems.<sup>10</sup> In assessing the molecular weight of the **PM** samples, we compared the theoretical  $M_n$  based on conversion, the  $M_n$  calculated from <sup>1</sup>H NMR spectroscopy, and the relative  $M_n$  estimated by SEC using PS standards. The values for the three methods were similar ( $\sim 100$  kg mol<sup>-1</sup>), with narrow PDI values (1.07) that showed that the polymerization was well controlled.

Similar to commercially available styrenic materials, **PLA** endblocks was targeted with relatively small molecular weights of 5 kg mol<sup>-1</sup> and 10 kg mol<sup>-1</sup>, respectively. In order to synthesize PLA-PM-PLA triblock copolymers, D,L-lactide (**LA**) was also polymerized via tin catalyzed ROP from the hydroxy groups in the **PM** macroinitiator. After the polymerization, the resonance for the methine protons at  $\delta$  3.33 ppm adjacent to the hydroxy end groups of **PM** disappeared completely and a new resonance for the terminal methine protons of PLA endblocks at  $\delta$  4.36 appeared in the <sup>1</sup>H NMR spectrum (Figure 1. A(b)). The triblock copolymers possess only two distinct resonances at  $\delta$  172.9 and 169.3 ppm associated with the carbonyl groups of the **PM** midblock and **PLA** endblocks, suggesting that transesterification was minimal (Figure 1. B).<sup>11</sup> Molecular weight evaluation as described above showed  $M_n$  values of approximately 110 and 120 kg mol<sup>-1</sup> for the two types of PLA-PM-PLA copolymers, respectively, with narrow molecular weight distributions (1.07–1.09).



**Figure 1.** A. Expanded <sup>1</sup>H NMR spectra (500 MHz, CDCl<sub>3</sub>) of (a) PM, and (b) PLA-PM-PLA(10-100-10). B. <sup>13</sup>C NMR spectra for carbonyl carbons of (a) PM, (b) PLA-PM-PLA(5-100-5), (c) PLA-PM-PLA(10-100-10), and (d) PLA (as a reference; poly(D,L-lactide)). Reprinted with permission from Shin, J.; Martello, M. T.; Shrestha, M.; Wissinger, J. E.; Tolman, W. B.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 87-94. Copyright (2011) American Chemical Society.

Differential scanning calorimetry (DSC) and small-angle x-ray scattering (SAXS) showed the degree of immiscibility and morphology of the renewable triblock copolymers. The DSC curves contain two glass transition temperatures ( $T_g$ ) at  $-22$  °C and  $53$  °C which correspond to the PM midblock and PLA endblocks of the copolymers. SAXS analysis at ambient temperature showed principal reflections by which the principal domain spacings could be determined. The DSC and SAXS analysis is consistent with microphase separation in the triblock copolymers.

### Adhesive Behavior

We determined that our renewable triblock was miscible with rosin ester (RE) tackifier through simple compatibility tests. Solution mixtures in toluene stayed transparent even after 10 days, and the laminated mixture film also exhibited clear transparency, an important property for applications (Figure 2). It was concluded that rosin ester tackifier had excellent compatibility with our green triblock copolymers.

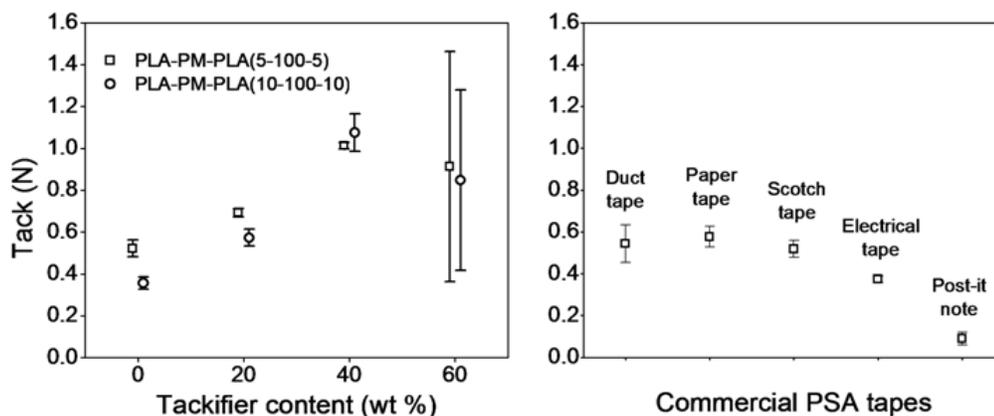


**Figure 2.** Compatibility tests. (a) a mixture of PLA-PM-PLA(10-100-10)/rosin ester (RE) tackifier in toluene, and (b) a transparent film from the PLA-PM-PLA(10-100-10)/RE tackifier. Reprinted with permission from Shin, J.; Martello, M. T.; Shrestha, M.; Wissinger, J. E.; Tolman, W. B.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 87-94. Copyright (2011) American Chemical Society.

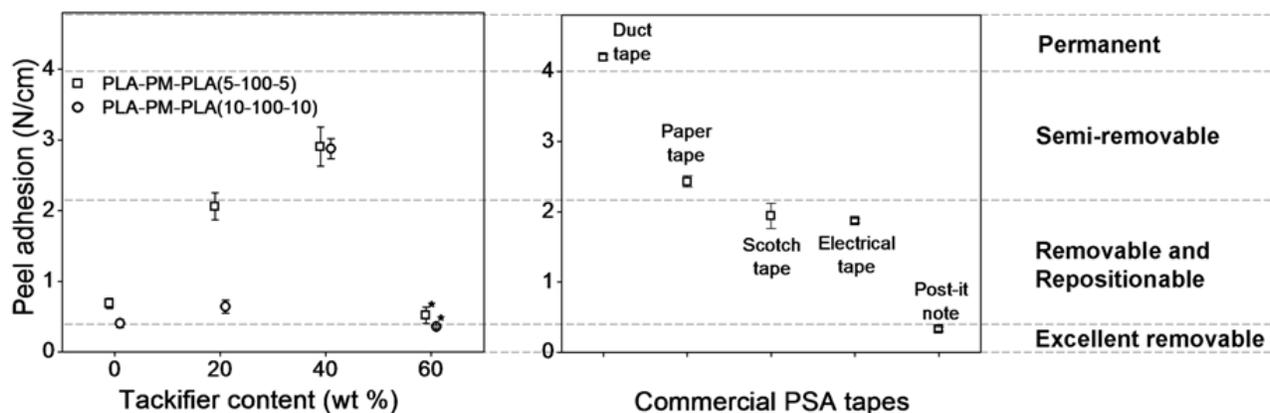
To evaluate the properties of the PSA system, eight PSA samples were formulated by combining the two triblock copolymers with 0 to 60 wt % RE tackifier. Comparative probe tack, peel adhesion, and shear strength tests were performed for our PSA samples and for commercial PSA-containing products such as duct tape, paper tape, Scotch tape, electrical tape, and Post-it notes (Figure 3).<sup>12</sup>

We found that tack force and peel adhesion improved as the RE tackifier content was increased from 0 to 40 wt%. The maximum values were 1.1 N and 3.2 N cm<sup>-1</sup> at 40 wt% RE tackifier, respectively. Interestingly, our renewable triblock copolymers showed some degree of tack force and peel adhesion without adding RE tackifier. However, large standard deviations and cohesive failures at each test were observed when 60 wt% tackifier was used. Shear strength average values of 2000 min were seen for all content levels of RE tackifier. Taken together, these results demonstrate that the performance of our green PSA is comparable to commercial samples.

### A. Probe tack test



### B. Peel adhesion test



**Figure 3.** **A.** Effect of RE tackifier content on the tack of the renewable PSA systems (left graph). The tack of commercial PSA tapes (right graph). **B.** Effect of RE tackifier content on the peel adhesion of the renewable PSA systems (left graph). The peel adhesion of commercial PSA tapes (right graph). The properties of commercial PSAs tapes were classified in the figure. \*The adhesive were partially separated from backing, which is called ‘cohesive failure’. Reprinted with permission from Shin, J.; Martello, M. T.; Shrestha, M.; Wissinger, J. E.; Tolman, W. B.; Hillmyer, M. A. *Macromolecules* **2011**, *44*, 87-94. Copyright (2011) American Chemical Society.

### Summary and Future Work

We have described green pressure-sensitive adhesives (PSAs) derived entirely from plant-based resources. Importantly, not only were we able to synthesize well-defined renewable block copolymers as PSA elastomers, but through fabrication and evaluation of the PSA properties of copolymer/rosin ester systems the potential for widespread applications was demonstrated.

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