

Development of High Biomass Content Hot-melt Pressure-Sensitive Adhesives

A THESIS  
SUBMITTED TO THE FACULTY OF THE  
UNIVERSITY OF MINNSOTA  
BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR THE DEGREE OF  
MASTER OF SCIENCE

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August, 2014

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## ACKNOWLEDGMENTS

This thesis represents not just only the research work I have finished as a graduate student, it is an achievement I would never made without the help of my committee members, friends and family.

First and foremost, I would like to express my deepest gratitude to Dr. Steve Severtson, my advisor, also my mentor for his professional guidance, constant patience and continuous encouragement throughout my master project. He is always an approachable, knowledgeable and helpful person from my perspective and his enthusiasm and wisdom in science research have exerted massive influence on me and inspired my passion and aspiration to devote more of myself into graduate study. I would never expect to be able to finish my thesis if he was not there lighting the way for me.

I would also like to thank all the members in the Dr. Steve Severtson's group, who have kindly provided help for me on my way to be prepared for a master degree. I would like especially to thank Dr. Matthew Dubay who helped formulate the goals for my project and generously shared his suggestions, knowledge and experience with me to conduct a meaningful and successful study. Also, I would like to thank Dr. Gang Pu for his substantial amount of friendly instruction and advice with respect to conducting experiments and running equipment in the laboratory.

In addition, I really appreciated that my other two committee members, Dr. William Tze and Dr. Paul Chen, put their valuable time and effort in reviewing this thesis and offered instrumental advices and guidance.

I want also to acknowledge the great help of Franklin International, especially Dr. Larry Gwin, who has strong expertise in my research area and meanwhile is extremely nice to cooperate with. It is his continuous supply of invaluable technical assistant and reliable

samples testing support that lead me to finally make progress in the project. I would also like to acknowledge that this project was funded in part by a grant from the United States Postal Service, Stamp Acquisition and Distribution. And I want to thank NatureWorks for donating high quality L-lactide for this project.

At last, I want to say that I hold my greatest gratitude for my beloved family for their endless love and selfless support. I would never try to go this far in my education without them.

## ABSTRACT

A new approach was introduced for incorporating renewable biomass into existing commercial pressure-sensitive adhesive (PSA) polymers in the form of acrylated macromonomers (MM). MM were prepared with L-lactide and  $\epsilon$ -caprolactone via a bulk ring-opening polymerization initiated by *N*-hydroxyethyl acrylamide (HEAA). Acrylic adhesive copolymers were synthesized by free-radical solution polymerization in presence of 2-ethylhexyl acrylate (EHA), acrylamide and macromonomers. This approach was achieved without sacrificing adhesive performance. Incorporation of the MM into the polymers was confirmed via proton NMR. Properties and adhesive performance of the new polymer were compared with its 100% acrylic commercial version. When synthesized using the same approach, the biomass-containing PSA had a lower molecular weight, higher glass transition temperature ( $T_g$ ) and lower melt viscosity. Introduction of MM had little impact of tack force, shear time and shear adhesion failure temperature and peel strength increased substantially. Influence of HEAA capped L-lactide/ $\epsilon$ -caprolactoneMM composition on acrylic hot-melts was also reviewed. A series of MMs, synthesized using catalyzed ring-opening polymerizations, were produced containing a broad range of lactic acid and caprolactone repeat units. Results indicate that the properties and performance of adhesive polymers are strongly dependent on lactide composition. In general, increasing lactide content increases polymer hardness enhancing cohesive strength, while reducing it (i.e., increasing caprolactone content) softens the polymer. Optimal adhesion is found to require a balance between these tendencies as indicated by the existence of a clear maximum in both tack and peel data. The results demonstrate that a broad range of properties is achievable through relatively minor modifications to MM composition. It is expected that these hybrid materials can be optimized for a variety of self-adhesive applications.

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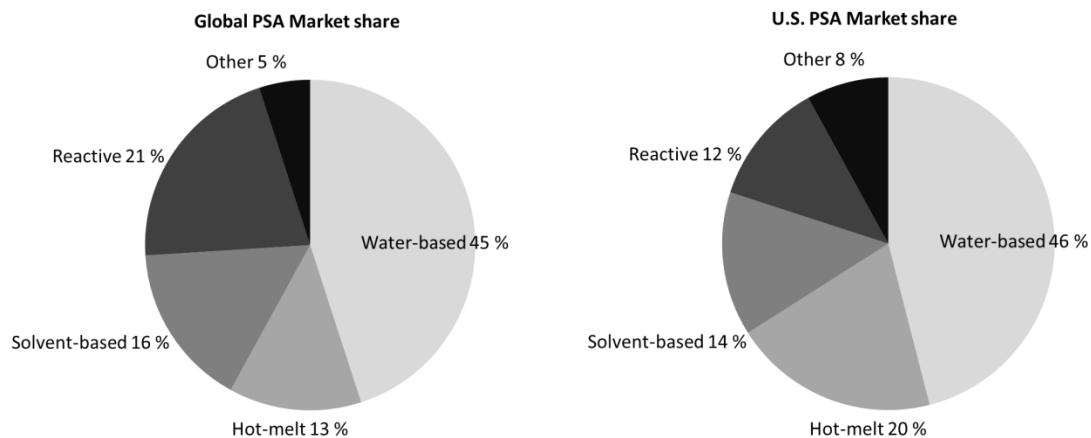
## CHAPTER 1 – INTRODUCTION

### BACKGROUND

Pressure-sensitive adhesives (PSAs) are the most common type of adhesive used in our daily life. They have seen considerable development and expanding applications in the past decade with the appearance of new materials and technologies. PSAs are rapidly replacing traditional adhesive due to their convenience, safe manipulation and relative low cost. PSAs, also known as self-adhesives, are polymeric materials that are highly viscous and sticky to touch. They flow under light pressure to wet a wide variety of substrates and retain sufficient cohesion to form adhesive bonds.<sup>1-3</sup> Usually a modulus below  $10^5$  Pa at room temperature is required for these types of materials as described by the well-known Dalquist criterion<sup>4</sup>.

A variety of PSA systems are utilized commercially. Most can be found in products such as sticky notes, tapes, labels, stamps and construction materials. The global adhesive market is mainly shared by water-based, solvent-based and hot-melt adhesives. They differ in their chemical composition, additives, processing to manufacture products and in use. Figure 1 shows the global and U.S. PSA market share by type in 2012.<sup>5</sup> It is clear that water-based PSA dominates, accounting for about half of the market. This type of PSAs is formulated and processed in aqueous systems. They are emulsions often times consisting of a complex mixture including polymer, tackifiers, emulsifiers, wetting agents, rheology modifiers, defoamers etc.<sup>6,7</sup> Formulations are designed to aid in the manufacturing of adhesive products as well as for adhesive stability and performance.<sup>8,9</sup> Two major types of emulsions commonly utilized are rubber and acrylics systems. Rubber systems refers to latexes containing natural rubber or synthetic copolymer of butadiene and chloroprene.<sup>10</sup> Acrylic systems utilize monomers such as 2-ethylhexyl acrylate, n-butyl acrylate, ethyl acrylate, methyl acrylate, styrene and some other functional monomer used to manipulate the PSA formulation to achieve specify properties.<sup>11,12</sup> Similar to water-based PSAs, Solvent-based PSAs are split mainly into rubber and acrylics systems, two main categories in terms of the

base polymer used. The main different is that their reaction is carried out in organic solvent. A trend of reduced use of solvent-based PSAs has occurred primarily due to safety issues and environmental concerns related to handling of the solvent, such as solvent exposure, flammability and VOCs.<sup>13</sup>



**Figure 1.** The global and U.S. pressure sensitive adhesive market in 2012.

Hot-melt PSAs are 100% solid, thermoplastic materials. They are quite different from water-based and solvent-based PSAs since there is no need to handle them in aqueous or organic solutions during the transportation and use. Hot-melt PSAs becomes molten upon heating allowing for processing including their application to carriers to produce PSA products. Moreover, hot-melt PSAs are less complex than water-based and solvent-based PSAs, consisting of only a few components. Most will contain roughly equal levels of a base polymer or polymer blend, tackifying resin, plasticizer. Antioxidants are usually added at very low concentrations to inhibit oxidation and degradation. Hot-melts commonly used commercially include styrene block copolymers (SIS, SBS, SEBS), thermoplastic acrylics, ethylene vinyl acetate copolymer (EVA), polyolefins (PE, PP, APAO), etc.<sup>14,15</sup> Styrene block copolymers, a commonly used base polymer for hot-melt PSA, consist of higher glass transition temperature ( $T_g$ ) styrene segments in combination with lower  $T_g$  (more rubbery) polymeric components such as ethylene-propylene, ethylene-butene, isoprene or butadiene.

The styrene and rubbery blocks are incompatible and form separate phases. The rubbery phase provides PSAs with flow ability while the styrenic glassy phase acts as physical cross-links.<sup>16</sup> This chemical structure provides opportunities for manipulation of mechanical properties through the use of tackifying resins and plasticizers specific for the different microphases that are formed. The most common tackifying resins used in thermoplastic formulations are low molecular weight species of amorphous structures such as rosin acid and hydrocarbon derivatives.<sup>15</sup> The role of plasticizers in hot-melt formulations is usually to reduce viscosity and lower cost. Common plasticizers include low molecular weight orthophthalate liquids, terephthalate liquids and oils composed of complex mixtures of paraffinic aromatic, naphthenic and cycloaliphatic species. Hot-melt PSAs are now experiencing increasing prevalence due to their unique advantages such as the absence of an organic solvent, superior recyclability, ease of application, rapid bond development.

A significant drawback of all types of PSA in their current form is that they barely biodegrade in landfills. Typical PSAs such as hot-melts are mostly prepared from materials as acrylates (poly(butyl acrylate), poly(2-ethylhexyl acrylate), styrenic block copolymers (SIS), which are petroleum-derived, non-renewable, non-biodegradable. Moreover, PSAs severely interfere with the lifecycles of other materials they come into contact with such as paper and plastic bottles, resulting in an even greater environmental impact. The increasing demand and consumption of PSAs make it important to develop more sustainable and environmental friendly PSA products. A potential solution to these problems is to replace the petrochemicals with degradable, plant-derived components such as derivatives from soybean, vegetable oils and starches.<sup>17,18</sup> Incorporation of these biomass components into commodity polymeric materials offers a variety of benefits. Often the presence of biomass provides the material with the ability to partially or fully biodegrade. Also, renewable raw materials represent an alternative to traditional monomers currently derived from sources such as petroleum and natural gas. Renewable materials that could be feasibly utilized for replacing traditional petroleum-derived chemicals used in PSAs industry are fatty acids, triglycerides, polyols, lactone and lactide.<sup>17,19-22</sup> A considerable amount of effort have been

placed on this topic. Recent examples of PSA fully or partially made from biorenewable materials include epoxidized and dihydroxyl soybean oils, poly(lactide)-poly(isoprene), fatty-acid based polyesters, polyamides of dimerized fatty acids.<sup>23-28</sup> Nevertheless, these PSAs materials more or less suffered from problems such as poor adhesive performance and stability and high cost, which prevented their commercialization.

In this thesis, I review an approach used to generate a new type of renewable polymeric material that is considered promising as a candidate for application as hot-melt PSA. Lactide was selected as the major biorenewable raw material in the project since it can be easily derived from crops such as corn and its homopolymer is a well-known degradable polyester. Generated bio-based polymers contain 50% biomass content and show competitive adhesive properties against commercial hot-melts products under standard adhesive performance tests. In previous publications, our group has demonstrated a biomass pedant group attachment method to generate water-based acrylic PSAs with high biomass content. This polymer shows desirable adhesive properties.<sup>29</sup> The general approach, which was first introduced by Ishimoto *et al.*, involves preparing acrylated poly(lactic acid) (PLA) macromonomers via ring-opening of L-lactide with 2-hydroxyethyl methacrylate (HEMA) as initiator for future use in free-radical copolymerizations.<sup>30,31</sup> We employed a similar technique on a current acrylic hot-melts formula. This technique contains two steps. The first step is the formation of oligomeric biomass macromonomer, which can be described as introducing unsaturated acrylic groups (hydroxyethyl acrylamide (HEAA)) to renewable materials (L-lactide and  $\epsilon$ -caprolactone) by building up copolymers of the latter two upon the primary hydroxyl groups of the acrylic initiators via ring-opening polymerization (ROP). The second step involves a subsequent free-radical copolymerization of macromonomers with acrylic monomers commonly used in commercial PSA formulations. Resulting polymeric materials were subjected to four standard adhesive performance property measurements include loop tack, peel, shear and shear adhesive failure temperature (SAFT).<sup>32-35</sup> Among these tests, loop tack is a measure of the ability of an adhesive to rapidly wet a surface and form an adhesive bond. Peel tests measure the force or energy necessary to pull an adhesive from a given surface,

typically stainless steel plate. Shear testing involves the application of a constant shear stress to a laminate and measurement of the time required for cohesive strength failure. Another type of shear test, commonly used with hot-melt PSAs, is SAFT. It is similar to the shear test but rather than time, SAFT measures the temperature at which a laminate fails. The SAFT value is taken as an indication of the temperature at which the PSA is too soft to be used as an adhesive.



## **Research Goals**

The objective of this study is to develop a new type of hot-melt adhesives that possesses high content of bio-renewables. It is also expected that generated bio-based hot melt adhesive could have competitive adhesive performance properties well against current commercial hot-melt pressure-sensitive adhesive (PSA) products and conceivably be commercialized in the short term. To this end, a biomass macromonomer approach was employed. Macromonomer containing renewable L-lactide raw materials were produced to substitute soft acrylic monomers that are largely used in existing hot-melt PSA formula. Standard adhesive performance tests commonly used in PSA industry are utilized to demonstrate the excellent performance of generated high biomass content hot-melt. In addition, macromonomers of variety composition were made to investigate the influence of its composition on the overall properties of adhesive polymers materials that generated from them.

## **CHAPTER 2 – HOT-MELT PRESSURE-SENSITIVE ADHESIVES CONTAINING HIGH BIOMASS CONTENTS**

### **INTRODUCTION**

Given their convenience, versatility and low cost, the use of pressure-sensitive products continues to expand. Recently, an approach was outlined for introducing high levels of biomass into commercial water-based, pressure-sensitive adhesive (PSA) polymers.<sup>29,36</sup> These products demonstrate performance properties consistent with current commercial (permanent) PSAs. The substituted biomass is believed to make the formulations more biodegradable, but more importantly, provides an alternative renewable raw material source for their production. In this article the synthesis and properties of a hot-melt or thermoplastic pressure-sensitive adhesive (PSA) generated using a similar approach is reviewed.

While water-based PSA composes a majority of the self-adhesive materials market, hot-melt PSA accounts for a smaller yet significant portion. When only considering label grade products, often designed to be disposable, water-based formulations dominate and hot-melt technology is the only other major alternative in the marketplace. There are advantages and disadvantages to both of these types of PSAs, which will not be reviewed here. Like water-based PSA, hot-melt technology is considered more environmentally friendly due to the absence of an organic solvent in the coating process. The rheological properties of hot-melt systems, specifically their melt processing, provides for coating and product options not available with water-based formulations, and it is expected that hot-melts will remain a significant part of the PSA market in the future.

Currently, the most common types of hot-melt PSAs are those formulated using styrenic block copolymers, which combine harder styrene blocks with more rubbery components such as isoprene or butadiene.<sup>8,37</sup> These products often consist of equal portions of base polymer, tackifier resin and plasticizer.<sup>38</sup> The hot-melt PSA introduced here is based on acrylic

copolymers composed primarily of 2-ethylhexyl acrylate (EHA). For these hot-melts, property manipulation is achieved through synthesis, not formulation, which makes them an ideal platform for acrylated biomass macromonomers (MMs). The MMs utilized for this work are synthesized by building chains of L-lactide and  $\epsilon$ -caprolactone on a hydroxy acrylate monomer through catalyzed ring-opening polymerization. The generated MMs possess a reactive double bond allowing for their participation in copolymerization with acrylic monomers traditionally used in the generation of adhesive materials.<sup>30,31,39-42</sup>

As described below, the hot-melt PSA is generated by first synthesizing and characterizing the MMs, which are dissolved in an organic solvent and copolymerized with acrylic monomers to generate the adhesive polymer. This technology has one major advantage over the high-biomass-content, water-based PSA described in previous publications in that there appears to be few barriers to its commercial production. The water-based system is synthesized using miniemulsion polymerization. The size and limited solubility of the MMs necessitates the use of this technique. The cost associated with generating miniemulsions makes the water-based technology commercially infeasible. Current efforts on this technology are focused on synthesis using conventional emulsion polymerization. For the hot-melt technology, little in the synthesis is changed due to the introduction of the high-biomass MMs. With the proper choice of solvent, the MMs readily copolymerize with traditional acrylic monomers. As will be discussed, even with the use of MM contents as high as 50 wt%, the properties of the generated hot-melts are nearly identical and even enhanced relative to those of the commercial form of the PSA generated without the MMs.

## **MATERIALS AND METHODS**

### **Chemicals and Materials.**

L-lactide (L300, melting temperature 95-98 °C) was provided by Natureworks LLC (Minnetonka, MN), while the  $\epsilon$ -caprolactone was donated by Perstorp (Toledo, OH).

Solvents (reagent grade toluene, acetone and tetrahydrofuran), monomers (*N*-hydroxyethyl acrylamide, 2-ethylhexyl acrylate, acrylamide), initiators (including 2,2'-Azobis(2-methylpropionitrile), di-*t*-butyl peroxide), and catalyst (stannous octoate) were all purchased from Sigma-Aldrich (St. Louis, MO) and used as received. The deuterated chloroform (CDCl<sub>3</sub>) used to dissolve MMs and the hot-melt adhesive polymers for <sup>1</sup>H-NMR analysis was purchased from Cambridge Isotope Laboratories (Andover, MA).

### **Synthesis of Macromonomer.**

Macromonomers were synthesized using *N*-hydroxyethyl acrylamide (HEAA)/L-lactide/ $\epsilon$ -caprolactone molar ratios consistently at 1:5:4. Prior to ring-opening polymerizations, the reactants were heated and stirred continuously in a round-bottom flask, and the contents were purged with N<sub>2</sub> gas for approximately 5 min. The flask was then sealed and lowered into an hot oil bath and heated to 140 °C prior to the introduction of 0.1 molar% stannous octoate, Sn(Oct)<sub>2</sub>, via a syringe. This reaction temperature was maintained up to 24 h under constant mixing. The products were cooled and washed by 3:1 *n*-pentane/ethanol solution twice to eliminate residual reactants and the catalyst, and the MM was dried in a vacuum oven for 24 h.

### **Synthesis of the Adhesive Polymer.**

Tetrahydrofuran (THF), acetone, acrylamide (AAm), 2-ethylhexyl acrylate (EHA), and MMs were added to a flame-dried 250 mL round bottom flask. The mixture was continuously stirred and purged with N<sub>2</sub> gas for at least 5 minutes. After heating the mixture to 50 °C (vapor temperature  $\approx$  28 °C), azobisisobutyronitrile (AIBN) was introduced via a syringe from a toluene solution. The system was then purged again with N<sub>2</sub> gas for at least 5 mins and heated to reflux for 24 hours. The contents were cooled to 50 °C, di-*t*-butyl peroxide (DTBP) was added, and cooling was allowed to continue to room temperature. After the polymer was synthesized, the solvents were removed via distillation at liquid temperatures in excess of 150 °C for up to 4 hours. Vacuum ( $\sim$ 20 in Hg) was then applied to the distillation apparatus for 30 mins or until the vapor temperature decreased below 70 °C. Then, without

vacuum, 2.5 mL of DDI water was added in 0.5 mL increments. The temperature was allowed to recover between increments of water. Vacuum was again applied for at least 30 minutes to remove trace amounts of water and solvent. After cooling, the contents were poured out and stored at room temperature. At this point the polymer is a viscoelastic solid that can be heated to form a low-viscosity melt.

### **Characterization Methods.**

The conversion and structure of MM and adhesive polymer were determined by Proton NMR.  $^1\text{H}$  NMR spectra were recorded in  $\text{CDCl}_3$  using a Varian (Palo Alto, CA) Unity 300 spectrometer (with a Varian Inova console). The molecular weight and distribution were determined by gel permeation chromatography (GPC) (Agilent 1100 equipped with refractive index (RI) detector) with tetrahydrofuran as the eluent. The sample solution was subjected to filtration to remove impurities prior to injection. The test was performed at a flow rate of 1mL/min in styragel columns using polystyrene standards as reference. Differential scanning calorimetric (DSC) cooling curves were obtained with a Q2000 DSC (TA Instruments, New Castle, DE) with a liquid nitrogen cooling system (LNCS) capable of cooling to  $-160\text{ }^\circ\text{C}$ . Carefully weighed amounts of the polymer, 5-10 mg, were placed in Tzero™ aluminum pans. The specimens were heated and held isothermally at  $35\text{ }^\circ\text{C}$  for 5 min. The temperature was then decreased at a rate of  $5\text{ }^\circ\text{C}/\text{min}$  until the specimen reached the final temperature. The final temperature was chosen to be below the transitions exhibited by the sample, which was between  $-40$  to  $-80\text{ }^\circ\text{C}$ . Since the polymer exhibits a simple glass transition, the transition temperature was determined by locating the peak in the derivative of the heat flux with respect to temperature. Viscosity profiles were obtained using a Brookfield high-temperature viscosity test. The test was run using a Brookfield Hot-melt Viscometer. The temperature was ramped from  $93\text{ }^\circ\text{C}$  to  $177\text{ }^\circ\text{C}$  and the spindle speed was increased with increasing temperature to keep the test result in the 20-80% range of full scale of the viscometer for each test condition. Measurements were taken about every  $10\text{ }^\circ\text{C}$  to produce the viscosity profiles.

### **Performance Property Testing of Hot-melt PSAs.**

For performance property testing, the generated polymer was dissolved in an equal mass of acetone and coated onto pre-weighed 2 mil poly(ethylene terephthalate) (PET) films. The adhesive films were then dried and covered with release liner for protection. Samples of the film were cut and weighed to confirm coating weights of  $25 \pm 3 \text{ g/m}^2$  ( $\approx 1 \text{ mil}$ ). The peel, loop tack, shear and shear adhesion failure temperature (SAFT) were measured for the adhesive films using standard ASTM tests<sup>32-35</sup> including: ASTM D903–98(2010) Standard Test Method for Peel or Stripping Strength of Adhesive Bonds; ASTM D6195–03(2011) Standard Test Methods for Loop Tack; ASTM D6463/D6463M-06(2012) Standard Test Method for Time to Failure of Pressure Sensitive Articles Under Sustained Shear Loading; and ASTM D4498-07 Standard Test Method for Heat-Fail Temperature in Shear of Hot-melt Adhesives. The same procedure was used in characterizing the performance properties of the commercial hot-melt formulations.

## **RESULTS AND DISCUSSION**

### **Characterization of Macromonomers.**

High-biomass contents MMs were generated with L-lactide and  $\epsilon$  caprolactone. The use of L-lactide was based on previous work indicating it provides for enhanced performance properties relative to other forms of lactide.<sup>36</sup> Oligomer chains were grown on N-hydroxyethyl acrylamide (HEAA) molecules, which possess a reactive vinyl group allowing for the copolymerization of formed MMs with other acrylic species. The HEAA was selected based on the performance of the resulting adhesives after a screening process that examined a wide variety of potential initiators.<sup>43,44</sup> The feed ratio used in bulk polymerization reactions was aimed at producing oligomer chains composed of 10 L-lactic acid (L) units and 4 units of  $\epsilon$ -caprolactone (C) per HEAA unit, referred to here as the L<sub>10</sub>C<sub>4</sub> MMs. The renewable biomass content of such structures is debatable. Lactide is derived from plant material and is a well-established and economically viable building block for making renewable polymeric

materials,<sup>45</sup> while  $\epsilon$ -caprolactone is currently derived primarily from fossil fuels, although pathways do exist for its extraction from renewable sources.<sup>21,46</sup> Thus, only considering the lactide as renewable, the conservative estimate based on repeat unit molecular weights would put the renewable content of the MMs at 56 wt%. However, it is expected that the MMs are completely biodegradable under the proper conditions.<sup>47,48</sup>

Figure 2 shows the  $^1\text{H}$  NMR spectra for the generated MMs. Plausible assignments are shown. The reaction of MMs appears to go to completion as indicated by the absence of lactide and  $\epsilon$ -caprolactone monomer peaks. Peaks for the acrylic head-group, HEAA, were identified at  $\delta = 6.26, 6.14, 5.64$  ppm for protons located at the vinyl group, and  $\delta = 3.61, 4.27$  ppm for protons between the amide group and first most adjacent biomass unit (either L-lactic acid or  $\epsilon$ -caprolactone). The  $\epsilon$ -caprolactone and lactic acid repeat units formed copolymers and could be quantitatively characterized by peaks i, e and j, which are exactly the same as argued previously.<sup>29</sup> It was noticed that both of the i and e peaks are split corresponding to either  $\epsilon$ -caprolactone- $\epsilon$ -caprolactone or  $\epsilon$ -caprolactone-lactic acid dyads. The comparable integration values of areas of each dyad indicate a statistically random arrangement for the copolymers along MM backbones.

Peak integration resulted in a number-average molecular weight ( $M_n$ ) of 1415 g/mol and the formula was found to be  $\text{L}_{10.94}\text{C}_{4.48}$ , which is close to the feeding ratio of two monomers. However, the distribution of the lactic acid and  $\epsilon$ -caprolactone between the 2 protic functional groups could not be determined.

Table 1 lists properties for the MMs including the DSC-determined glass transition temperature ( $T_g$ ) and the NMR and gel permeation chromatography (GPC) determined molecular weights. The DSC thermograms indicate a single and distinct glass transition occurring at about  $-15$  °C. Acrylic-based PSAs are composed mainly of low- $T_g$  monomers. The two most common are n-butyl acrylate (BA) and 2-ethylhexyl acrylate (EHA).<sup>49</sup> These

monomers have  $T_g$  values in their homopolymer forms of -54 and -85 °C, respectively,<sup>50</sup> and their purpose is to provide the PSA with the ability to flow and wet substrates under light pressures. The aim of the research here is to replace a portion of these soft monomers with the high-biomass-content MMs. However, lactide is generally considered a hard monomer with a  $T_g$  value in its homopolymer form ranging from 35 to 60 °C depending on the form of lactide utilized.<sup>51</sup> The sole purpose for incorporating  $\epsilon$ -caprolactone is to lower the  $T_g$  of the lactide-based MM, which is why it is often referred to as an organic modifier. The poly( $\epsilon$ -caprolactone) homopolymer has a reported  $T_g$  value of -71 °C.<sup>52</sup> On the basis of the Fox equation, the estimated  $T_g$  for the L<sub>10</sub>C<sub>4</sub> MMs is -5 °C using 50 °C as the  $T_g$  for PLA and 70.6 °C as the  $T_g$  for HEAA.<sup>43,53</sup> This is close to the value obtained, but is significantly higher than that for BA and EHA. However, it was found previously with the water-based PSA that the higher  $T_g$  did not lead to a reduction in adhesive performance, possibly due to the fact that the MM essentially act as pendant groups and are not a member of the main polymer chain.

From <sup>1</sup>H NMR, the number-average molecular weight ( $M_n$ ) was determined to be 1415 g/mol, which is lower than that found with GPC, which was 1774 g/mol. Also, both  $M_n$  values are higher than the predicted  $M_n$  based on feed ratios (i.e., 1292 g/mol). This variation does not appear unreasonable given the typical variations found in such reactions. An important reason for duplicating molecular weight measurements using GPC is to obtain a molecular weight distribution. The measured weight-average molecular weight ( $M_w$ ) found using GPC was 3408 g/mol, yielding a polydispersity index (PDI) of 1.92 for the generated MM.

### **Characterization of Adhesive Polymer.**

Figure 3 reviews the mechanism of the free radical copolymerization for making the MM-containing adhesive polymers. The figure also shows the <sup>1</sup>H NMR spectra for the generated polymer. As shown in the scheme, the MMs were copolymerized with EHA and acrylamide (AAm). As discussed above, EHA provides the PSA with the ability to flow and wet surfaces. It acts as a so-called “soft monomer”. Acrylamide plays the role of a “hard



monomer” in the polymer, providing the adhesive with greater cohesive strength to inhibit shear or creep and maintain adhesive bonds. To achieve polymers with good adhesive properties, the monomers were fed with a fine-tuned ratio.

The details of incorporation and conversion were indicated by the  $^1\text{H}$  NMR spectra for the EHA-co-AAm-co-MM copolymer. It is expected that the conversion of the copolymerization will be dictated by the MM due to its bulky structure relative to other monomers involved in the reaction. Nevertheless, it appears that MMs were almost fully incorporated in the formed terpolymers, indicated by the absence of peaks in the  $^1\text{H}$  NMR spectra near  $6.26 < \delta < 5.64$  ppm, where peaks identifying the reactive vinyl groups of the MM were located. Subsequent to the reaction, peaks for protons associated with HEAA show chemical shifts at around 2.35 and 1.85 ppm labeled as peaks a and b, respectively. Peaks of other protons were also assigned from the spectrum. No peaks could be assigned for the amide group of AAm. This is reasonable since it only accounts for 7.38wt% of the polymer and the peak associated with the protic end group is too weak to be observed. The polymer structure can be roughly determined by peaks h & j at  $\delta = 0.89$  ppm and peak a at  $\delta = 5.15$  ppm. Peaks h & j are assigned to the 6 protons on the two end methyl groups of EHA while peak s represents the 9 non-end-unit  $\alpha$ - protons on lactic acid, which could be further utilized to determine the amount of MM incorporated. A mass ratio of EHA repeat units to MM repeat units in the copolymer was calculated to be 0.81:1, which was close to the feed ratio of 0.85:1, so the expected structure was formed.

Table 2 lists molecular weight, polydispersity for both the MM-containing adhesive polymer as well as the commercial polymer on which it is based. Both polymers were synthesized using the same procedure, but the MM-containing version appears to have a  $M_n$  value that is about half that of the commercial adhesive, and a significantly lower  $M_w$ . The reason for this may be a lower relative solubility and/or reactivity of the much larger MM, which could result in the premature quenching of the free-radical during polymerization reactions. The MM-containing polymers also have a much narrower molecular weight distribution.

As with the MM,  $T_g$  values for the adhesive polymers were determined using DSC. Given that the commercial adhesive polymer contains mainly EHA, a low  $T_g$  is expected. Substitution of about 60 wt% of this mass with the MM should significantly increase the  $T_g$ , which is observed. It is interesting that the substitution of EHA with the MM results in a lower molecular weight, harder adhesive polymer. The lower molecular weight would be expected to increase the aggressiveness of the adhesive, while a harder monomer should increase cohesive strength. In other words, the influence of these changes on adhesive performance would tend to offset each other. If this is indeed the case, the challenge will be finding the proper balance in the MM-containing PSA in order to provide properties comparable to those of the commercial form of the adhesive.

Figure 4 plots the melt viscosity versus temperature for both polymers. The melt viscosity and its temperature dependency are important issues for hot-melt PSAs. These determine what equipment can be used to coat the adhesive in the production of laminate structures. A discussion of PSA coating techniques is beyond the scope of our discussion. Of interest here is how the curve for the commercial polymer changes with the introduction of the MM. It can be seen that the MM-containing hot-melt exhibits a lower viscosity than the commercial hot-melt on which it is based. The disparity tends to decrease with temperature. From the previous discussion, we know that the main structural differences between the MM-containing PSA and its commercial counterpart are a lower molecular weight and the presence of lactic acid/caprolactone pendant groups. It is well established that the melt viscosity of polymers is dependent on molecular weight. Generally, a reduction in molecular weight results in a lower melt viscosity, which is consistent with Fig. 4. This dependency is monotonic for smaller polymers and stronger for polymers above a critical chain length, which tends to be quite high relative to the polymers tested here. It is also true that the introduction of branching can influence melt viscosity. Commonly, side chains will increase chain entanglements and viscosity, but only for larger polymers above their critical chain lengths. Given that the adhesives polymers possess relatively low molecular weights, it is likely that the behavior observed is governed primarily by molecular weight.<sup>54</sup>

### **Performance Properties of Hot-melt PSAs.**

Figure 5 compares performance properties of the MM-containing PSA with two commercial, acrylic hot-melt products. As with the water-based PSAs, key performance properties for hot-melt PSA includes tack force, peel strength and shear times. However, for hot-melts, a fourth important gauge of performance is the shear adhesion failure temperature or SAFT. The SAFT of a hot-melt PSA indicates at what temperature a  $\approx 1$  mil (25.4  $\mu\text{m}$ ) adhesive film becomes too soft to carry a modest shear load (typically 500 g). In other words, it indicates the temperature where the cohesive strength of the PSA is too low to provide adequate adhesive performance. A disadvantage of hot-melt PSAs is their loss in performance with increasing temperature, which is why SAFT is typically reported along with tack, peel and shear data.

Comparisons of results for these four tests are shown for the hot-melt containing 50 wt% MM with 2 off-the-shelf, commercial acrylic hot-melt PSA products. These were used rather than the adhesive version synthesized in our laboratory to provide for a more realistic comparison of the properties achieved. Commercial hot-melt PSA 1 is the formulation that was modified by introducing biomass-containing MM at levels of 50 wt% of the monomer content. The literature associated with this PSA promotes its high peel strength and loop tack. The second PSA used in this comparison, Commercial hot-melt PSA 2, is from the same family of acrylic hot-melt PSA products and possesses a slightly different acrylic monomer composition. The literature for this product claims it exhibits a balanced level of peel and tack and excellent shear strength and creep resistance.

From reviewing Fig. 5, it can be seen that the replacement of 60 wt% EHA with the MM does little to diminish performance properties. In fact, introduction of the MMs results in a significant increase in peel strength. The choice of this particular MM formulation, which provides similar performance, involved some trial and error. However, the structure is by no means optimized. These efforts are already underway to determine the best acrylic and MM content as well as the optimal MM size and structure. Although not tested in a formal way,

test laminates produced by coating the hot-melts on PET label stock were clear, i.e., the presence of the high-biomass MM showed no detectable impact on optical clarity. Commercial hot-melt PSA 2 possesses much greater cohesive strength than both commercial hot-melt PSA 1 and its biomass-modified version. This particular adhesive is cross-linked to a small extent, which explains the drop in tack and peel that accompanies the increase in strength and hardness as gauged by shear times and SAFT, respectively. The results indicate that with this family of acrylic hot-melt PSA, the biomass-containing MMs can be used to augment formulations and provide for enhanced properties not possible with tradition acrylic monomers.

## CONCLUSIONS

A new type of hybrid hot-melt adhesive is introduced. The polymer is based on a commercial acrylic hot-melt PSA composed primarily of EHA. Although neither the MM nor the polymer structure have been optimized for adhesive performance, industrial tests for tack force, shear strength and temperature resistance indicate that the incorporation of the biomass has little impact on these performance properties. Furthermore, inspection of films cast on PET label stock indicates that the presence of the MM had no impact on film optical clarity. The one property affected is peel strength, which increased nearly 90% with the addition of the MM. Characterizations via DSC and GPC show the PSA generated with biomass-containing MM were harder and of lower molecular weight. The increase in  $T_g$  was not surprising given that the MMs have substantially greater  $T_g$  values than the homopolymer of EHA. The lower molecular weight is likely what is producing to low melt viscosities, which may need to be controlled for proper application.

The hybrid PSA was also compared with a second commercial hot-melt PSA from the same product line. This adhesive polymer had a different monomer composition and contained some cross-linking. These comparisons indicate the MMs could be introduced in the

generation of these hot-melt PSAs to provide for use with a variety of applications. It is expected that along with molecular weight and monomer composition, the structure and composition of the MMs will have a significant impact on adhesive properties. Thus, in addition to providing the PSA with greater renewable biomass content, the use of MMs may actually enhance the applicability of the acrylic hot-melts. It is also expected that the addition of the lactide-based MMs will increase the degree to which the adhesive biodegrades. This issue is currently under investigation.

## TABLES

**Table 1.** Characteristics of HEAA-L<sub>10</sub>C<sub>4</sub> MM<sup>a</sup>

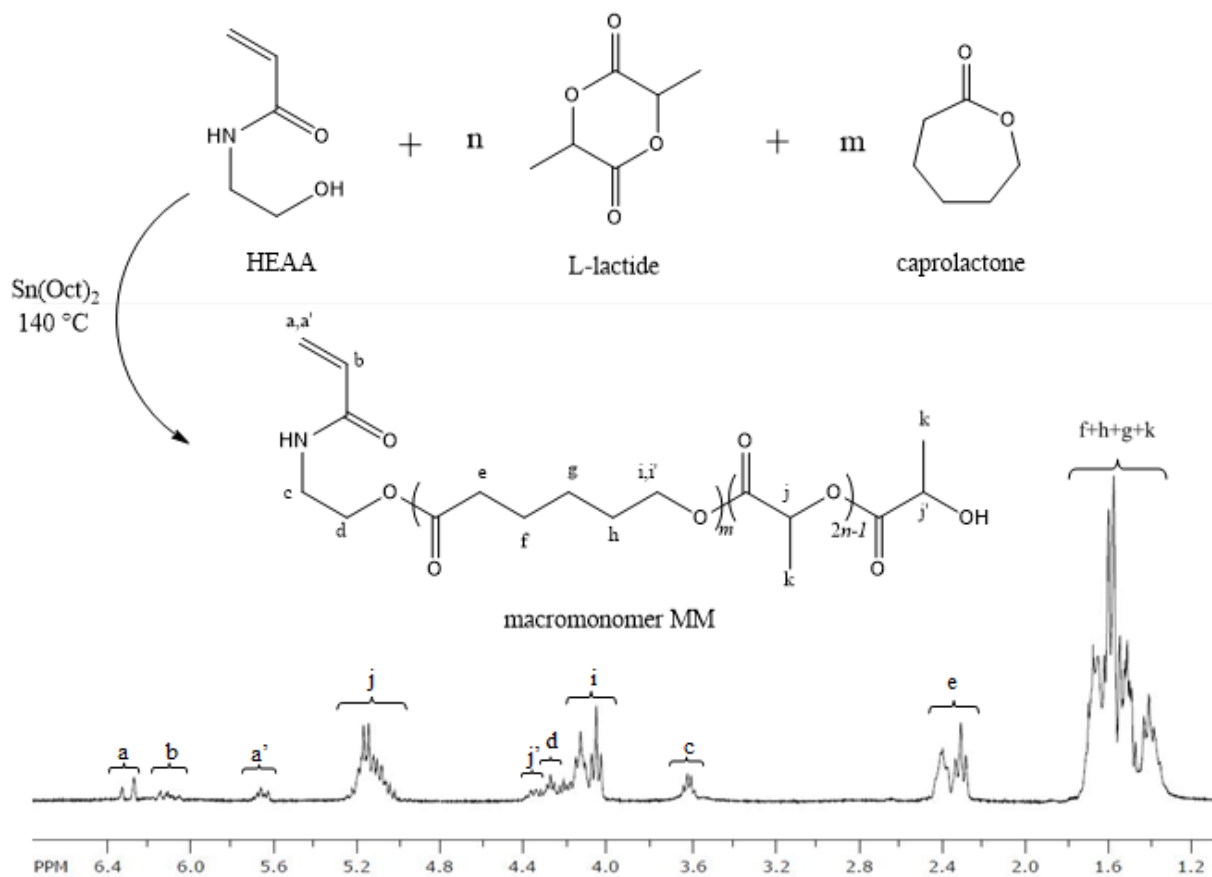
M <sub>n</sub> (Theoretical) g·mol <sup>-1</sup>	M <sub>n</sub> ( <sup>1</sup> H NMR ) g·mol <sup>-1</sup>	M <sub>n</sub> (GPC) g·mol <sup>-1</sup>	M <sub>w</sub> ( GPC) g·mol <sup>-1</sup>	PDI (GPC)	T <sub>g</sub> (DSC) °C
1292	1415	1774	3408	1.92	-14.44

<sup>a</sup>The theoretical value was calculated on the basis of the feed ratio.

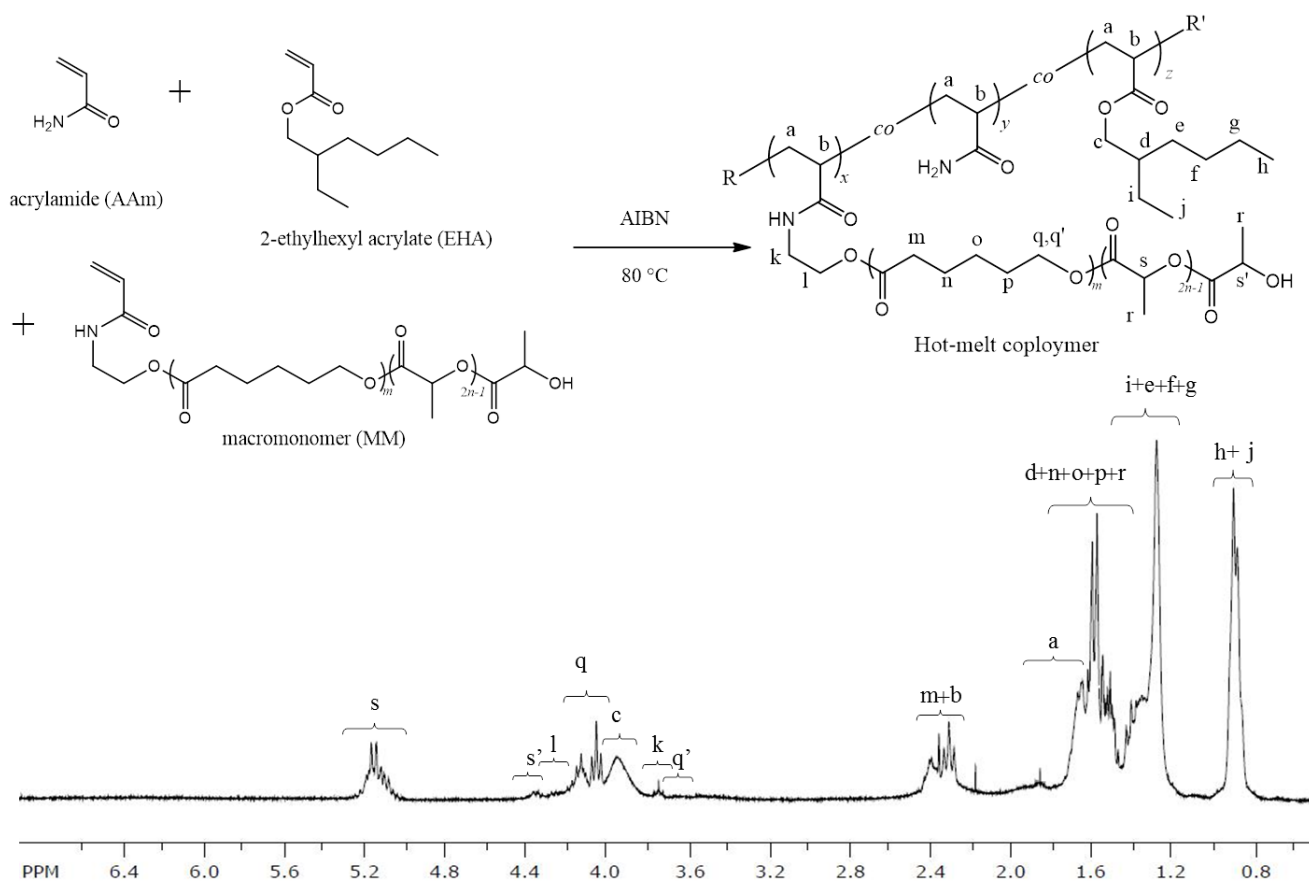
**Table 2.** Characteristics of Hot-Melt PSAs

	M <sub>n</sub> (GPC) (g·mol <sup>-1</sup> )	M <sub>w</sub> ( GPC) (g·mol <sup>-1</sup> )	PDI (GPC)	T <sub>g</sub> (DSC) (°C)
MM-containing hot-melt PSA	6008	15251	2.54	-14.8
commercial hot-melt PSA	13164	57408	4.36	-59.85

## FIGURES

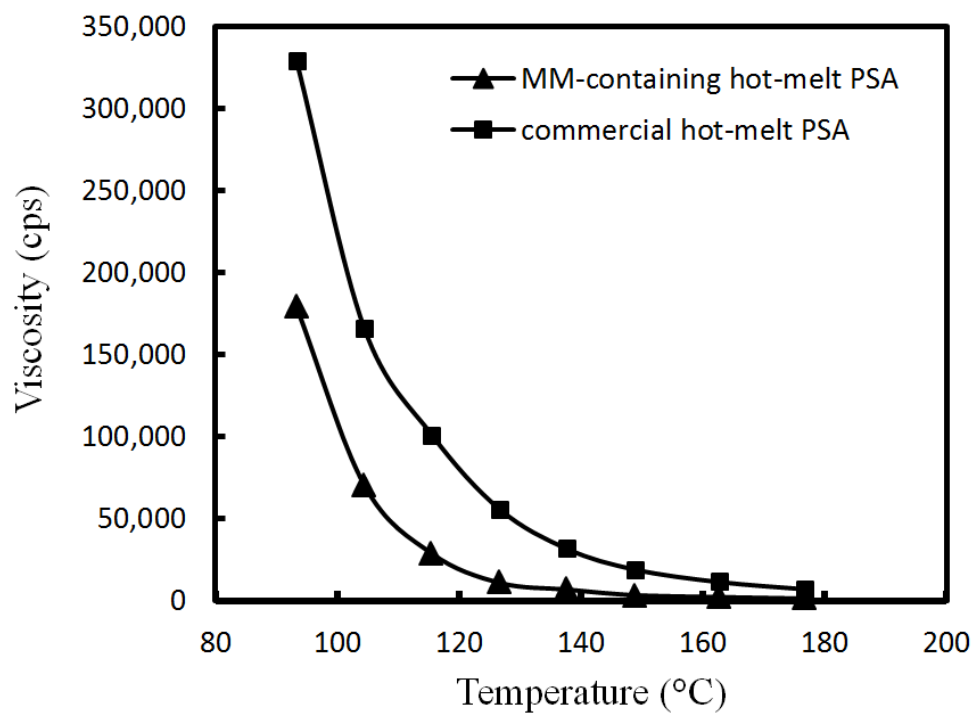


**Figure 2.** Ring-Opening polymerization scheme and  $^1\text{H}$  NMR spectra for the high biomass content macromonomers (MMs).

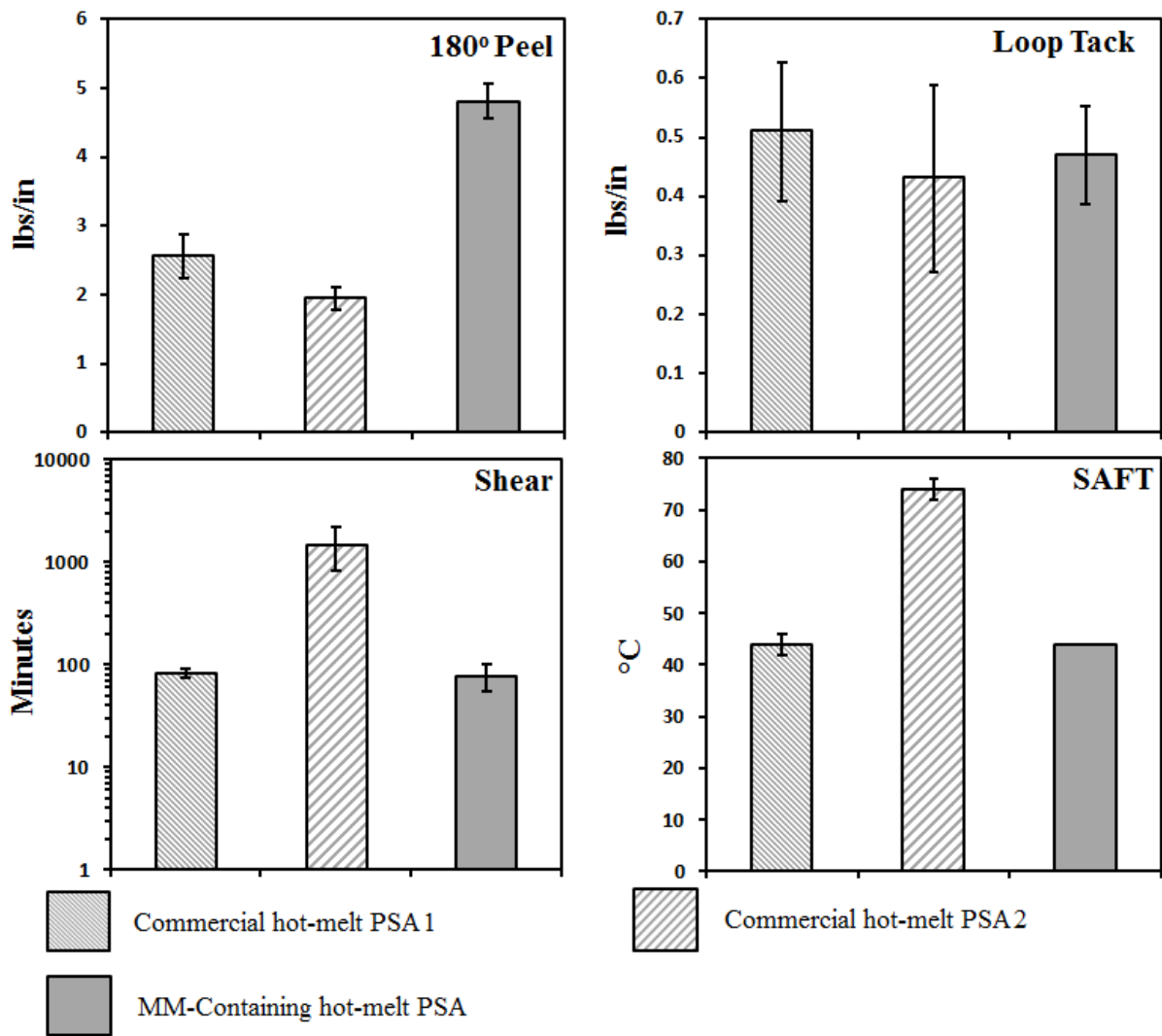


**Figure 3.** Synthesis scheme and  $^1\text{H}$  NMR spectral results for MM-containing hot-melt copolymer generated via free-radical polymerization.





**Figure 4.** Viscosity versus temperature curve obtained for both the MM-containing hot-melt and commercial hot-melt PSAs via Brookfield high temperature sweep.



**Figure 5.** Comparison of performance properties for the MM-containing hot-melt PSA with 2 commercial hot-melt PSAs.

## **CHAPTER 3 – EFFECT OF POLY(L-LACTIDE-CO- $\epsilon$ -CAPROLACTONE) MACROMONOMER COMPOSITION ON THE PROPERTIES OF HOT-MELT ADHESIVES WITH HIGH BIOMASS CONTENTS**

### **INTRODUCTION**

Hot-melt pressure-sensitive adhesive (PSA) accounts for a significant portion of the self-adhesive sold worldwide.<sup>5</sup> As was discussed in the previous chapters, the use of pressure-sensitive (PS) products is expanding due to their convenience and relative low cost.<sup>8,49</sup> The drawback is that current forms of PSA are not sustainable. These materials do not readily biodegrade and there is currently no method available to recycle discarded adhesive products. This problem is compounded by the fact that the presence of PSA can interfere with processes used in the recovery of other materials such as paper and plastics. The use of plant-derived chemicals in lieu of more traditional monomers can enhance the biodegradability of polymeric materials possibly providing for more sustainable disposal such as compostability. Furthermore, the development of such alternative raw components provides a means to combat shortages and price instability as was seen for acrylic acid, the precursor for many acrylic monomers, over the past decade.

Previously, it was shown that a high-biomass, hot-melt, acrylic PSA could be generated via solution polymerization. The synthesis involves the copolymerization of acrylic monomers with lactide-based macromonomers (MMs). Macromonomers were prepared with L-lactide and  $\epsilon$ -caprolactone via catalyzed bulk ring-opening polymerization using N-hydroxyethyl acrylamide (HEAA) as the initiator. This provides the poly(L-Lactide/ $\epsilon$ -caprolactone) oligomers each with an approximate composition of 10 moles of lactic acid repeating units (5 lactide units) and 4 units derived from  $\epsilon$ -caprolactone. The MMs contain a reactive double bond allowing for their participation in copolymerization reactions. In this case, the recipe for a commercial acrylic, hot-melt PSA is modified to generate the high biomass content adhesive. The commercial polymer is composed primarily of 2-ethylhexyl acrylate (EHA)

with lesser amounts of acrylamide (AAm). The MMs were synthesized to possess low glass transition temperatures ( $T_g$ s) and act as a substitute for the soft monomer, EHA. More than half the EHA monomer mass is replaced in the generation of the hot-melt PSA, which contain 50 wt.% MM. The results indicated that the adhesive provides performance properties that match or exceed that of the product upon which it is based. In fact it is shown that the peel strength is increased significantly, a general result observed with other polymers when L-lactide is incorporated into the structure. Given that the polymer is generated using the same laboratory procedure as that used to produce the commercial formulation, the results are promising for the practical application of this approach to generate adhesive materials.

As discussed in the introduction of this new adhesive material, no effort was made to determine the importance of the MM content in determining properties and performance. It can be expected that the MM governs adhesive performance to some extent. This is based on previous work involving a water-based formulation for which a lactide/caprolactone MM was used as a substitute for *n*-butyl acrylate (BA) in a commercial formulation also containing vinyl acetate (VA) and methacrylic acid (MAA). For this system, the MM was initiated using hydroxyethyl methacrylate (HEMA). The adhesive polymer, i.e., poly(BA/VA/MAA0.5-co-MM0.5), also contained 50 wt.% MM. Results indicate a strong dependency of adhesive polymer  $T_g$ s on the lactide and caprolactone contents as well as a less substantial dependency for the performance properties. It was found that increasing lactide levels increased  $T_g$ , while a higher  $\epsilon$ -caprolactone decreased it. Both relationships obeyed the rule of mixtures or Fox Equation. It is interesting to note that various forms of lactide were used in the generation of the polymer, and L-lactide provided the clearly superior adhesion performance. This observation appears to transcend the synthesis method and composition of co-monomers of the polymer, thus L-lactide is the sole form currently used in generating new adhesive polymers.

The key advantage of the hot-melt PSA over the water-based approach is that the procedure used to incorporate biomass can be more easily duplicated on a commercial scale. Here a study of the role played by the MMs in determining the behavior of adhesive polymers is summarized. The general influence of MM composition on properties and adhesive performance is reviewed. The results show that MM composition can be used to provide a broad range of adhesive properties ranging over an entire acrylic hot-melt product line for which performance is tailored through the use of a variety of traditional acrylic monomers. In addition to the use of renewable biomass and the increased sustainability, the ability to prepare adhesives for such a range of applications through relatively minor modifications in the biomass composition demonstrates the values of this approach for producing new adhesive materials.

## **MATERIALS AND METHODS**

The materials, synthesis techniques, chemical analysis and materials testing have been describe in Chapter 2, but are repeated here along with a few minor modifications for the convenience of the readers.

### **Chemicals and Materials.**

L-lactide (L300, melting temperature 95-98 °C) was provided by Natureworks LLC (Minnetonka, MN), while the  $\epsilon$ -caprolactone was donated by Perstorp (Toledo, OH). Solvents (reagent grade acetone, tetrahydrofuran and hexane), monomers (*N*-hydroxyethyl acrylamide, 2-ethylhexyl acrylate, acrylamide), initiators (including 2,2'-Azobis(2-methylpropionitrile), ditert-butyl peroxide), and catalyst (stannous octoate) were all purchased from Sigma-Aldrich (St. Louis, MO) and used as received. The deuterated chloroform (CDCl<sub>3</sub>) used to dissolve MMs and the hot-melt adhesive polymers for <sup>1</sup>H-NMR and <sup>13</sup>C NMR analysis was purchased from Cambridge Isotope Laboratories (Andover, MA).

### **Synthesis of Macromonomer.**

Macromonomers were synthesized using various molar ratios of *N*-hydroxyethyl acrylamide (HEAA)/L-lactide/ $\epsilon$ -caprolactone. Prior to ring-opening polymerizations, reactants were heated and stirred continuously in a round-bottom flask, and the contents were purged with N<sub>2</sub> gas for approximately 10 min. The flask was then sealed and lowered into a hot oil bath and heated to 140 °C prior to the introduction of 0.1 molar% stannous octoate, Sn(Oct)<sub>2</sub>, via a syringe. This reaction temperature was maintained up to 24 h under constant mixing. The products were cooled and washed by hexane solution twice to eliminate residual reactants and the catalyst, and the MM was dried in a vacuum oven for 24 h.

### **Synthesis of the Adhesive Polymer.**

Tetrahydrofuran (THF), acetone, acrylamide (AAM), 2-ethylhexyl acrylate (EHA), and MMs were added to 250 mL round bottom flask. The mixture was continuously stirred and purged with N<sub>2</sub> gas for at least 5 minutes. After heating the mixture to 50 °C (vapor temperature  $\approx$  28 °C), azobisisobutyronitrile (AIBN) was introduced via a syringe from 4 mL THF solution. The system was then purged again with N<sub>2</sub> gas for at least 5 minutes and heated to 65 °C under cold reflux for 24 hours. The contents were cooled to 50 °C, di-*t*-butyl peroxide (DTBP) was added and cooling was allowed to continue to room temperature. After the polymer was synthesized, the solvents were removed via distillation at liquid temperatures in excess of 110 °C for up to 4 hours. Obtained polymer sample was then purified in large amount of hexane and subjected to another 4 hours of distillation at 110 °C. Vacuum ( $\sim$ 20 inHg) was then applied to the distillation apparatus for 30 minutes or until the vapor temperature decreased below 70 °C. After cooling, the contents were poured out and stored at room temperature. At this point the polymer is a viscoelastic solid that can be heated to form a low viscosity melt.

### **Characterization Methods.**

Conversion and structure of MM and adhesive polymer were determined by Proton NMR and <sup>13</sup>C NMR. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> using a Varian (Palo Alto, CA)

Unity 300 spectrometer (with a Varian Inova console).  $^{13}\text{C}$  NMR spectra were acquired in  $\text{CDCl}_3$  using a Bruker Advance 400 spectrometer (Bruker, Germany). Molecular weight and distribution were determined by gel permeation chromatography (GPC) (Waters Modular Room Temperature System equipped with Waters 2410 Refractive Index (RI) Detector) with tetrahydrofuran as the eluent. Sample solution was subjected to filtration to remove impurities prior to injection. The test was performed at a flow rate of 1 mL/min in styragel columns using polystyrene standards as reference. Differential scanning calorimetric (DSC) cooling curves were obtained with a Q2000 DSC (TA Instruments, New Castle, DE) with a liquid nitrogen cooling system (LNCS) capable of cooling to  $-90\text{ }^\circ\text{C}$ . Carefully weighed amounts of the polymer, 5-10 mg, were placed in Tzero<sup>TM</sup> aluminum pans and loaded in auto sampler. The specimens were heated and held isothermally at  $35\text{ }^\circ\text{C}$  for 5 min and subjected to a Heat-Cool process to remove thermal history. Temperature was then increased at a rate of  $5\text{ }^\circ\text{C}/\text{min}$  from  $-80\text{ }^\circ\text{C}$  to  $140\text{ }^\circ\text{C}$  to locate the glass transitions exhibited by the sample, which was between  $-40$  to  $-80\text{ }^\circ\text{C}$ .

#### **Performance Property Testing of Hot-melt PSAs.**

For performance property testing, the generated polymer was dissolved in THF at a mass ratio of 1:1.25 and coated onto pre-weighed 2 mil poly(ethylene terephthalate) (PET) films with wire wound drawdown rod. The adhesive films were then dried and covered with release liner for protection. Samples of the film were cut and weighed to confirm coating weights of  $25 \pm 3\text{ g}/\text{m}^2$  ( $\approx 1\text{ mil}$ ). Peel, loop tack, shear and shear adhesion failure temperature (SAFT) were measured for the adhesive films using standard ASTM tests<sup>32-35</sup> including: ASTM D903-98(2010) Standard Test Method for Peel or Stripping Strength of Adhesive Bonds; ASTM D6195-03(2011) Standard Test Methods for Loop Tack; ASTM D6463/D6463M-06(2012) Standard Test Method for Time to Failure of Pressure Sensitive Articles Under Sustained Shear Loading; and ASTM D4498-07 Standard Test Method for Heat-Fail Temperature in Shear of Hot-melt Adhesives.

## RESULTS AND DISCUSSION

The synthesis routes for MMs and graft adhesive polymers are shown in Scheme 1. The HEAA-capped MMs are oligomeric copolymers containing combinations of L-lactide and  $\epsilon$ -caprolactone. The HEAA head groups allow for subsequent copolymerization of MMs with EHA and AAm carried out with free-radical solution polymerization to produce what appears to be a comb-shaped adhesive polymers. Both EHA and AAm are monomers commonly used in commercial acrylic hot-melt production. They were used here in combination with various MMs to modulate the polymer properties to pursue optimal adhesive performance.

### Characterization of Macromonomers.

Table 3 lists several measured properties for the eleven samples of MMs produced by the described synthesis route. Each sample was composed of different L-lactide and  $\epsilon$ -caprolactone combinations and was assigned with a unique sample name based on its theoretical composition calculated from feed ratios. Specifically, the L and C numbers denote the theoretical mean number of lactic acid and caprolactone repeat units in the MMs. For example, L<sub>10</sub>C<sub>4</sub> refers to the MMs that on average contain 10 lactic acid and 4 caprolactone repeat units. For this study, two series of MM samples were generated using the L<sub>6</sub>C<sub>4</sub> as a reference point. In the first series, the caprolactone is maintained at 4 units in MMs while the number of lactic acid units is increased from 6 to 22. For the second series, the number of lactic acid units in the MMs is held constant at 6 and the number of caprolactone units is increased from 2 to 16. The series of samples were all subject to investigation with the aim of understanding the influence of changing lactic acid/caprolactone composition on the properties of resulting MMs and the branched copolymers containing them.

Proton NMR spectroscopy was utilized for conversion and compositional analysis of MMs. A representative <sup>1</sup>H NMR spectrum of L<sub>10</sub>C<sub>4</sub> MM including plausible peaks assignments is shown in Figure 6a. The MM was obtained from the reaction of L-lactide/ $\epsilon$ -



caprolactone/HEAA at a ratio of 5/4/1. The spectrum confirmed a copolymer structure and indicates that the ring-opening reaction went to completion. As argued in previous chapter, MMs emerged as random copolymers containing lactic acid and caprolactone units. Statistical random structure is supported by two obvious splits of comparable peak area for both peak e and J, which correspond to either caprolactone-caprolactone or caprolactone-lactic acid dyads. MMs were found to be mainly terminated by lactic acid units based on the single alkyl proton peak at  $\delta = 4.35$  ppm. Non-terminal lactic acid and caprolactone moieties are evident from the spectrum at  $\delta = 5.15$  ppm and  $2.30 \text{ ppm} < \delta < 2.38$  ppm, respectively. A similar  $^1\text{H}$  NMR analysis was carried out for each of the MMs generated. Figure 6b shows the  $^{13}\text{C}$  NMR spectrum for the same  $\text{L}_{10}\text{C}_4$  sample, in which all plausible peak assignments are made. The interpretation of the  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra are consistent with the proposed structures of the MMs.

By integrating above mentioned peaks associated with caprolactone and lactic acid along with that for HEAA, the average numbers of lactic acid and caprolactone units incorporated in a given MM sample as well as the number average molecular weight can be determined. These values are contained in the table for all eleven MM samples. It can be seen that the  $^1\text{H}$  NMR determined compositions are fairly close to those estimated from feed ratios, i.e., target MM compositions were nearly quantitatively obtained. Number average ( $M_n$ ) and weight average ( $M_w$ ) molecular weights of MMs were also gauged by gel permeation chromatography (GPC).  $M_n$  value for each MM samples determined by GPC was fairly close to theoretical and  $^1\text{H}$  NMR-determined values. Most MMs samples exhibited  $M_w$  values that are twice to three times greater than their  $M_n$  values, which lead polydispersity values between 2 to 3 for these generated MMs samples. One issue related to composition is the calculation of renewable content of the formed MM. The last column in Table 1 lists the percentages of lactide wt.% in each of the MMs as determined via  $^1\text{H}$  NMR.

Insights on the kinetics of the MM ring-opening polymerizations were obtained from monitoring the reaction to form the  $\text{L}_{10}\text{C}_4$  MM. Small aliquots were extracted from the

reaction vessel at regular time intervals and quenched. The samples were analyzed using  $^1\text{H}$  NMR. The spectra for these samples are plotted together in Figure 1 to allow for a direct comparison. It can be seen that HEAA is an effective initiator and the initiation proceeds rapidly. Almost all of the HEAA was found to be involved in initiating chain growth as indicated by the shift of peaks for the two methylene linkages located at  $\delta = 3.7, 3.45$  ppm. These methylene groups are located between amide and end hydroxyl functional groups in the HEAA monomers and the shift is an indication of the participation of HEAA in the ring-opening process. It was also observed that L-Lactide was generally more reactive than  $\epsilon$ -caprolactone, consistent with literature.<sup>55-58</sup> From Figure 6b, it can be seen that most of the L-lactide is consumed in the first 2 hours of the reaction. This is indicated by the disappearance of its monomer peak at  $\delta = 5.07$  ppm. Full incorporation of  $\epsilon$ -caprolactone, on the other hand, as indicated by the disappearance of the peak at  $\delta = 2.6$  ppm, did not occur until after 12 hours of reaction time. However, due to the considerable overlap area of pure L-lactide and polylactide peaks ( $\delta = 5.07, 5.15$  ppm, respectively) and large monomer conversion, a quantitative analysis of the reactivity ratio of L-lactide to  $\epsilon$ -caprolactone in the ring-opening polymerization reaction was not possible from these spectra and needs to be investigated further. After 20 hours of reaction time at a temperature  $140^\circ\text{C}$ , both the L-lactide and  $\epsilon$ -caprolactone appear to be completely consumed to form the and high biomass content MMs.

Figure 7 plots DSC-determined  $T_g$ s of MMs against their lactide contents calculated by peak integration of the  $^1\text{H}$  NMR spectra. For each MM, only one distinct  $T_g$  was observed from DSC thermograms. Glass-transition data for both MM series are displayed and superimposed. It can be seen that this produces a linear relationship. In general,  $T_g$  increases with increasing lactide content and decreases with increasing caprolactone content. This result is not surprising given that polylactide tends to have a relatively high  $T_g$  ( $35 - 60^\circ\text{C}$ ),<sup>51</sup> while polycaprolactone tends to be quite soft in the homopolymer form with a  $T_g$  around  $-70^\circ\text{C}$ .<sup>52</sup> In fact, the primary purpose for introducing caprolactone is to provide for softer MMs, which are more conducive with producing softer adhesive polymers. Another important point

indicated by this linear plot was that for low molecular weight oligomeric MMs, the  $T_g$ s were relatively independent of the molecular weight of MMs. That is,  $T_g$  is mainly dictated by composition. For example, from the  $^1\text{H}$  NMR analysis,  $\text{L}_6\text{C}_2$  ( $M_n = 1110$  kg/mol) and  $\text{L}_{10}\text{C}_4$  ( $M_n = 1500$  kg/mol) have nearly identical lactide contents (about 55%) and exhibited almost identical  $T_g$  values of about  $-14$  °C. For the  $\text{L}_6\text{C}_{16}$  MM a crystallization point is observed at  $-7.7$  °C and melting peak is clearly present in the thermogram at  $27.5$  °C (Figure 7c). This indicates that for those MMs of high caprolactone contents and high molecular weight, bulk amount of long polymer chain sections solely comprised of pure caprolactone existed and were capable of pack themselves together in an ordered way. No evidence for crystallization was observed for the high L-lactide content MMs, even for  $\text{L}_{22}\text{C}_4$ . Reciprocals of  $T_g$  values were plotted against the lactide mass fraction in MMs to produce a linear relationship consistent with the Fox equation (Figure 7b).<sup>53</sup>

$$\frac{1}{T_g MM} = \left( \frac{1}{T_g L} - \frac{1}{T_g C} \right) \text{WtL}\% + \frac{1}{T_g C}$$

where  $T_g MM$  is the  $T_g$  of MM and  $T_g L$  and  $T_g C$  are  $T_g$ s of homopolymers of L-lactide,  $\epsilon$ -caprolactone, respectively.  $\text{WtL}\%$  is the lactide mass fraction in the MM. Roughly estimates of  $T_g$ s for polylactide and polycaprolactone homopolymers without considering the HEAA head group were  $60$  °C and  $-65$  °C, respectively, consistent with values reported in the literature.

### **Characterization of Adhesive Polymers.**

The lactide-caprolactone MMs were generated for use as a substitute for the soft monomer in the generation of acrylic hot-melt PSA. The most commonly used monomers for this purpose are BA and EHA, which have  $T_g$ s in their homopolymer forms of  $-54$  and  $-85$  °C, respectively. The MMs have  $T_g$  values for the oligomers from  $-52.6$  to  $9.5$  °C, which are slightly high in comparison. However, as will be shown, the performance properties formed with the MMs are quite reasonable, which is the focus of the next section. Here the physical properties of formed adhesive polymers are reviewed.

Figure 8 shows the  $^1\text{H}$  NMR spectrum for an adhesive polymer generated via solution polymerization. More than half of the EHA used in the polymer has been replaced by the  $\text{L}_{10}\text{C}_4$  MM. In fact, the MM composes 50 wt.% of the polymer weight. The plot includes reasonable peak assignments for the polymer resulting from copolymerization of EHA, AAm and  $\text{L}_{10}\text{C}_4$ . From the spectrum, complete conversion of feeding monomers were clearly supported by the disappearance of all the vinyl peaks located around  $\delta = 6.26\text{-}5.64$  ppm, which are associated with both the MMs and acrylic monomers. These three components were already incorporated onto the polymer backbone and represented their saturated vinyl group at peak a and b ( $\delta = 2.35, 1.85$  ppm). The MM and EHA composition in the adhesive polymers can be roughly determined by integration of peak s and Peak h,j. Peak s identified the non-terminal lactic acid units in the MM-branch moieties and h,j represented the six hydrogens located at the two end methyl groups of EHA moieties. HEAA peaks were not obvious in the spectrum mainly due to their relatively low feeding ratio and were not assigned. Since MMs were acrylated and fairly similar to the other two acrylic monomers with respect to head structural characteristics, all generated biomass containing adhesives polymers were considered to be of comb-shaped and statistically random arrangement copolymer structures. Nevertheless, due to the various compositions and chain lengths possessed by different MMs, the reactivity might vary for MMs and the copolymerization process would change accordingly as well.

Table 4 lists properties for the high biomass containing adhesive polymers including the GPC determined molecular weights and DSC determined  $T_g$ s. We have demonstrated a new way to add MMs into existing commercial adhesive polymer formulations via solution copolymerization in previous work. Of interest here is how the MMs of different compositions and chain lengths would affect the polymerization process and the properties of the generated graft copolymers. To this end, adhesive polymers were prepared by EHA (soft monomer), AAm (hard monomers) and various different MMs in THF/Acetone mixture solution at  $65\text{ }^\circ\text{C}$  using AIBN as the initiator. The feeding mass ratios of EHA/AAm/MM/AIBN were kept at 42.6/7.4/50/0.16 so all the adhesive polymer samples contained 50

wt% biomass macromonomer, i.e., poly(EHA0.43-co-AAm0.07-co-MM0.5). The free-radical polymerizations produced soluble and homogeneous graft copolymers after a 24 hours reaction. Corresponding to their base MMs components, adhesive samples were identically divide into two series with the copolymer containing the L<sub>6</sub>C<sub>4</sub> as the reference from which the lactide and caprolactone content is increased.

From the table, it can be seen that all of the adhesive polymers have molecular weights,  $M_w$ , ranging from 32000 to 47000 g/mol. Molecular weight decreased as the number of lactic acid repeat units was increased in the MMs. This tendency was expected. The larger and more polar MMs are less soluble, diffuse more slowly and increase solution viscosity limiting contact with free radicals and likely leading to premature quenching of reactions.<sup>59-61</sup> However, a second trend observed in the data is that increasing caprolactone repeat units increased the polymer molecular weight. One possible explanation is the GPC-determined  $M_w$  deviated more from real  $M_w$  when more caprolactone composition presented in the polymer, which might be correlated to the polystyrene standard used in the characterization. The overall influence of acrylated lactic acid and caprolactone MMs on the generated graft polymer could be complicated and a multitude factors might need to be taken into account.

Glass transition temperatures for the adhesive polymers generated with the different MMs were determined using DSC. Thermograms are consistent with an amorphous structure and showed only a single  $T_g$  for each sample. Polymers, generated with the EHA/AAm/MM/AIBN 42.6/7.4/50/0.16 mass feed ratios, possessed  $T_g$  values very close to their base MMs, especially for those made from low lactide content MMs. Values ranged from -52.9 to 5.1 °C and show a trend similar to that observed for the MMs,  $T_g$  values increase with higher lactide content and decrease with greater caprolactone content. Displayed in Figure 9 are  $T_g$ s of the adhesive polymers plotted against the lactide content in the MMs determined from <sup>1</sup>H NMR spectroscopy. It can be seen that this produces a straight line. Similar to what was found for the MMs, the Fox equation provides an accurate fit of the relationship between  $T_g$  with lactide mass fraction.<sup>53</sup>

$$\frac{1}{T_g HM} = \frac{50}{100} \left( \frac{1}{T_g L} - \frac{1}{T_g C} \right) WtL\% + \left( \frac{50}{100} \frac{1}{T_g C} + \frac{42.6}{100} \frac{1}{T_g EHA} + \frac{7.4}{100} \frac{1}{T_g AAm} \right)$$

where  $T_g HM$  is the  $T_g$  of MM containing hot-melt adhesive sample,  $T_g L$ ,  $T_g C$ ,  $T_g EHA$  and  $T_g AAm$  are  $T_g$ s for the homopolymers of L-lactide,  $\epsilon$ -caprolactone, EHA and AAm, respectively.  $WtL\%$  is the lactide mass fraction in the MM.

### **Performance Properties of Hot-melt PSAs.**

In previous chapter, it was demonstrated that replacement of 50 wt% of acrylic polymers with  $L_{10}C_4$  MMs did not diminish adhesive performance compared to commercial products. Here, it is shown that properties of adhesives can be controlled through modifications of MM composition. Figure 10 outlines results obtained for the primary performance tests used to evaluate hot-melt PSA. The tests include tack force, peel strength, shear strength and the shear adhesion failure temperature (SAFT). The dashed lines represent the test results of control samples as reference. The control sample is a 100% acrylic commercial-grade version on which the MM-containing hot-melt is based.

Loop tack is considered a measure of the ability of a PSA to rapidly flow and wet a surface to form an adhesive bond. It is sometimes said to measure the aggressiveness of a PSA. It can be seen that loop tack passes through a maximum when plotted against MM lactide content. The greatest tack value obtained was for the polymer generated with the  $L_6C_4$  MM, which corresponds to a lactide level of 45 wt.% in the MM. Values decrease from this formulation with either increasing lactide or increasing caprolactone contents. These results are consistent with a qualitative assessment of tack, which indicates that the hot-melt generated with 50 wt.% of the  $L_6C_4$  MM is significantly tackier to the touch compared with other formulations. The results demonstrate the balance required in PSAs. While the ability to flow, requiring a softer, less cohesive structure is important to providing the adhesive with greater tack, cohesive strength is necessary to maintain the adhesive bond. It appears this balance can be controlled through the composition of the MMs. A final point with regard to tack that cannot be emphasized enough is the magnitude of measured values here. A value >

4 lbs./in. is obtained for the best formulation. This is quite high relative to typical commercial hot-melt formulations.

Peel strength testing provides a relative indication of the strength of an adhesive bond. In this case between flexible adhesive materials and a rigid metal substrate. A similar trend as was observed for tack is seen here, i.e., values pass through a maximum. For peel, this occurs for the polymer generated with the L<sub>6</sub>C<sub>2</sub> MM, corresponding to 55 wt.% lactide, i.e., shifted to slightly higher lactide contents relative to maximum for loop tack values. Peel values decrease from this composition with either increasing lactide or increasing caprolactone contents. The explanation is similar to that provided for the loop tack in that adhesion for a PSA requires a balance between the ability to wet and form the bond and the strength to maintain it. Caprolactone is a primary contributor to the former, while lactide is important for the latter. Again, it should be emphasized, the maximum value obtained here is nearly 7 lbs./in, which is considered high relative to that observed for typical commercial, hot-melt PSA.

Shear tests are aimed at gauging PSA cohesive strength. The test measures the time required for the film to fail under a constant shear load. As would be expected, shear times increase with lactide contents in the MM. Values are quite modest until lactide levels exceed about 60 wt.% (i.e., for the L<sub>10</sub>C<sub>4</sub> MM). At this MM composition, shear times start to asymptotically climb to extremely high values reaching almost 4000 minutes for adhesive made with MMs containing 74 wt.% lactide (i.e., the L<sub>22</sub>C<sub>4</sub> MM). On the high caprolactone side, values appear to plateau at around 5 minutes, far too low to allow its use for practical applications. Testing of SAFT is quite similar to that for shear except that the control variable is temperature, not time, i.e., films heated to failure while under a constant shear load. SAFT measurements are not typically carried out on water-based formulations but are commonly used in the characterization of hot-melt PSAs to determine the temperature where the adhesive is too soft to function. It can be seen that the SAFT results are quite similar to

the shear results. With relatively modest values being observed up until lactide levels exceed 60 wt.%.

## CONCLUSIONS

Results presented demonstrate that hot-melt PSA containing high renewable biomass contents can be generated via solution polymerization. The MMs contain a HEAA cap. This is an alternative initiator from what has previously been reported.<sup>29</sup> The HEAA provides for rapid synthesis of target MM using catalyzed bulk polymerization. It was shown that the  $T_g$  of MMs was controlled in a significant and systematic way through changes in lactide composition. The  $T_g$  data were fit accurately by the Fox model. A similar relationship was found for adhesive polymers when produced with the MMs. Molecular weight of adhesive polymers varied modestly with use of the different MMs. Higher lactide content MMs produced lower molecular weights, while the opposite relationship is seen for the higher caprolactone content MMs. Performance properties taken individually provide outstanding results. That is, for any of the 4 performance property tests, a MM composition could be identified that provided excellent adhesive performance. For tack force and peel strength, values passed through a maximum with increasing MM lactide content. For shear and SAFT testing, results asymptotically climb to extremely high values with increasing lactide content. Unfortunately, the outstanding performance compositions showed minimal overlap with tack and peel values being optimized below 60 wt.% lactide and shear and SAFT climbing to reasonable values for commercial products above this composition. Thus, compromise is the key in developing products using the current materials, but a broad range of properties is achievable with just a single acrylic formulation.



## TABLES

**Table 3.** MMs synthesized via ring-opening polymerization

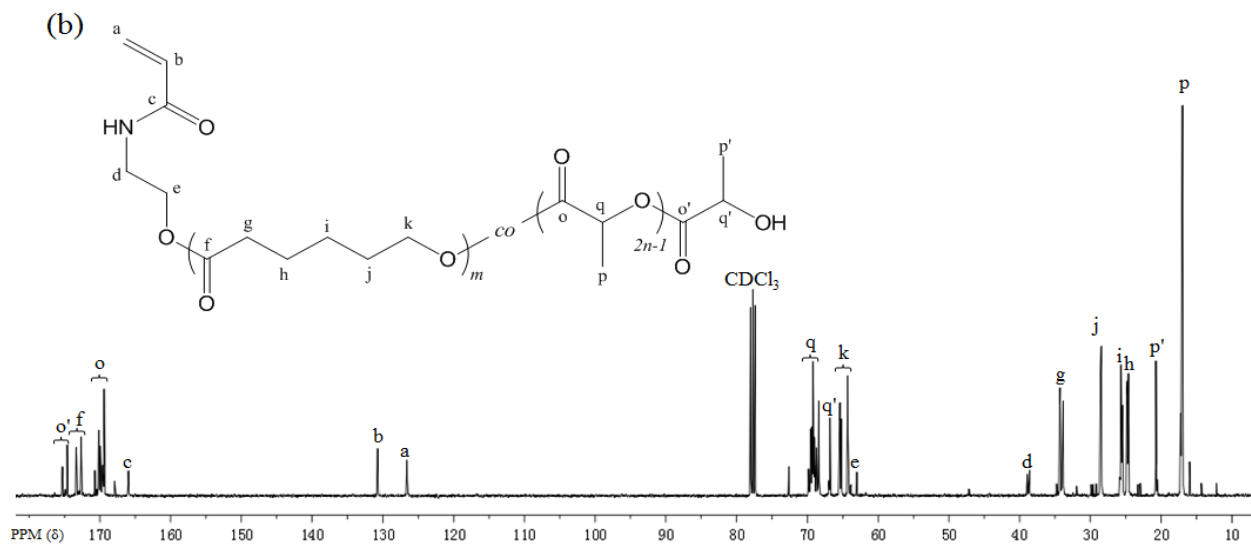
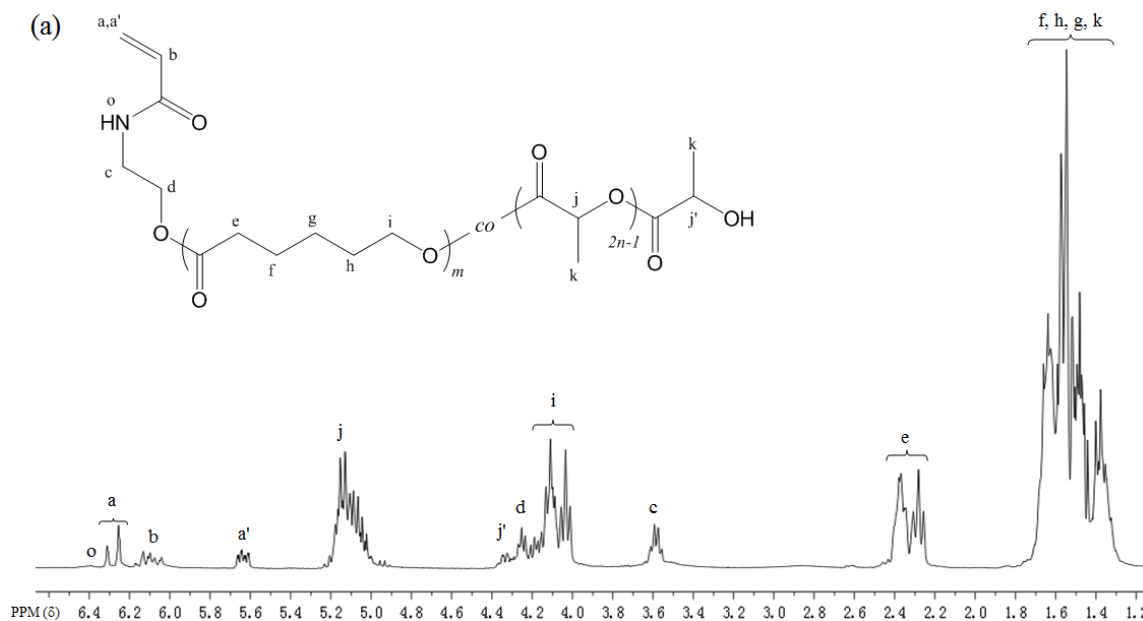
MM <sup>a</sup> sample	feed molar ratio L-LA/CL/HEAA	MM ( <sup>1</sup> H NMR)		M <sub>n</sub> (kg/mol)			PDI GPC	T <sub>g</sub> (°C)		L wt % ( <sup>1</sup> H NMR)
		L	C	theor	<sup>1</sup> H NMR	GPC		DSC		
L22C4	11/4/1	24.1	4.3	2157	2350	2100	2.7	9.5	74	
L18C4	9/4/1	20.0	4.4	1869	2060	1740	2.8	3.9	70	
L12C4	6/4/1	15.4	5.5	1436	1850	1680	2.6	-7.7	60	
L10C4	5/4/1	11.4	4.9	1292	1500	1430	2.7	-14.2	55	
L8C4	4/4/1	8.9	4.8	1148	1300	1120	2.1	-19.9	49	
L6C4	3/4/1	6.9	5.1	1004	1190	930	2.3	-27.9	42	
L6C2	3/2/1	8.7	3.3	776	1110	740	1.5	-14.3	56	
L6C6	3/6/1	6.9	7.5	1232	1360	1430	2.5	-36.4	37	
L6C8	3/8/1	6.2	8.2	1461	1490	1760	2.6	-41.7	30	
L6C12	3/12/1	5.9	11.9	1917	1900	1970	2.9	-48.9	22	
L6C16	3/16/1	5.7	15.0	2373	2240	1940	3.0	-52.6	18	

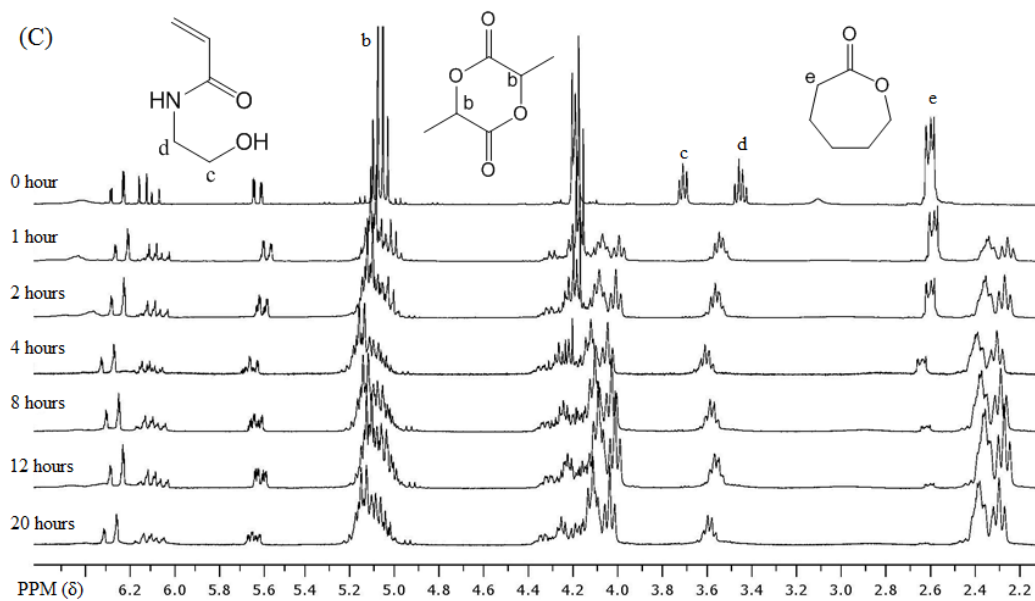
<sup>a</sup>Theoretical values for L and C were calculated on the basis of feeding molar ratio.

**Table 4.** Properties of MM-Containing Adhesive Copolymers

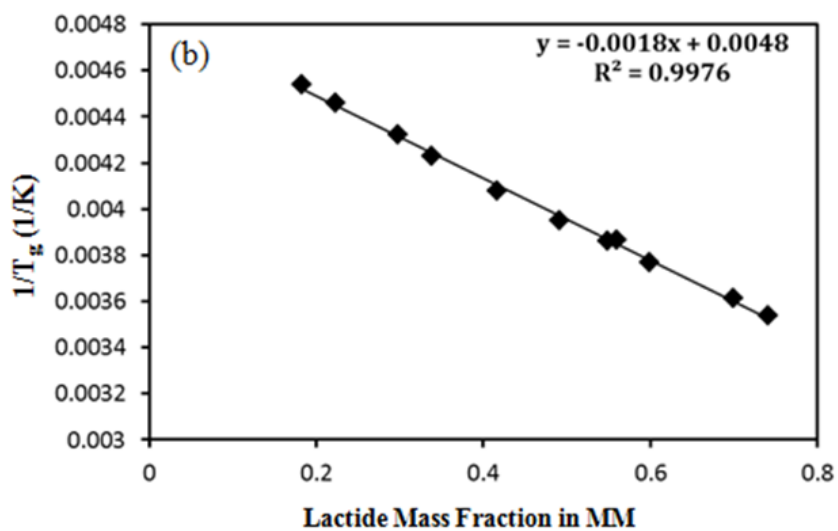
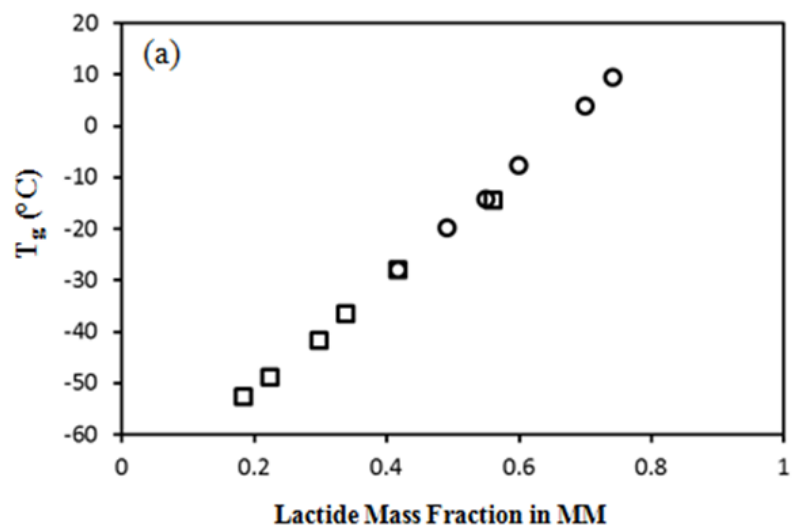
Hot-melt sample	MM (theor) used in copolymerization	M <sub>w</sub> (kg/mol)	PDI	T <sub>g</sub> (°C)
		GPC	GPC	DSC
1	L22C4	32500	2.6	14.6
2	L18C4	36200	2.9	5.1
3	L12C4	38900	2.6	-5.7
4	L10C4	39000	2.6	-15.7
5	L8C4	40000	2.8	-20.4
6	L6C4	43100	2.7	-27.1
7	L6C2	40500	2.8	-9.4
8	L6C6	38600	2.9	-35.5
9	L6C8	43000	2.7	-43.4
10	L6C12	46000	2.6	-47.6
11	L6C16	46700	2.5	-52.9

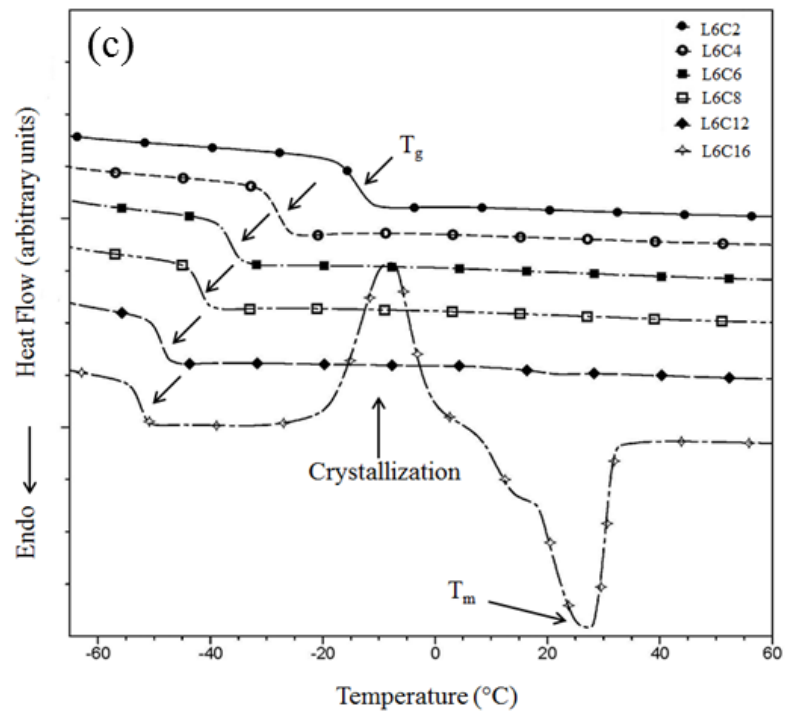
# FIGURES



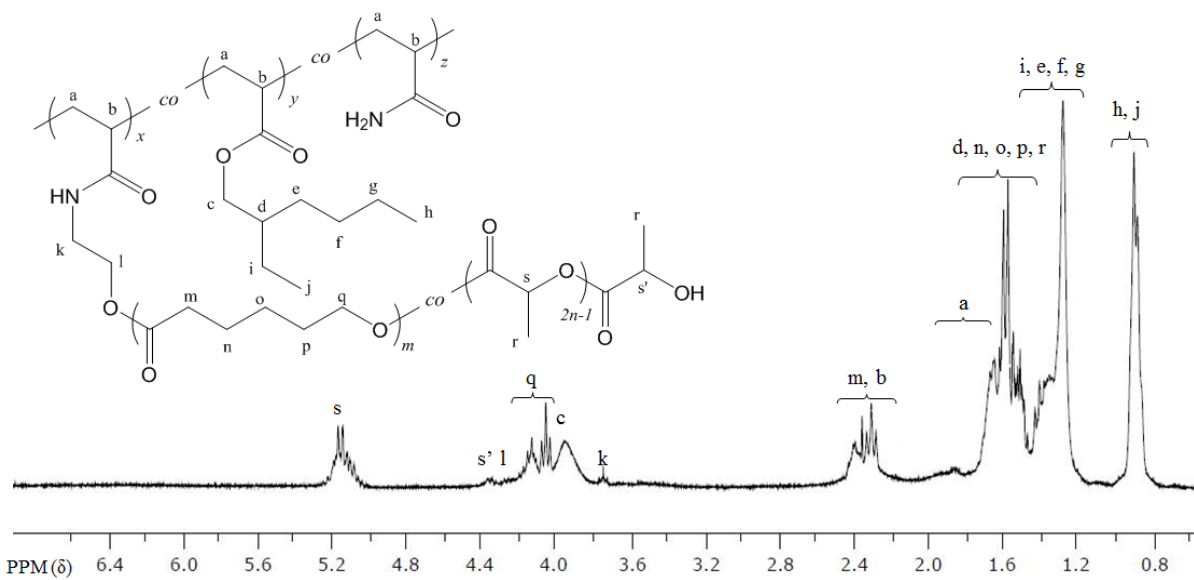


**Figure 6.** a.) 300 MHz  $^1\text{H}$  NMR spectrum of  $\text{L}_{10}\text{C}_4$  MM, b.) 400 MHz  $^{13}\text{C}$  NMR spectrum of  $\text{L}_{10}\text{C}_4$  MM and c.) 20 hours kinetic study of ring-opening polymerization of  $\text{L}_{10}\text{C}_4$  MM by  $^1\text{H}$  NMR spectroscopy.

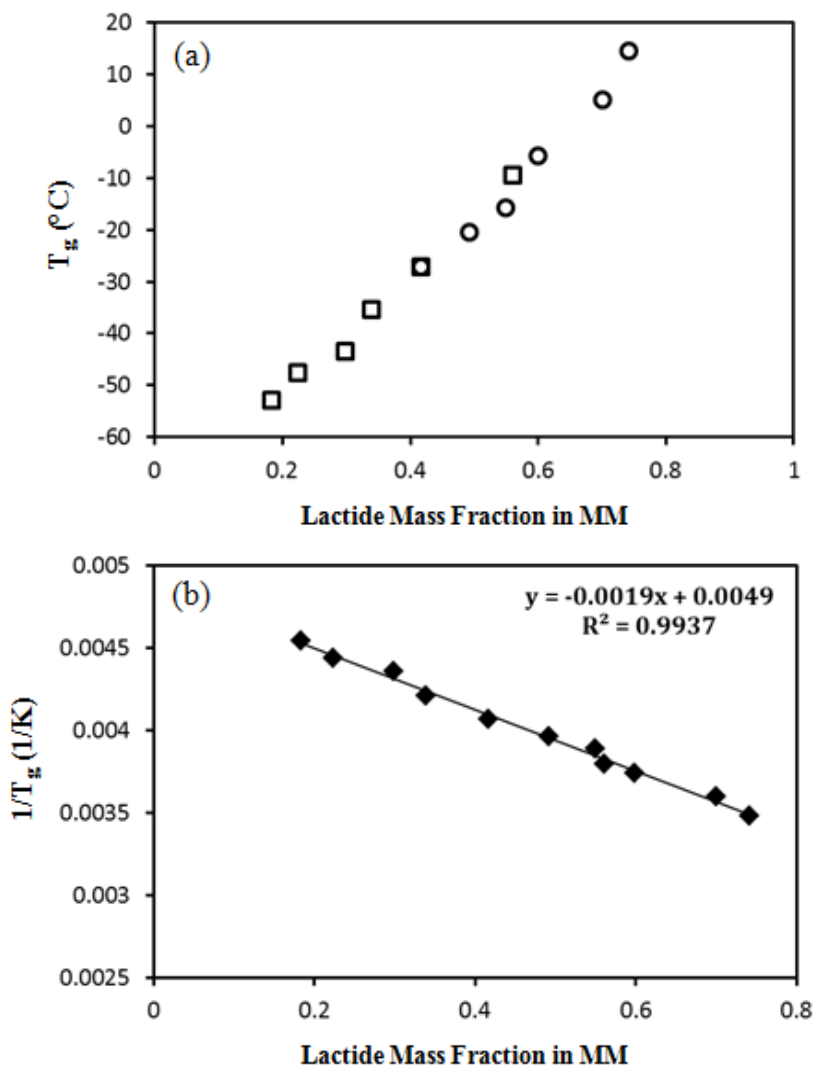




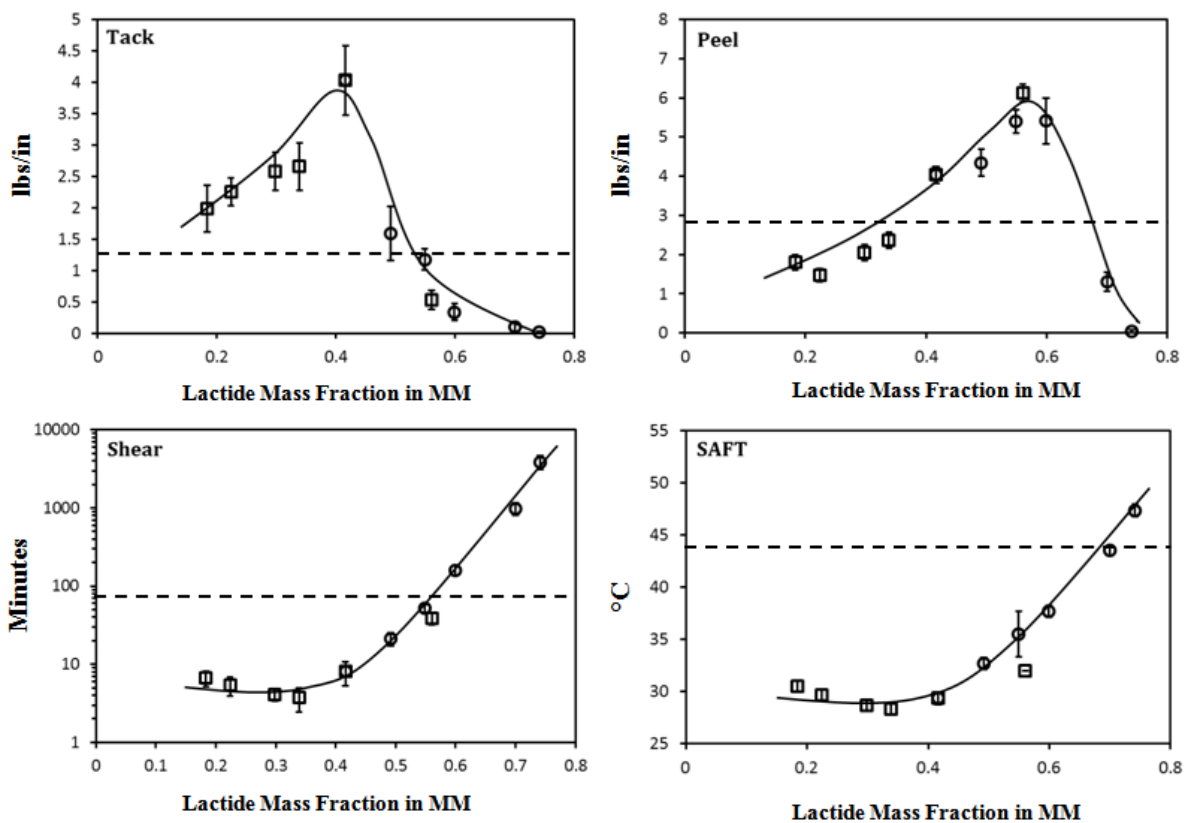
**Figure 7.** a.) Dependence of glass transition temperature ( $T_g$ ) on lactide mass fraction for MM. Open squares denote MMs made at constant lactide content with increasing caprolactone content and open circles denote MMs made at constant caprolactone content with increasing lactide content. b.) The inverse of  $T_g$  as a function of lactide mass fraction for MM fit using the Fox equation. c.) Differential scanning calorimetry (DSC) thermograms for determination of  $T_g$  for a series of MMs with constant lactide content. For the L<sub>6</sub>C<sub>16</sub> MM, crystallization and a melting point were also observed.



**Figure 8.** <sup>1</sup>H NMR spectra of L<sub>10</sub>C<sub>4</sub> MM-containing hot-melt copolymer.



**Figure 9.** a.) Dependence of  $T_g$  of hot-melt copolymer on lactide mass fraction in MM used in copolymerization. Open squares indicate adhesive copolymers containing MMs made at constant lactide content with increasing caprolactone content and open circles indicate adhesive copolymers containing MMs made at constant caprolactone content with increasing lactide content. b.)  $T_g$  plotted as a function of lactide mass fraction in MM used in copolymerization for adhesive copolymers, which is fit by the Fox equation.

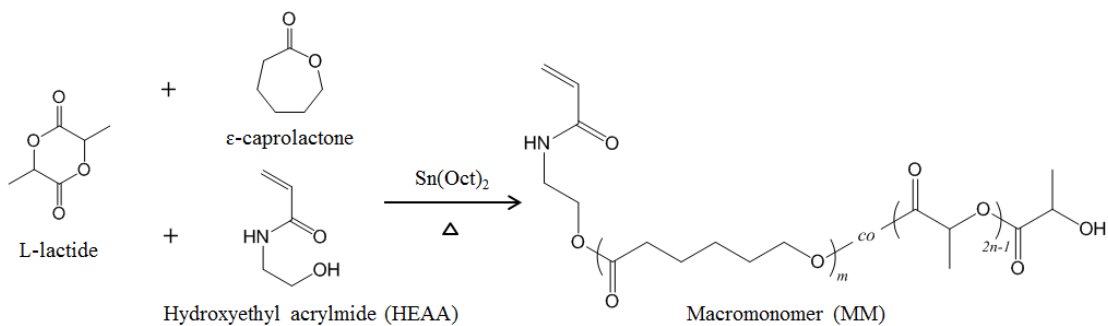


**Figure 10.** Dependence of performance properties of adhesive films cast from MM-containing adhesive copolymers versus MM lactide mass fraction. Four standard adhesive performance tests were carried out including a.) (maximum) tack force, b.) peel strength, c.) shear time and d.) SAFT. Open squares indicate hot-melt copolymers containing MMs made at constant lactide content with increasing caprolactone content and open circles indicate hot-melt copolymers containing MMs made at constant caprolactone content with increasing lactide content.

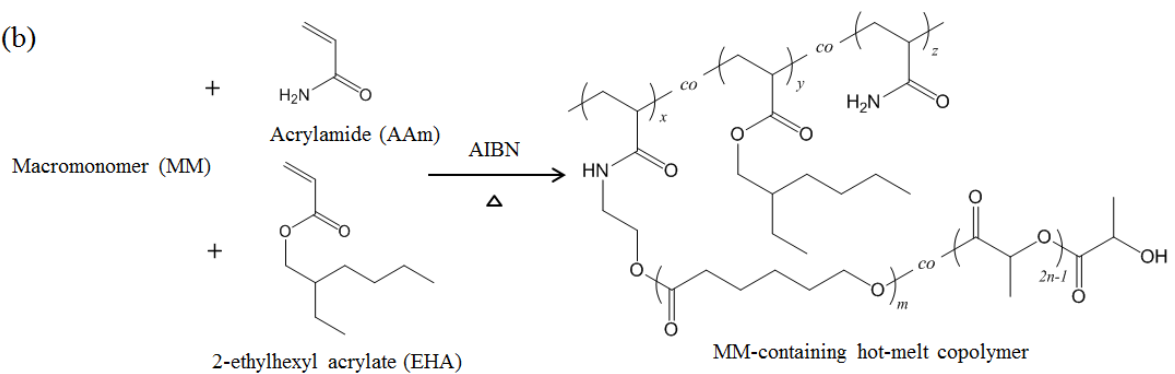


## SCHEMES

(a)



(b)



**Scheme 1.** Synthesis outline of the a.) macromonomer (MM) and b.) MM-containing adhesive copolymer.

## SUMMARY OF CONCLUSIONS AND FUTURE WORK

A new type of hot-melt pressure-sensitive adhesive (PSA) was generated containing a high content of renewable biomass. The new polymer is based on a commercial hot-melt acrylic formula containing primarily 2-ethylhexyl acrylate (EHA) and acrylamide (AAm). It is synthesized with a majority of the EHA (approximately 60%) replaced with a macromonomer (MM) prepared with L-lactide and  $\epsilon$ -caprolactone via catalyzed bulk ring-opening polymerization using N-hydroxyethyl acrylamide (HEAA) as the initiator. Generated hot-melt polymer is of a comb-shape structure with biomass containing MM as branches. Adhesive Films cast from this type of hot-melt polymer provided good optical clarity. Characterization by differential scanning calorimetric (DSC) and gel permeation chromatography (GPC) indicate hot-melt PSA produced with biomass-containing MM have relatively higher glass transition temperature ( $T_g$ ) and low molecular weight compared to its non-biomass version, which means it is harder and of lower melt viscosity. Due to these changes of polymer properties, interesting adhesive performance were observed for this type of materials. It is demonstrated that incorporation of 50 wt.% MM in acrylic polymer did not lead to reduction of performance properties of adhesive polymers. Without any optimization, bio-based hot-melt exhibited excellent adhesive performance properties including look tack, peel, shear and shear adhesion failure temperature (SAFT). The overall properties of this new hot melt match well against the commercial hot-melt polymer on which it is based. With the incorporation of MMs, peel strength increase nearly 90%, and other three properties are comparable. This comparison confirmed that adding MMs is a feasible way in generation of high biomass contents hot-melt PSAs that are qualified for a variety of applications.

Results from a study of the influence of macromonomer (MM) composition on the properties of a high biomass content adhesive polymer are also reported. A variety of different MMs were synthesized via changing the HEAA/L-Lactide/ $\epsilon$ -caprolactone feeding ratio. Target MMs were almost quantitatively obtained and proposed compositions and structures were clearly supported by  $^1\text{H}$  NMR and  $^{13}\text{C}$  HMR. From the investigation of DSC results, it is

concluded that the  $T_g$  of MMs was controlled in a significant and systematic way through changes in lactide composition, the trend were accurately characterized by Fox model. A series of hot-melt PSAs were produced with these MMs at a constant EHA/AAm/MM/Initiator feeding ratio. Molecular weight of produced polymers showed slight disparities as with different MM being used. At selected feeding ratio, adhesive polymers have  $T_g$  values fairly close to those of their base MMs and produced a similar relationship with the lactide content in MMs when fit in Fox equation. Adhesive performance properties of polymers showed strong dependency on MM composition. For loop and peel, maximum values were reached at a medium lactide mass fraction in MM. Shear and SAFT values monotonically increase with lactide mass fraction in MM indicated a better cohesion provided by more lactide component. It is also noticed that performance properties taken individually from each test provide excellent results. However, at current feeding ratio of solution polymerization, the window for optimization of overall performance is small since the outstanding performance compositions showed minimal overlap. Adhesion and cohesion properties need to be balanced and adjusted according to specific hot-melt applications.

The work in this thesis can be described as exploring a feasible way to incorporate significant amount of biomass (lactide) into existing commercial hot-melt PSA formula. Current results proved that a broad range of adhesive performance properties can be achieved with the best properties well above those of commercial products. However, the narrow window for manipulating and optimizing adhesive performance properties turned out to be its drawback. Given the great flexibility of this approach, there will be several directions to improve this technology. First, in current study, we were focusing on the relation of adhesive performance with MM compositions so that EHA/AA/MM/Initiator ratio was held constant. In order to obtain broader range of performance properties and enlarge the optimization window, the EHA/AAm composition can be also varied in combination with changing MMs compositions. In that case, we will have two hard monomers (L-lactide and AAm) and two soft monomers ( $\epsilon$ -caprolactone and EHA) to manipulate the formulation, and better properties are likely to result. Second direction for improving this technology will be to use different head groups.

Other effective head group could be utilized as initiator of MMs to manipulate MM and adhesive polymer structures and polymerization process. These head groups probably need reactive vinyl groups and one or more protic groups such as amine, hydroxyl for ring-opening polymerization of MMs. Then the movement of property windows via MM structural and component changes can be further investigated. Another option for future work on the basis of current procedure is to design a functionalized base-polymer and post-add biomass such as L-lactide onto the polymer. This post-add method reorganizes the reaction process which means the ring-opening polymerization will be performed after the free-radical copolymerization. Functional groups need to be effective for initiating ring-opening reaction and are put in the adhesive backbone ahead of time. Post-add method is expected to eliminate low reactivity and solubility problems of MMs and increase the molecular weight of polymers. It also makes the production of adhesive polymers easier to be carried out. Last but not least, one purpose of developing biomass-containing hot-melt PSAs is to make this type of materials biodegradable, however this topic is not investigated in this thesis. Therefore, a very important work in the future is to measure the degradability this new adhesive material as adhesive composition and chemical structures varies. In short, it is hoped that with further improvement, this technology is able to produce adhesives products for various applications and be commercialized in the near future.

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