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Preparation and Characterization of a Renewable Pressure-Sensitive Adhesive System Derived from ε-Decalactone, L-Lactide, Epoxidized Soybean Oil, and Rosin Ester

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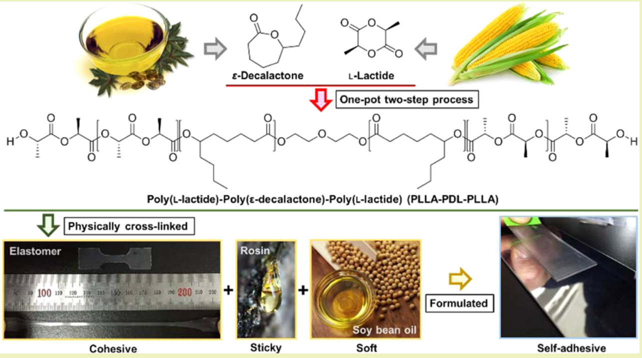
Supporting Information



ABSTRACT: Pressure-sensitive adhesives (PSAs) are prepared with plant-based thermoplastic polyester elastomers (TPPEs), rosin ester tackifier, and epoxidized soybean oil plasticizer. Controlled bulk ring-opening transesterification polymerization of ε-decalactone and L-lactide using diethylene glycol as an initiator gives ABA type block polyesters via a one-pot, two-step process with only tin(II) ethylhexanoate. Three semicrystalline poly(L-lactide)−poly(ε-decalactone)−poly(L-lactide) (PLLA−PDL−PLLA) triblock copolymers are prepared containing 100 kg mol^{-1} PDL midblocks and 8−30 wt % PLLA end blocks with narrow dispersities. The mechanical behavior of the triblock architectures is investigated by tensile experiments. The triblocks are combined with the tackifier of 50 wt % and the plasticizer of 15−30 wt %. The thermal, viscoelastic, and morphological properties of the elastomers and the adhesive formulations are determined with differential scanning calorimetry, thermal gravimetric analysis, dynamic mechanical analysis, and atomic force microscopy. The renewable self-adhesive performance is evaluated showing peel strength of 1.9−2.6 N cm^{-1}, probe tack of 2.2−3.0 N, and static shear strength of >20 000 min comparable to current thermoplastic elastomers and PSAs. These novel materials could hold promise for sustainability and high adhesive performance.

KEYWORDS: *Sustainable polymer, Pressure-sensitive adhesives, Thermoplastic polyester elastomers, Block copolymers, Microphase separation*

INTRODUCTION

Pressure-sensitive adhesives (PSAs) are a special category of viscoelastic materials that firmly adhere to various dissimilar surfaces upon a mere finger or hand contact, showing ubiquitous applications in numerous industries, especially in the electric, automotive, packing, and medical industries.[1] PSAs should possess both liquid-like viscosity to wet quickly surfaces for good sticky contact and solid-like elasticity for resistance to flow during a separation or debonding process.[2,3] The conflicting properties of PSA are difficult to achieve within a single material. Viscoelastic fine-tuning in PSAs is known to control adhesive properties. To perform the specialized functions, PSAs should be formulated including a variety of additives such as tackifier resins (30−60 wt %), plasticizer (0−30 wt %), and stabilizer used to inhibit degradation (0.1−2 wt %) based on an elastomeric base polymer (20−50 wt %) such as acrylic copolymers, ethylene−vinyl acetate copolymers, rubber, silicone, and styrenic block copolymers (SBCs).[4−8] Typically utilized SBCs including ABA architecture consist of higher T_g value styrene segments (A) for a hard phase and lower T_g value ethylene−propylene, ethylene−butene, isoprene, or butadiene segments (B) for a soft and rubbery phase.[9,10] The immiscible property between the glassy and the rubbery blocks at ambient temperature provides microphase separation in the polymer matrix, which means that the copolymers are physically cross-linked with the hard domains to enhance creep resistance caused by a loose but sufficiently connected network of chains.[11] Tackifying resin miscible with rubbery phase of PSA base polymer generates adhesive properties and typically increases the T_g value of the rubbery phase. The roles of a plasticizer are to reduce cost, decrease hardness, and decrease the T_g value of the rubbery phase, inducing the low-temperature tack of an adhesive.[12−16]

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The growing movement in the chemical industry to develop greener products and to find novel growth strategies based on renewable alternatives is being driven by global warming, current technology, general demand from consumers, and government regulations.[17,18] However, for soft landing of the renewable models in petroleum-based industry application, renewable feedstock should simultaneously address sustainability objectives and provide high performance materials through intended design derived from natural sources.[19−22] The shift toward sustainable solutions for adhesive materials could have a significant impact on the environment and society.[23] The design of PSAs derived from renewable materials has attracted significant attention in the industrial adhesive community. Vegetable oils are currently one of the most abundant, less toxic, biodegradable, and less expensive renewable raw materials, which have been widely used as promising monomers of thermosetting composites in various applications such as foams, elastomers, coatings, and paint resins.[24−26]

Plant-oil-based PSAs were first developed using epoxidized soybean oil (ESO), dihydroxyl soybean oil (DSO), fatty acid methyl ester (FAME), and phosphoric acid as a cross-linker through a simple curing process, showing attractive thermal stability for heat-related applications, transparency, and tolerance to organic solvents as well as clear removal and peel strength comparable to commercial PSA tapes such as Post-it notes and Scotch Magic Tape.[27−29] Renewable self-adhesive coatings having tunable viscoelastic properties caused by careful selection of the network precursors such as well-defined amounts of carboxylic acid groups were prepared with hydroxyl-telechelic polyester architectures by melt polycondensation of dimerized fatty acids with fatty diols or isosorbide, which was subsequently followed by curing with maleic anhydride-modified triglycerides or epoxidized plant oils.[30,31] To generate a new class of PSAs based on renewable materials, ESO or epoxidized fatty acids (EFAs) were polymerized and cross-linked with a dicarboxylic acid such as dimer acid (DA), sebacic acid, adipic acid, and a polymerized DA incorporated with a small amount of phenylene-containing monomer, bisphenol A diglycidyl ether (BPAGE). The thermoset polyester as PSAs had reasonable peel strength, loop tack, shear strength, and good aging resistance.[32−34] Recently, a partially sustainable approach was introduced to incorporate *N*-hydroxyethyl acrylamide capped poly(L-lactide-*co*-ε-caprolactone) macromonomers into an existing commercial 2-ethylhexyl acrylate hot-melt PSAs without sacrificing adhesive performance, which was significantly dependent on the lactide content to increase polymer hardness relevant to cohesive strength of adhesives.[35−37] However, there are few reports to develop PSAs including renewable thermoplastic block copolymers as the base elastomers in SBC-based PSAs. A self-adhesive system composed of renewable poly(lactide)−poly(menthide)−poly(lactide) (PLA−PM−PLA) triblock polyesters combined with a rosin ester (RE) tackifier was prepared. Maximum values of peel adhesion (3.2 N cm^{-1}) and tack (1.1 N) were shown at the PSA formulation of 40 wt % tackifier and 60 wt % elastomer. The unbalanced PSA formulation having relatively larger amounts of the elastomer without plasticizer derived from bioresources, when compared to commercial SBC PSA formulation, was caused by the weak mechanical strength of the biobased triblocks, which is not acceptable in the adhesive industry.[38]

Herein, we report the development of a renewable PSA system obtaining poly(L-lactide)−poly(ε-decalactone)−poly(L-lactide) (PLLA−PDL−PLLA), RE, and ESO as a base elastomer, a tackifier, and a plasticizer, respectively. Using ring-opening transesterification polymerization (ROTEP) of ε-decalactone (DL) subsequently followed by the addition of L-lactide (LLA) to form a hard segment in the triblock via a one-pot, two-step process, the preparation and characterization of the renewable triblock thermoplastic elastomers (TPEs) were also shown.[39,40] On the basis of previous literature, we hypothesized that the crystal structure of PLLA hard domains in the PLLA−PDL−PLLA(20−100−20), when compared to the amorphous phase of PLA segments in PLA−PM−PLA(20−100−20), could enhance mechanical properties, which results in reduced amounts (up to 20−40 wt %) of a base elastomer used for PSA formulation.[41,42] We also pursued an optimized protocol for wholly sustainable PSA formulation using a plant-oil-based plasticizer, ESO, as well as the process mentioned in the previous literature.[38] Herein, we describe (a) a method for preparing PLLA−PDL−PLLA triblock copolymers with low distributions through a one-pot, two-step method, (b) the characterization of the triblocks and PSA formulations using NMR spectroscopy, size-exclusion chromatography (SEC), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), dynamic mechanical analysis (DMA), atomic force microscopy (AFM) or tensile testing, and (c) combination of these triblocks with variable amounts of a plant-based RE tackifier and a vegetable-oil-based ESO plasticizer showing excellent adhesive performance as demonstrated by peel adhesion, probe tack, and shear strength tests.

■ EXPERIMENTAL SECTION

Materials. All air or/and moisture sensitive materials were stored in a nitrogen charged glovebox after purification. ε-Decalactone (DL) (Sigma-Aldrich) was purified by distillation under reduced pressure over calcium hydride, which was subsequently passed through a column of activated basic alumina (Sigma-Aldrich) under nitrogen atmosphere. Diethylene glycol (DEG) (Sigma-Aldrich) was distilled under reduced pressure over sodium. L-Lactide (LLA) and D,L-lactide (LA) (Purac) were recrystallized twice from toluene prior to being stored in a glovebox. Tin(II) 2-ethylhexanoate (Aldrich) was distilled (5×). Toluene was dried using sodium and benzophenone, and distilled under reduced pressure. Chloroform (B&J, HPLC grade) and methanol (B&J, HPLC grade) for polymer precipitation were purchased and used without purification. Glass pressure vessels, Teflon caps, and Teflon-coated magnetic stir bars were fully dried at 130 °C prior to use in the glovebox. Poly(styrene)−poly(isoprene)−poly(styrene) (PS−PI−PS) having a styrene and residual diblock (PS−PI) content of approximately 15 and 19 wt % (Kraton D1161, Kraton Performance Polymers Inc.), respectively, and poly(methyl methacrylate)−poly(*n*-butyl acrylate)−poly(methyl methacrylate) (PMMA−PBA−PMMA) having methyl methacrylate (MMA) content of 23 wt % without any diblock (Kurarity LA2140e, Kuraray Co., Ltd.) were obtained from the manufacturers. The rosin ester (RE) tackifier (Sylvalite RE 80HP, Arizona Chemical Company, LLC) and epoxidized soybean oil (ESO) plasticizer (Sajo Haepyo Corp.) were used as received. All other solvents were used as received from commercial sources without further purification. The backing film for the adhesive test was a poly(ethylene terephthalate) sheet (PET, thickness: 50 μm).

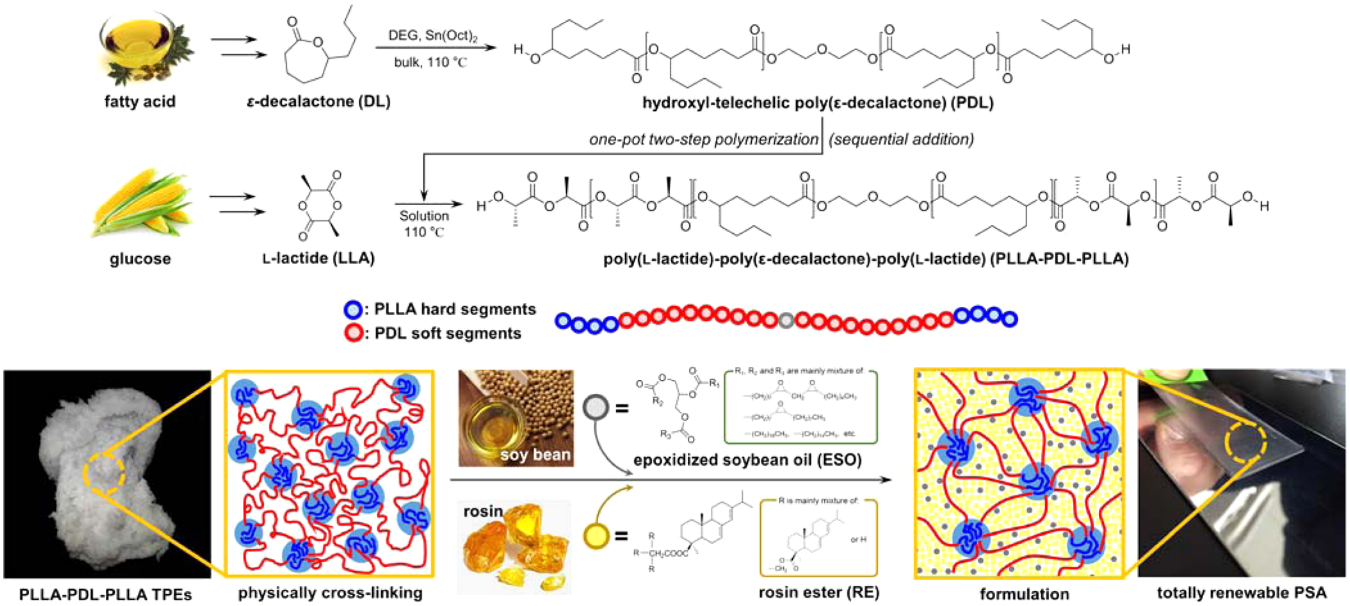
Measurements. The ^1H and ^{13}C NMR spectra of the polymeric compounds dissolved in $CDCl_3$ were obtained using a Bruker DPX-500 spectrometer (500 and 125 MHz, respectively). Tetramethylsilane (TMS) was used as the internal standard. Size-exclusion chromatography (SEC) was conducted on an Agilent 1260 LC system equipped with a refractive index detector. The samples were diluted in CHCl$_3$ (mobile phase) and passed through one PLgel guard column (5 μm, 50 × 7.5 mm) and three PLgel Mixed-C columns (5 μm, 300 × 7.5 mm) at 35 °C under a constant flow rate of 1 mL min^{-1}. The molar mass (M_n and M_w) was calculated by the calibration curve, which was fitted with polystyrene standards (Shodex). Differential scanning calorimetry (DSC) analysis was performed on a TA Q-1000 DSC instrument under a nitrogen atmosphere. The polymer samples (5−10 mg) were scanned from 25 to 150 °C and held for 5 min; then, they were allowed to cool to −80 °C and held there for 1 min. The samples were reheated to 230 °C. The rates of heating and cooling were 10 °C min^{-1}. The transition temperatures were obtained from the second scan. Thermal gravimetric analysis (TGA) was performed by a TA Q-500 TGA instrument under a nitrogen atmosphere at heating rate of 10 °C min^{-1} in a temperature range from 25 to 600 °C. Tensile testing of the triblock copolymers was conducted using a universal testing machine (QRS-S11H, Quro) at room temperature. Tensile properties of the ASTM D1708 microtensile bars, which were prepared by solvent casted films with chloroform as the solvent with a uniform sheet thickness (~0.30 mm), were tested at a strain rate of 130 mm min^{-1} with a 100 N load cell; all values were reported as the average and standard deviation of at least four samples. Dynamic mechanical analysis (DMA) was conducted with an ARES-G2 rotational rheometer (TA Instruments) under nitrogen conditions. The shear modulus with temperatures from −70 to +140 °C was measured in a rectangular torsion fixture at ω = 1.0 rad s^{-1} and γ = 1.0%. The frequency sweep mode was implemented from 0.1 to 100 rad s^{-1} at 25 and 80 °C. The tapping mode AFM measurements were performed by a Multimode Nanoscope system (Bruker). Samples were prepared by spin coating of a 3.0% (w/v) solution in dichloromethane on a Si wafer (1 × 1 cm) at 3000 rpm. Thermal annealing of the triblocks sample was done in a vacuum oven at 150 °C for 24 h.

Preparation of Semicrystalline and Amorphous Polyester Elastomers..[21,38−40] *One-Pot, Two-Step Process for Synthesis of Poly(L-lactide)−Poly(ε-decalactone)−Poly(L-lactide) (PLLA−PDL−PLLA) and Poly(D,L-lactide)−Poly(ε-decalactone)−Poly(D,L-lactide) (PLA−PDL−PLA).* First, PDL to target molar mass of 100 kg mol^{-1} was synthesized by ring-opening transesterification polymerization (ROTEP) of ε-decalactone (DL). DEG (1 equiv), Sn(Oct)$_2$ (1 equiv), and DL (640 equiv) were transferred to a pressure vessel with a magnetic stir bar in a nitrogen-filled glovebox. The sealed vessel was taken out of the glovebox and placed a thermoset oil bath at a 110 °C for 40 h (ca. 93% conversion of the monomer and 80−90% isolated yield based on the product weight calculated by the conversion). Density: 0.974 ± 0.007 g cm^{-3} for PDL(100). ^{1}H NMR (500 MHz, CDCl$_3$) in Figure S1A: δ 4.83 (quin, J = 6.3 Hz, 588H, H$_d$ from the repeating unit of PDL), 4.22 (t, J = 4.9 Hz, 4H, H$_c$ from incorporated initiator), 3.67 (t, J = 4.9 Hz, 4H, H$_b$ from incorporated initiator), 3.57 (br, 2H from the end unit of PDL), 2.25 (t, J = 7.6 Hz, 1176H from the repeating unit of PDL), 1.65−1.55 (m, 1176H from the repeating unit of PDL), 1.54−1.47 (m, 2352H from the repeating unit of PDL), 1.36−1.17 (m, 3528H from the repeating unit of PDL), 0.88−0.85 (t, J = 7.0 Hz, 1764H from the repeating unit of PDL). ^{13}C NMR (125 MHz, CDCl$_3$): δ 173.3, 73.8, 34.5, 33.8, 33.7, 27.5, 25.0, 24.9, 24.8, 22.6, 14.0. After the vessel cooled to room temperature, it was brought into the glovebox. Finally, the vessel was charged with toluene and reheated to 135 °C for 30 min to dissolve the polymer. The vessel was cooled to room temperature and L-lactide (75, 150, and 300 equiv to target molar masses of 10, 20, and 40 kg mol^{-1} as PLLA hard domains in the triblock copolymers) or D,L-lactide (300 equiv to target molar mass of 40 kg mol^{-1} as PLA hard domains in the triblock copolymer) was added into the reaction vessel in the glovebox without any additional amount of the catalyst. The vessel was sealed and returned to 110 °C for 12 h (ca. 96−97% conversion of L-lactide and D,L-lactide). The reaction was quenched by exposure to the air, diluted with chloroform (10% w/v solution), and precipitated into methanol at −70 to −60 °C. The recovered triblocks were dried at 90 °C in a vacuum oven (90−95% isolated yield based on the product weight calculated by the conversion). Densities for PLLA−PDL−PLLA(5−100−5, 10−100−10, and 20−100−20): 1.006 ± 0.002, 1.024 ± 0.001, and 1.060 ± 0.008 g cm^{-3}. ^{1}H NMR (500 MHz, CDCl$_3$) for PLLA−PDL−PLLA(5−100−5, 10−100−10, 20−100−20 (in Figure S1B,C)): δ 5.15 (q, J = 7.1 Hz, 126, 280, and 598H, H$_f$ from the repeating unit of PLLA), 4.83 (quin, J = 6.3 Hz, 588H, H$_d$ from the repeating unit of PDL), 4.36 (m, 2H, H$_e$ from the end unit of PLLA), 4.22 (t, J = 4.9 Hz, 4H from incorporated initiator), 3.67 (t, J = 4.9 Hz, 4H from incorporated initiator), 2.25 (t, J = 7.6 Hz, 1176H from the repeating unit of PDL), 1.65−1.55 (m, 1176H from the repeating unit of PDL and 189, 420, and 897H from the repeating unit of PLLA), 1.54−1.47 (m, 2352H from the repeating unit of PDL), 1.36−1.17 (m, 3528H from the repeating unit of PDL), 0.88−0.85 (t, J = 7.0 Hz, 1764H from the repeating unit of PDL). ^{13}C NMR (125 MHz, CDCl$_3$): δ 173.3, 169.6, 73.8, 69.0, 34.5, 33.8, 33.7, 27.5, 25.0, 24.9, 24.8, 22.6, 16.6, 14.0. Density for PLA−PDL−PLA(20−100−20): 1.064 ± 0.010 g cm^{-3}. ^{1}H NMR (500 MHz, CDCl$_3$) for PLA−PDL−PLA(20−100−20): δ 5.25−5.13 (m, 610H from the repeating unit of PLA), 4.83 (quin, J = 6.3 Hz, 588H from the repeating unit of PDL), 4.35 (m, 2H from the end unit of PLA), 4.22 (t, J = 4.9 Hz, 4H from incorporated initiator), 3.67 (t, J = 4.9 Hz, 4H from incorporated initiator), 2.25 (t, J = 7.6 Hz, 1176H from the repeating unit of PDL), 1.64−1.49 (m, 3528H from the repeating unit of PDL and 915H from the repeating unit of PLA), 1.36−1.17 (m, 3528H from the repeating unit of PDL), 0.88−0.85 (t, J = 7.0 Hz, 1764H from the repeating unit of PDL). ^{13}C NMR (125 MHz, CDCl$_3$): δ 173.3, 169.6−169.1, 73.8, 69.2, 69.0, 34.5, 33.8, 33.7, 27.5, 25.0, 24.9, 24.8, 22.6, 16.7−16.6, 14.0.

Compatibility Tests and PSA Films Preparation for Adhesive Tests. The compatibility of the renewable triblock elastomers, tackifier and plasticizer was estimated by the following simple tests. First, the liquid phase separation of the adhesive solution was examined. Individual solutions of PLLA−PDL−PLLA(10−100−10 or 20−100−20) in chloroform (7 wt %), rosin ester (RE) tackifier in chloroform (10 wt %) and epoxidized soybean oil (ESO) plasticizer in chloroform (3 wt %) were prepared, to make the total solid content 20 wt %. The same amounts of two solutions were mixed in a vial using a stirring bar for 1 h, respectively. The solution was transferred to a test tube, allowed to stand for 10 days at room temperature and then visually observed. Second, the 20 wt % chloroform solutions of the adhesive systems were cast on a PET sheet. After chloroform was evaporated at 80 °C for 10 min, the transparency of the film was visually observed. The resulting systems layer had thickness of ca. 10 μm. Ten PSA films from our renewable PSAs system were prepared for performing adhesive tests or/and measuring the thermal properties. PLLA−PDL−PLLA(5−100−5, 10−100−10, and 20−100−20), PLA−PDL−PLA(20−100−20), PMMA−PBA−PMMA(Kurarity LA2140e), and PS−PI−PS/PS−PI(Kraton D1161) were used as elastomers. Rosin ester and epoxidized soybean oil were used as a tackifier and a plasticizer. The concentration of the elastomer/tackifier/plasticizer in chloroform solution was 20 wt %. The 10 wt % elastomer/plasticizer ratio was 7/3 or 4/6, keeping the concentration of tackifier 10 wt %, based on the total solid content (20 wt %). Selected amounts of six solution samples having PLLA−PDL−PLLA triblocks were dried at 90 °C in a vacuum oven to evaporate completely chloroform and anneal overnight. They were used for preparing DSC and TGA samples. The solutions of the PSAs in chloroform were coated on the PET sheets (thickness 50 μm), using a draw-down caster and a wire-wound rod, and were dried in a 80 °C oven for 10 min. The cast films were transferred to a room with controlled temperature and humidity of 22 ± 1.5 °C and 50 ± 2.0% and remained in the room for at least 12 h before testing. The target thickness of the cast adhesive after drying was ca. 10 μm. PSA sample performance was evaluated using the following adhesive tests.

Adhesive Tests. *180° Peel Test.* The peel strength was measured by ASTM D3330: Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape with 180° Peel Adhesive Testing Machine (PA-1000-180, ChemInstruments, Inc.) at a peeling rate of 305 mm min^{-1}. The PET strips with 1 in. width were attached on Pressure-Sensitive Tape Council, PSTC-grade polished stainless steel test panels (ASTM A666) as an adherend with the constant pressure by a 4.5 Lb ASTM quality hand roller. The average peel force and standard

Scheme 1. Synthesis of Semicrystalline Thermoplastic Polyester and Renewable PSA Formulation Thereof



deviation were collected after 1 in. was peeled and were reported from at least three tests for each sample.

Probe Tack Test. Tack force was measured by ASTM D2979: Standard Test Method for Pressure-Sensitive Tack of Adhesives Using an Inverted Probe Machine with Polyken Probe Tack (PT-1000, ChemInstruments, Inc.). The probe with a diameter of 5 mm contacted the adhesive film, was held for 1 s, and then removed from the surface at 610 mm min^{-1}. The probe was cleaned after every test and the resulting maximum force was reported. The average tack force and standard deviation from at least 10 tests were reported for each sample.

Shear Test. Shear test was performed by modified ASTM D3654: Standard Test Methods for Shear Adhesion of Pressure-Sensitive Tapes with Room Temperature 10 bank Shear Tester (SS-RT-10, ChemInstruments, Inc.). PSA strip was attached with a contact area of 1 × 1 in. on PSTC-grade polished stainless steel panel. The sample was rolled with a 4.5 lb ASTM quality hand roller. The average time and standard deviation of failure in minutes under shear loading of 500 g, instead of 1000 g, to the bottom of the test strip were reported from at least three tests for each sample.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Semicrystalline Polyester Elastomers. We developed a one-pot, two process method to synthesize semicrystalline poly(L-lactide)−poly(ε-decalactone)−poly(L-lactide) (PLLA−PDL−PLLA) triblock copolymers. First, as shown in Scheme 1, α,ω-hydroxyl functionalized PDL was prepared by ring-opening trans-esterificatgion polymerization (ROTEP) of ε-decalactone (DL) using tin(II) ethylhexanoate (Sn(Oct)_2) as a catalyst and diethylene glycol (DEG) as a difunctional initiator in a bulk system (see Experimental Section for synthetic details). An initial DL/DEG ratio of 640:1 was chosen to target molar mass of 100 kg mol^{-1}, designated as PDL(100). ^{1}H NMR spectroscopy was used to monitor monomer conversion (ca. 93%), determine DEG chain connectivity, and calculate M_n from relative integration of PDL repeating units and incorporated DEG in PDL. On the basis of the conversion and the starting monomer-to-initiator content, the theoretical M_n value for PDL(100) was 101 kg mol^{-1}. The M_n value of 100 kg mol^{-1} was also obtained by calculation of the relative integration between the methylene protons of the DEG initiator fragment at δ 4.22 and 3.67 ppm (8 protons in total) and the methine protons at δ 4.83 ppm from the repeating units of the ester chain in the ^{1}H NMR spectrum of telechelic hydroxyl PDL (Figure S1C). The number-average molar mass (M_n) determined by ^{1}H NMR spectroscopy and the calculated theoretical M_n were in excellent agreement. Furthermore, the dispersity determined by size exclusion chromatography (SEC) relative to poly(styrene) standards was narrow ($Đ$ = 1.07 and M_n = 146 kg mol^{-1} in Figure 1 and Table S1).

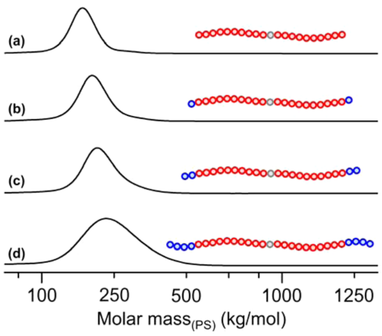


Figure 1. Size-exclusion chromatography data (1 mg mL^{-1} chloroform) for (a) PDL(100), (b) PLLA−PDL−PLLA(5−100−5), (c) PLLA−PDL−PLLA(10−100−10), and (d) PLLA−PDL−PLLA(20−100−20).

ABA triblock polyesters were prepared by the addition of L-lactide (LLA) and toluene to hydroxyl-telechelic PDL, which was not isolated in a one-pot two step method (Figure S1b). The polymer compositions were facilely controlled by adjusting the weight fraction of LLA to that of difunctional PDL. Initial PDL macroinitiator/LLA ratios of 1:75, 1:150, and 1:300 were chosen to target molar masses of 10, 20, and 40 kg mol^{-1}, designated as PLLA−PDL−PLLA(5−100−5, 10−100−10, and 20−100−20). Upon completion of the reaction, the signal for the terminal methine protons of PDL at δ 3.57 ppm disappeared and new signals for the methine protons from

Table 1. Characterization Data of Renewable Triblock Copolymers[a] and Commercial Elastomers

ABA triblock copolymers	$f_{\text{hard block}}$[b]	T_g (°C)[c]	T_m (°C)[c]	ΔH_f (J g^{-1})[d]	crystallinity (%)[e]	T_d (°C)[f]	Young's modulus, E (MPa)[g]	tensile strength, σ_b (MPa)[g]	strain at break, ε_b (%)[g]	storage modulus, G' (MPa)[h]
PLLA–PDL–PLLA(5–100–5)[i]	6.3	−50, +53	159	0.2	2.7	284	1.13 ± 0.1	0.14 ± 0.1	323 ± 10	0.63
PLLA–PDL–PLLA(10–100–10)[i]	13.0	−50, +55	159	1.5	9.4	241	2.00 ± 0.2	4.23 ± 0.2	1420 ± 59	0.97
PLLA–PDL–PLLA(20–100–20)[i]	24.3	−49, +60	161	8.6	30.5	225	2.86 ± 0.3	13.6 ± 0.5	1212 ± 25	1.24
PLA–PDL–PLA(20–100–20)[j]	25.4	−49, +58				233	1.89 ± 0.4	1.70 ± 0.4	1249 ± 88	0.83
PMMA–PBA–PMMA(Kurarity LA2140e)[k]	23.2	−49, +109				347	1.00 ± 0.1	6.24 ± 0.5	543 ± 77	0.35[48]
PS–PI–PS/PS–PI(Kraton D)[l]	13.6	−59, +90				333	1.24 ± 0.1	13.6 ± 0.3	3235 ± 60	0.44[49,50]

[a]See Experimental Section for details. [b]Calculated volume fraction of hard block using the densities of PLLA, PLA, PS, PMMA, PDL, PBA, and PI of 1.290, 1.248, 1.035, 1.180, 0.974, 1.190, and 0.899 at 25 °C. [c]Determined by DSC (second heating cycle) at 10 °C min^{-1}. [d]Heat of fusion for the triblocks in J g^{-1}. [e]The percent of crystallinity based on the theoretical heat of fusion calculated 100% crystalline PLLA (i.e., $\Delta H_f^\circ = 94.0$ J g^{-1}). [f]5% weight loss determined by TGA at 10 °C min^{-1} in N_2. [g]Mechanical properties determined on an ASTM D1708 microtensile bars. [h]Determined by DMA with rectangular torsion fixture at 25 °C. Oscillation test from −70 to +140 °C at 3 °C min^{-1}, $\omega = 1.00$ rad s^{-1}, and $\gamma = 1.0\%$. [i]PLLA–PDL–PLLA: poly(L-lactide)–poly(ε-decalactone)–poly(L-lactide). [j]PLA–PDL–PLA: poly(D,L-lactide)–poly(ε-decalactone)–poly(D,L-lactide). [k]PMMA–PBA–PMMA: poly(methyl methacrylate)–poly(n-butyl acrylate)–poly(methyl methacrylate). [l]PS–PI–PS/PS–PI: poly(styrene)–poly(isoprene)–poly(styrene)/poly(styrene)–poly(isoprene) (81/19 wt %).

the repeating units of the ester chain and the terminal methine protons of PLLA end blocks appeared at δ 5.15 and 4.36 ppm, proving efficient initiation by the macroinitiator. On the completion of the reaction, typical conversions of LLA were ca. 96%. The molar masses of PLLA end blocks determined by ^{1}H NMR spectroscopy were 9, 20, and 43 kg mol^{-1}, which were well matched with the theoretical molar masses of 10, 21, and 42 kg mol^{-1}, respectively (Table S1). A constant ∼6% of residual DL content during the polymerization of LLA (Figure S1a) and only two distinct resonances for PDL and PLLA at δ 173.3 and 169.6 ppm in the ^{13}C NMR spectrum indicated that unreacted DL was little incorporated in the PLLA end block and the PDL middle block with minimal transesterification.[43,44] Compared to that of PDL(100), the SEC chromatograms for PLLA–PDL–PLLA triblocks showed an apparent shift to higher molar masses (Figure 1). The M_n values for the block polyesters calculated with poly(styrene) standards were 162, 173, and 191 kg mol^{-1}, still remaining narrow dispersities ($Đ$ = 1.08, 1.08, and 1.10) (Table S1) with no evidence of uninitiated PDL or PLLA homopolymer. After isolation, the purified triblock compositions were 8.2, 16.5, and 29.9 wt % end block PLLA (Table 1), in addition to 6.3, 13.0, and 24.3 vol % as the volume fractions of the PLLA hard segments. Taken together, all data related to the molar mass obtained by the one-pot, two-step method proved that the sequential polymerizations using a single catalyst did not cause adverse side reaction leading to cleavage or cross-linking of polymer chains. To compare mechanical properties and PSA performance of the triblocks including semicrystalline hard segment PLLA, poly(D,L-lactide)–poly(ε-decalactone)–poly(D,L-lactide) having amorphous end blocks to target molar mass of 40 kg mol^{-1} was also prepared via the one-pot, two-step process of ROTEP, which was designated as PLA–PDL–PLA(20–100–20) (see Experimental Section for synthetic details). The molar mass of PLA end blocks determined by ^{1}H NMR spectroscopy was 44 kg mol^{-1}, showing unimodal and narrow SEC dispersity ($Đ$ = 1.10). The weight and volume fractions of the amorphous PLA in the triblock were 30.6 wt % and 25.4 vol %, respectively.

The tensile properties of four prepared triblock copolymers having 8, 17, and 30 wt % semicrystalline PLLA and 31 wt % amorphous PLA as well as two commercial thermoplastic elastomers (TPEs) such as styrenic and acrylic copolymers were investigated (Table 1, Figures 2 and S2). Linear responses at low strains (Young's modulus) were observed in the stress–strain (S–S) curves for all elastomers. The curves of PLLA–PDL–PLLA(5–100–5, 10–100–10, and 20–100–20) demonstrated that tensile strength (0.1 to 13.6 MPa) and Young's modulus (1.1 to 2.9 MPa) were improved significantly with increasing PLLA content (8 to 30 wt %). Beyond the low strain elastic region, the PLLA–PDL–PLLA(10–100–10 and 20–100–20) samples showed strains in excess of 1200%. However, PLLA–PDL–PLLA(5–100–5) had relatively low ultimate strength and strain at break (0.1 MPa and 320%) due to the small portion of PLLA hard end blocks (8 wt %). PLA–PDL–PLA (20–100–20) having 30.6 wt % amorphous end blocks also reached Young's modulus (1.9 MPa), tensile strength (1.7 MPa), and elongation at break (ca. 1200%) relatively similar to those of PLLA–PDL–PLLA(10–100–10) obtaining 16.7 wt % semicrystalline hard segments, indicating that the crystal structure of hard domains in the triblocks induced significant increase of ultimate strength and Young's modulus for the

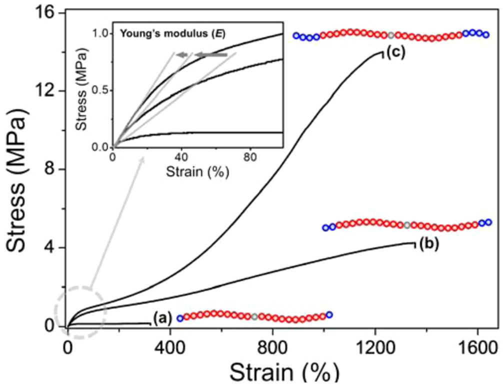


Figure 2. Representative stress–strain curves for (a) PLLA–PDL–PLLA(5–100–5), (b) PLLA–PDL–PLLA(10–100–10), and (c) PLLA–PDL–PLLA(20–100–20) of the triblock copolymers.

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elastomers. The stronger interaction among polymer chains with the same stereoconfiguration would lead to more enhanced physical cross-linking in the semicrystalline PLLA matrix, compared to the amorphous PLA phase.[41,45] These ultimate strengths and Young's moduli observed in PLLA–PDL–PLLA triblocks featuring relatively high amounts of end block (>ca. 17 wt %) were comparable or superior to those of commercial TPEs such as poly(styrene)–poly(isoprene)–poly(styrene) (PS–PI–PS)/poly(styrene)–poly(isoprene) (PS–PI), and poly(methyl methacrylate)–poly(*n*-butyl acrylate)–poly(methyl methacrylate) (PMMA–PBA–PMMA) (Table 1 and Figure S2). These ultimate elongations observed in the triblocks were significantly higher than that for the acrylic TPEs (540%) and lower than that for the styrenic TPEs (3200%). To fulfill the typical requirement of a self-adhesive to fail without leaving a sticky residue on the surface, elastomers in PSA formulations should show a strain-hardening property at high levels of strain.[1] The commercial TPEs and all the prepared triblock copolymers except PLLA–PDL–PLLA(5–100–5) exhibited variable degree of strain hardening in the *S*–*S* curves.

The thermal properties of the triblocks were studied by differential scanning calorimetry (DSC, Figure 3a and Table 1). DSC traces of the triblock copolymers revealed two glass transition temperatures ($T_{\mathrm{g\ PDL}} \approx -50$ °C and $T_{\mathrm{g\ PLLA}} \approx 53-60$ °C) and one melting temperature ($T_{\mathrm{m\ PLLA}} \approx 160$ °C) corresponding to the PDL midblock and the PLLA end blocks. This suggested that the glassy PLLA end blocks were not mixed but microphase-separated in the PDL rubbery phase. Although the former T_g value closely matched that of PDL(100), the latter T_g value was similar to that of pure high molar mass PLLA (60 °C). The degree of crystallinity (X_c) was calculated using the following equation:

$$X_c = (\Delta H_f/\Delta H_f^0 \cdot w_f) \times 100 \qquad (1)$$

where X_c is the degree of crystallinity, w_f is the weight fraction of PLLA in the copolymer, ΔH_f is the heat of fusion of the sample, and ΔH_f^0 is the heat of fusion of 100% crystalline PLLA (94 J g^{-1}). DSC traces of PLLA–PDL–PLLA(5–100–5, 10–100–10, and 20–100–20) showed different crystallinities of 2.7, 9.4, and 30.5%, respectively.[39,46,47] The thermal stability of the PLLA–PDL–PLLA(20–100–20) triblock copolymer was studied using thermal gravimetric analysis (TGA, Figure S3). Two stages appeared for the weight loss of the block copolymer; the first weight loss was attributed to the decomposition of PLLA at 200–270 °C and the second weight loss was from the decomposition of PDL at 300–370 °C.

Thermal, Dynamic Mechanical and Morphological Properties of the Biobased PSAs. The thermal properties of the PSAs were studied by differential scanning calorimetry. Eight formulations having PLLA–PDL–PLLA(20–100–20 and 10–100–10) with 0, 60, 70, or 80 wt % RE tackifier and four PSA formulations having the two triblocks (35 or 20 wt %) and RE resin (50 wt %) with ESO plasticizer (15 or 30 wt %) were prepared (Figures 3 and S4). DSC measurements for these elastomer/tackifier systems showed one distinct glass transition for the rubbery mixture including PDL and RE resin. Adding more tackifier caused a broadening in the rubbery phase T_g value and an in increase in the temperature of the PDL midblock in the blends because the RE tackifier had a relatively higher T_g value of ~36 °C, compared to that of the pure triblock copolymers ($T_{\mathrm{g\ PDL}} \approx -50$ °C). However, there was little change in the vague T_g value at 59 °C of the PLLA end blocks in the blend having 40 wt % PLLA–PDL–PLLA(20–100–20 and 10–100–10) and 60 wt % tackifier (Figures 3b and S4b). DSC analysis for these PSA systems gave one clear T_g value for the rubbery matrix composed of PDL, the resin, and ESO (Figures 3c and S4c). Addition of more the plasticizer led to a sharp decrease in the T_g value of the rubbery phase because ESO had lower T_g value of around −61 °C, relative to that of the elastomer/tackifier systems. The DSC results confirmed that the tackifier and the plasticizer in the triblocks were mostly miscible with the more hydrophobic PDL midblock.[38,51,52] The thermal stability of the PLLA–PDL–PLLA/RE/ESO PSA system was assessed using thermal gravimetric analysis (TGA; Figure S3). Four stages were shown in the weight loss of the PSA formulation; the first weight loss was attributed to the decomposition of PLLA of the triblock at 220–280 °C, the

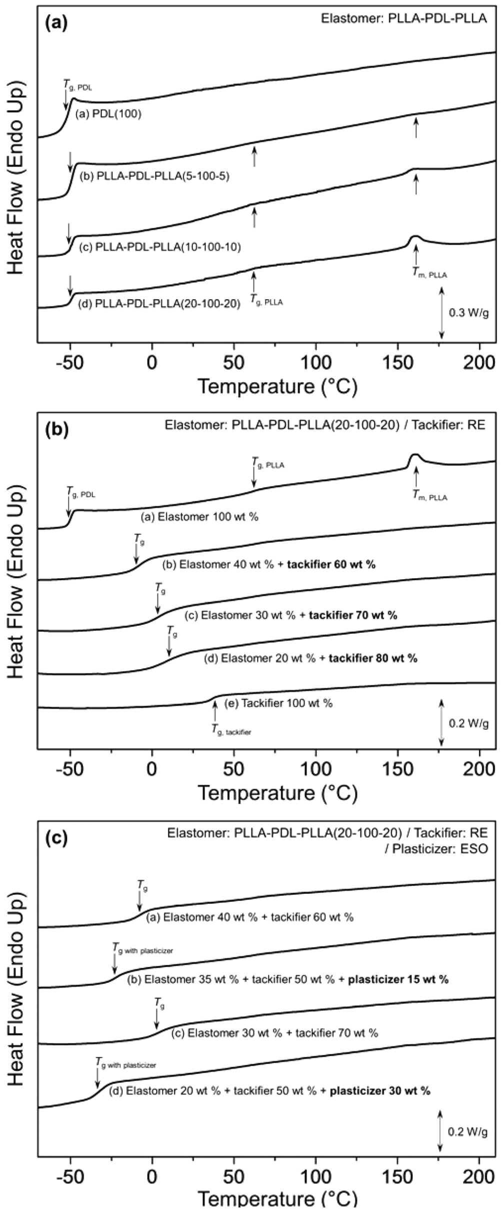

Figure 3. DSC analysis for (a) PDL and PLLA–PDL–PLLA triblock copolymers, (b) PLLA–PDL–PLLA(20–100–20)/rosin ester (RE) tackifier blends, and (c) PLLA–PDL–PLLA(20–100–20)/rosin ester (RE) tackifier/epoxidized soybean oil (ESO) plasticizer PSA formulations.

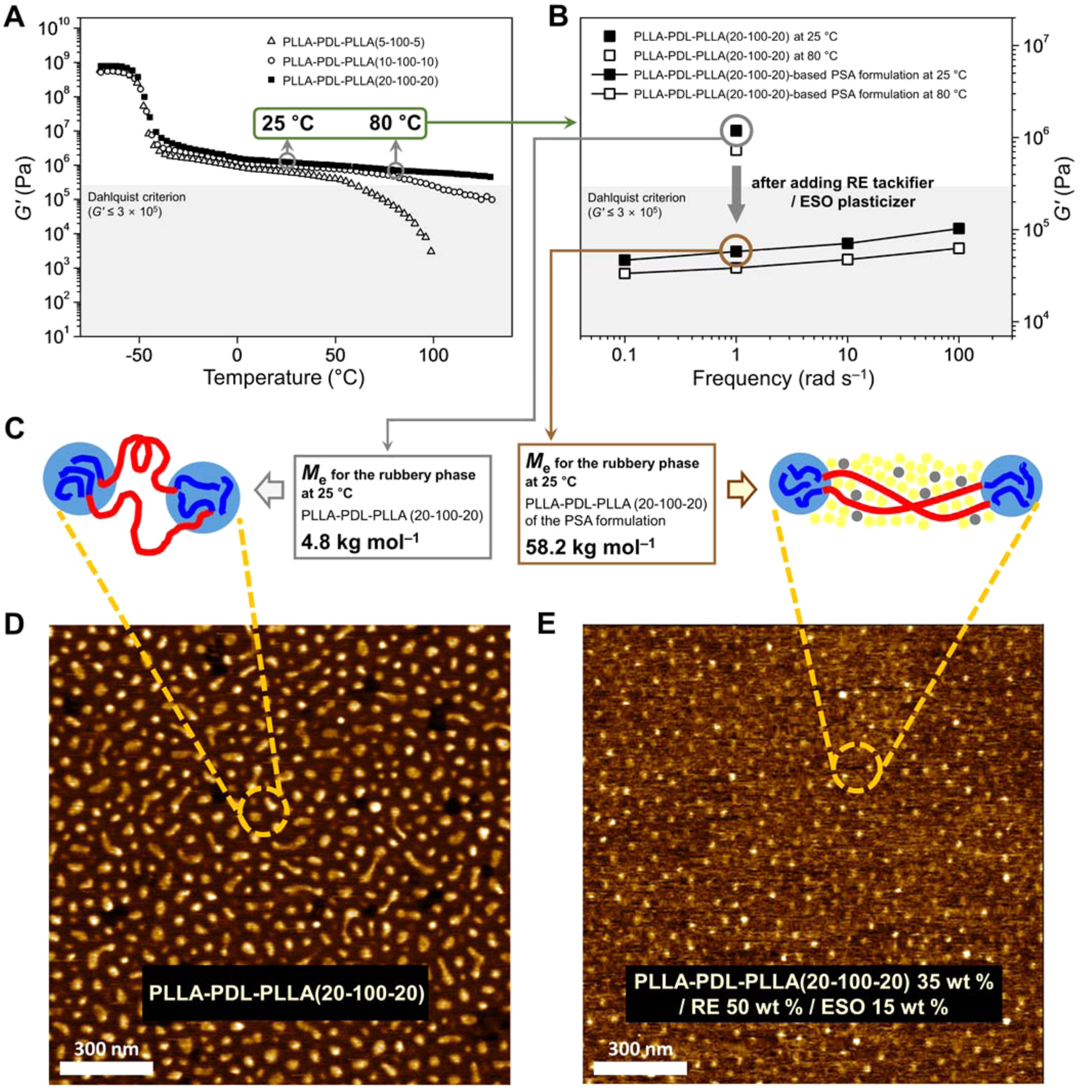

Figure 4. Viscoelastic properties (storage modulus, G') versus (a) temperature for triblock copolymers at 1 rad^{-1}, a strain around 1%, and a ramp rate of 3 °C, and (b) frequency at 25 and 80 °C for PLLA–PDL–PLLA(20–100–20) and the PSA formulation. (c) Calculated entanglement molar masses (M_e) and schematic diagram for entangled PLLA–PDL–PLLA(20–100–20) before and after adding RE tackifier and ESO plasticizer. 1.5 × 1.5 μm AFM phases of (d) a film of the pure polyester copolymer and (e) a film of the copolymer (35 wt %)-rosin ester (50 wt %)-epoxidized soybean oil (15 wt %) blend.

second weight loss was from the weight degradation of PDL in at 310–370 °C, and the following next phases were caused by weight degradations of the ESO plasticizer and RE tackifier at 380–415 and 420–470 °C, respectively. The TGA of the triblock in the PSA system in particular showed a slightly higher decomposition temperature (5% weight loss) than that of the pure triblock. Through simple compatibility tests using solution and film methods, we determined that the rosin ester tackifier (Sylvalite RE 80HP) and epoxidized soybean oil (ESO) plasticizer were seemingly miscible with the triblock (Figure S5).

Dynamic mechanical analysis (DMA) experiments of PLLA–PDL–PLLA triblock copolymers and the PSA formulations demonstrated the effect of temperature and frequency on dynamic elastic properties. The storage moduli (G') of the three triblocks as a function of temperature at low strain (1%) and the two PSAs as a function of frequency at 25 and 80 °C are shown in Figures 4 and S6. The low-temperature (<−50 °C) elastic moduli of the triblocks were constant at about 0.6–1.0 × 10^9 Pa. Pronounced drops in G' (Figure 4a) occurred around the T_g values (−52 to −48 °C) of the triblock samples; these drops were also observed by DSC (−50 to −49 °C). Therefore, the T_g values obtained from DSC and DMA were in good agreement. As the temperature was raised to 140 °C, a plateau in the storage modulus was observed until the onset of a more gradual drop in G' at 55 °C for PLLA–PDL–PLLA(5–100–5), at 80 °C for PLLA–PDL–PLLA(10–100–10), and at 140 °C for PLLA–PDL–PLLA(20–100–20), which were related to the domain disruption temperature (T_{dd}) depending on wt % and crystallinity of hard end blocks, molar masses of the blocks, and solubility parameters (χ) of the two blocks.[10] In general, two-phase structures of triblock copolymer still persist between the T_g and T_{dd} values of the hard phase due to polymer–polymer incompatibility. Microphase separated domains gradually disappear above T_{dd} owing to the intermixing of the components. The plateau moduli at 25 °C for the three triblocks were 0.6, 1.0, and 1.2 × 10^6 Pa, respectively. However, the plateau moduli (0.5 and 0.8 × 10^6 Pa) of only two PLLA–

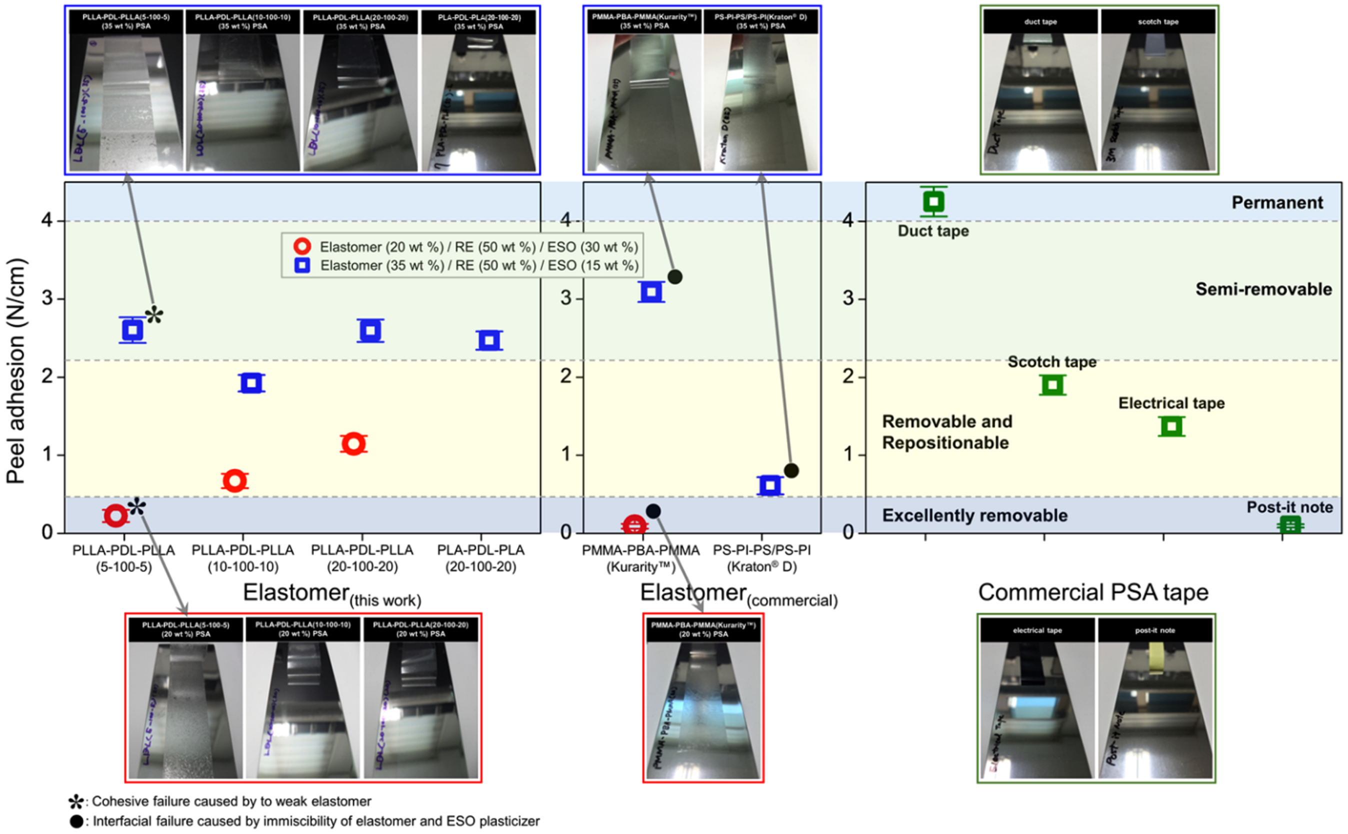

Figure 5. Effect of various elastomers with two different contents on the peel adhesion of the PSA systems (left and middle graph). In the case marked by an asterisk and a solid circle, the adhesive separated partially from the backing (i.e., cohesive or interfacial failure occurred). The peel adhesion of commercial PSA tapes (right graph). The properties of commercial PSAs were classified in the figure. Photographic images of clear removals and failure modes through peeling various PSA tapes from the stainless steel plate.

PDL−PLLA(10−100−10 and 20−100−20) samples were observed at 80 °C because the hard domains of PLLA−PDL−PLLA(5−100−5) were disrupted (Figure 4a). From the plateau modulus values of ABA triblock copolymers with spherical glassy domains, to which Holden applied the Guth−Smallwood equation:

$$G = \rho RT(1 + 2.5V + 14.1V^2)/M_e \tag{2}$$

where V was the hard phase volume fraction, ρ was the density of rubbery phase, R was the universal gas constant, T was the temperature, and G is the plateau storage modulus, the approximated entanglement molar masses (M_e) for PDL in the three triblocks were 4.6, 3.9, and 4.8 kg mol^{-1} at 25 °C, respectively.[53,54] Densities of 1.290 and 0.974 g cm^{-3} were used for PLLA and PDL. The M_e values per rubbery segments such as PDL, PBA and PI in PLA−PDL−PLA, PMMA−PBA−PMMA(Kurarity), and PS−PI−PS/PS−PI(Kraton D) at 25 °C (G' as plateau moduli = 0.83, 0.35, and 0.44 × 10^6 Pa) were also 7.2, 19.7, and 8.3 kg mol^{-1}, respectively, calculated using the equation. Densities of 1.190 and 0.899 g cm^{-3} were used for PBA and PI.[10,49]

However, these rubbery plateau moduli of the neat elastomers were usually too high for adequate tack of PSAs, indicating that these polymers were relatively entangled. To promote wetting and contact between adhesive and substrate at workplace temperature, PSAs should exhibit a dynamic elastic modulus below the Dahlquist criterion (shear modulus of $G' \leq 3 \times 10^5$ Pa at 1 rad s^{-1} or alternatively tensile (Young's) modulus of $E \leq 1 \times 10^5$ Pa).[55] The biobased tackifier (50 wt %) and plasticizer (15 or 30 wt %) miscible in the rubbery phase were added to lower the shear modulus, to dilute the entanglements, and finally to achieve PSA properties comparable to those of the commercial products.[51] Figures S6b and 4b demonstrated that the addition of tackifier resin (50 wt %) and plasticizer (15 wt %) to PLLA−PDL−PLLA(10−100−10 and 20−100−20) caused the decrease of the modulus (0.3−0.6 × 10^5 Pa at 25 and 80 °C keeping 1 rad s^{-1}) below the criterion for tack, compared to those of the neat elastomers. The G' values of the two PSAs over a frequency range from 0.1 to 100 rad s^{-1} were 0.3−1.0 × 10^5 Pa at 25 and 80 °C, respectively. The M_e values per PDL chain of the PSAs including the two elastomers, RE tackifier, and ESO plasticizer were 74.9 and 58.2 kg mol^{-1} at 25 °C and 1 rad s^{-1}, meaning the dilute entanglement of the rubbery matrix phase caused by the addition of tackifier and plasticizer, which induced the use of relatively small amounts of the triblocks for the PSA formulations. After the addition of petroleum-based tackifier (60 wt %) to the PS−PI−PS/PS−PI neat elastomer (40 wt %) having a styrene content of 14 wt % ($G' = 5.2 \times 10^5$ Pa and M_e = 6.6 kg mol^{-1} at 25 °C), the reduction of plateau modulus (G') and the increase of entanglement molar mass (M_e) in the PSA were also reported ($G' = 0.5 \times 10^5$ Pa and M_e = 54.4 kg mol^{-1} at 25 °C).[10]

The surface morphologies of spin coated thin films (see Experimental Section) prepraed by the triblock copolymer and the PSA formulation were investigated with atomic force microscopy (AFM). Figure 4d,e shows phase mode images for pure PLLA−PDL−PLLA(20−100−20) and the PLLA−PDL−

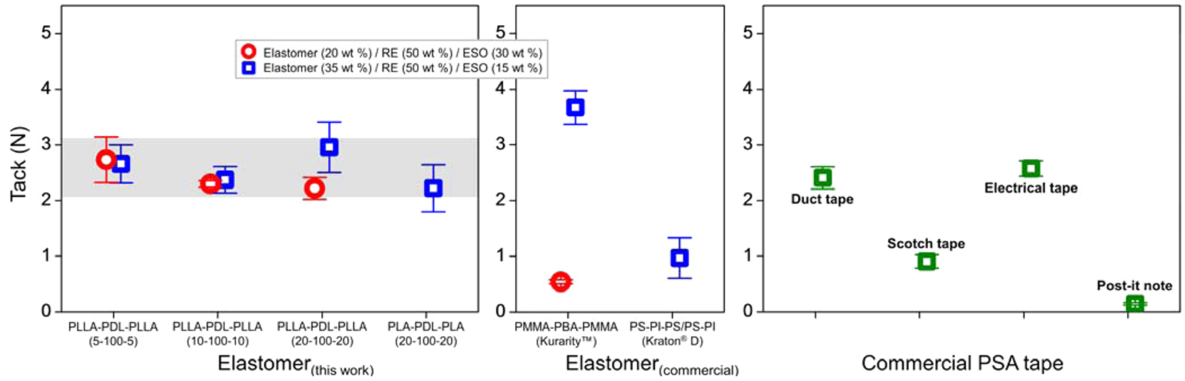

Figure 6. Effect of various elastomers with two different contents on the tack of the PSA systems (left and middle graph). The tack of commercial PSA tapes (right graph).

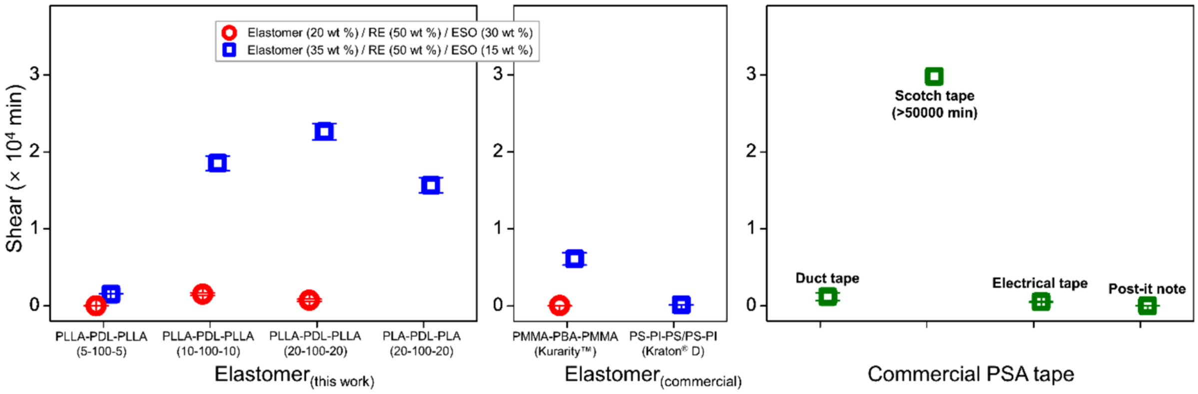

Figure 7. Effect of various elastomers with two different contents on the shear strength of the PSA systems (left and middle graph). The shear strength of commercial PSA tapes (right graph).

PLLA(20−100−20)-based PSA formulation (elastomer (35 wt %), RE tackifying resin (50 wt %), and ESO plasticizer (15 wt %)). PLLA domains appeared as bright circular features dispersed in the darker PDL matrix, proving microphase separation of the copolymer (Figure 4d). The PSA system also maintained a microphase-separated state. However, the PLLA domain size was decreased, indicating that the domain was partially miscibile with the plasticizer and/or the tackifier. In addition, the distance between the bright PLLA spheres was significantly increased, confirming that the tackifier resin and plasticizer were mainly incorporated in the PDL rubbery matrix (Figure 4e).[56,57] This result was also consistent with the calculated M_e values by DMA analysis (Figure 4c), representing the dilute entanglement of the PDL rubbery matrix phase caused by the addition of tackifier and plasticizer.

Adhesion Performance. Adhesion behaviors of the ten PSA systems having the renewable polyester triblocks or the aliphatic TPEs coated on a PET film and four commercial adhesive tapes have been investigated by 180° peel, probe tack, and shear static adhesion on stainless steel panel in Figures 5−7 (Table S2).[58] The peel test determines the force needed to tear a 25 mm-wide strip of tape from a solid substrate at a constant speed and is expressed herein as N cm^{-1}, tack (*N*) is the property that controls the instant formation of a bonding interaction between adhesive and substrate when they are brought into contact, and shear strength (min) is internal resistance of an adhesive to creep under an applied load.[6,59]

The peel adhesions developed with increasing the content of PLLA−PDL−PLLA(5−100−5, 10−100−10, and 20−100−20) samples from 20 to 35 wt % in the PSA systems and the molar mass of PLLA hard phases from 20 to 40 kg mol^{-1}, eventually reaching the values of peel adhesion (2.6 N cm^{-1}) without any adhesive residue (Figure 5), which explains that the cohesive strengths of the PSAs were much higher and were consistent with the trend of the storage moduli values and tensile properties of the triblocks (Table 1). Because the amount of RE tackifier was constant with 50 wt % in all the PSA formulations, relatively high tack forces (2.0−3.0 N) were observed regardless of the contents of the base polymers and ESO plasticizers (Figure 6). Increasing the amounts of PLLA−PDL−PLLA(10−100−10 and 20−100−20) samples from 20 to 35 wt % in the PSA systems and the molar mass of PLLA segments from 10 to 40 kg mol^{-1} at the elastomer of 35 wt % led to a considerable increase in shear strengths, ultimately obtaining shear strength (ca. 23 000 min) with enhanced cohesive strengths. However, there was no effect for shear strengths on the elastomer content at the PSA system using PLLA−PDL−PLLA(5−100−5) and the molar mass of hard domains at all triblocks of 20 wt % (Figure 7).

After the peel test of the PSA having PLLA−PDL−PLLA(5−100−5) (Figure 5), cohesive failure was evident owing to weak mechanical strength of the triblock having no strain hardening behavior in the *S*−*S* curve (Figure 2), although reasonable PSA performances appeared (Figure 5−7; Table S2). Furthermore, the PSA having amorphous PLA−PDL−PLA(20−100−20) elastomer afforded a decrease of adhesive behaviors such as values of peel adhesion (2.5 N cm^{-1}) without any adhesive residue, tack force (2.2 N), and shear strength (ca. 16 000 min) (Figures 5−7), when compared to those of the PSA formulation having the semicrystalline elastomers, because the tensile properties of the amorphous triblock were inferior or comparable to PLLA−PDL−PLLA(20−100−20 and 10−100−10) samples (Figures 2 and S2). The enhanced mechanical properties derived from the crystallinity of PLLA segments in the triblocks could afford superior cohesive strength in the PSA systems, improving adhesion properties in terms of peel adhesion and shear strength. The peel tests of PSA samples having the acrylic and styrenic TPEs left adhesive traces on stainless steel plates due to incompatibility of the commercial elastomers with the biobased RE tackifier and the renewable ESO plasticizer (Figure 5), even though the adhesive properties were accepted, shown in Table S2. By comparison, tests on commercial duct, Scotch, and electrical tapes under identical conditions gave values of peel adhesion (1.4−5.5 N cm^{-1}) without any adhesive residue (Figure 5), tack force (0.9−2.6 N), and shear strength (ca. 500−1100 min) except Scotch tape, which had a value of over 50 000 min (Figures 6 and 7). Moreover, in previous work, ABA triblock copolymers such as poly(D,L-lactide)−poly(menthide)−poly(D,L-lactide) (PLA−PM−PLA) with 100 kg mol^{-1} PM midblock and 6−11 kg mol^{-1} PLA end blocks were prepared using the plant-based monomers menthide and D,L-lactide. Subsequently, PLA−PM−PLA polyesters for a PSA base elastomer were formulated with a renewable rosin ester (RE) tackifier, which showed self-adhesive performances having maximum values of peel adhesion (3.2 N cm^{-1}), tack (1.1 N) and static shear strength (ca. 2500 min) at 40 wt % RE tackifier.[38] However, the PSA systems were unbalanced with relatively larger amounts (60 wt %) of the elastomers having weak mechanical properties (E = 0.32−0.45 MPa, σ_b = 0.02−0.03 MPa, and ε_b = 630−1210%) without biobased plasticizer, which could present some difficulty for commercial applications.[21,38]

Taken together, self-adhesive test data proved that PSA formulations including PLLA−PDL−PLLA triblock copolymers with commercially available and renewable RE tackifier and ESO plasticizer are not only effective but also competitive with commercial TPEs and PSA tapes. Most importantly, the self-adhesive properties can be controlled and tuned by the amount and amorphous/semicrystalline hard domain molar mass of the renewable triblock copolymers in the PSA formulation, even using relatively small amounts (20 to 35 wt %) of the elastomers.

■ CONCLUSION

A renewable pressure-sensitive adhesive system was designed using triblock copolymeric elastomers, tackifier, and plasticizer derived from natural resources such as fatty acid, corn starch, rosin, and soybean oil. PLLA−PDL−PLLA triblock copolymers having semicrystalline hard blocks with three molar masses of 10, 20, and 40 kg mol^{-1} were synthesized as the base elastomer for PSA formulations by the one-pot, two-step process of ring-opening transesterification polymerization (ROTEP) of DL and LLA in a bulk system. NMR spectroscopy confirmed well-defined polymer architectures and size exclusion chromatography proved controlled molar masses and narrow distributions, proving chiseled block copolymers. Phase separation was indirectly elucidated with differential scanning calorimetry and atomic force microscopy. The mechanical properties were demonstrated by tensile test and dynamic mechanical analysis (DMA), showing elastomeric behaviors dependent on the molar mass composition or amorphous/semicrystalline structure of end blocks in the triblocks. A renewable rosin ester and an epoxidized soybean oil were formulated with relatively small amounts (35 and 20 wt %) of the triblocks. Probe tack, peel adhesion, and static shear strength tests were performed to evaluate the self-adhesive properties. The results were consistent with considerable adhesive performance. The properties of PSA based on the biobased polyesters could be also tailored or controlled with amounts and crystallinity of the hard domains of the triblock copolymers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00580.

> Molar mass data for PLLA−PDL−PLLA triblock copolymers; ^{1}H spectra for sequential addition; *S*−*S* curves for the commercial TPEs; TGA, DSC, and compatibility tests, DMA for the PSA formulation; adhesive test details and comparisons to commercial PSA tapes (PDF).

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Notes

The authors declare no competing financial interest.

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