Tunable Adhesion Properties of Hydrolytically Degradable Aliphatic Polyester Triblock/Diblock Copolymer Blends

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Abstract

Tuning the molecular architecture of block copolymer blends is a powerful strategy to optimize their performance in pressure-sensitive adhesive (PSA) formulations. To improve the sustainability of the typical petroleum derived and non-degradable PSAs, aliphatic polyester block copolymer blends of poly(*L*–lactide)–*block*–poly(γ–methyl–ε–caprolactone)–*block*–poly(*L*–lactide) (LML) and poly(*L*-lactide)-*block*-poly(γ-methyl-ε-caprolactone) (ML) were prepared by combining sequential ring-opening transesterification polymerizations and copper-catalyzed alkyne-azido cycloaddition reactions. We systematically investigated the effects of blend compositions on their microstructural, thermal, mechanical, and adhesion properties in PSA formulations that included tackifier. Using optimized triblock contents and thermal annealing protocols, the tackified PSAs exhibited competitive adhesion properties when compared to established styrenic PSAs. For example, a PSA of LML/ML (mass ratio = 1:1) with 20 wt% tackifier showed a peel strength of 3.66 ± 0.33 N cm^{-1}, a shear resistance of 429 ± 62 min and the desired adhesive failure mode. The competitive adhesion performance is attributed to a balance between dangling and bridging PγMCL midblocks in the rubbery matrix that simultaneously allows interfacial adhesion and cohesive strength for favorable PSA bonding and debonding. The LML/ML-based PSAs are hydrolytically degradable into water soluble or dispersible compounds at 45 °C under basic conditions within 25 days. Our results indicate rationally tailoring the molecular architecture of polyester block copolymer blends is a convenient and robust strategy to optimize their adhesion properties for sustainable PSA solutions.

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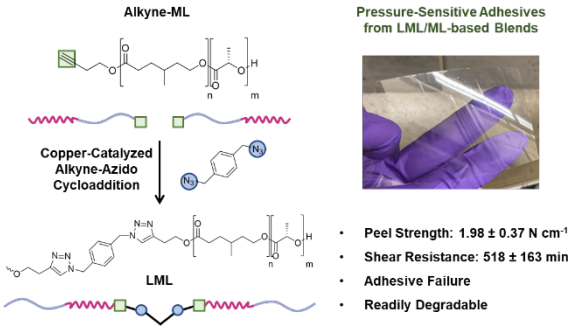


Introduction

Pressure-sensitive adhesives (PSAs) are soft solids that combine rapid substrate adhesion under light pressure, effective stress resistance once adhered, and clean removability without residue.[1-3] Ideal PSAs have complementary properties of viscous liquids and elastic solids, which necessitate precise design and engineering of their molecular characteristics, compositions, formulations, and processing techniques.[4-7] Among contemporary PSAs, tackified styrenic copolymers with a microphase-separated ABA triblock architecture are of particular interest due to their tunable mechanical properties and cost-effectiveness.[8-10] Styrenic ABA triblocks are typically comprised of 10–30 weight percent (wt%) glassy/minority "A" polystyrene (PS) blocks with the remainder being a chemically incompatible rubbery/majority "B" midblock (e.g., polyisoprene (PI) or polybutadiene (PB)) with a glass-transition temperature (T_g) well below room temperature.[8, 10] The rubbery "B" midblock forms a soft matrix to allow efficient interfacial adhesion and glassy, microphase-separated PS domains that act as physical cross-links provide cohesive strength and creep resistance under stress.[2] Blending tackifier that is chemically compatible with the rubbery midblock matrix results in selective midblock domain swelling. As a result, midblock entanglements are effectively diluted which promotes substrate adhesion.[11] These properties provide styrenic block copolymer-based blends with necessary adhesion properties for use in a wide range of applications, such as in tapes and labels.[1, 12]

Blending PS-*block*-PI-*block*-PS (SIS) triblocks with PS-*block*-PI (SI) diblocks is a convenient and robust strategy to optimize the mechanical properties and adhesion performance for PSAs.[10, 13-15] Compared to pure SIS or SI, previous work has shown that SIS/SI blends with 75 wt% SI diblock exhibited a significant increase in probe tack force and enhanced peel strength (the force per unit width required to debond a PSA from its substrate).[16] In this case, the SI diblock copolymer components were approximately half the molar mass of their SIS triblock analogs, while maintaining similar PS content. While the linear viscoelastic properties were comparable,[10] the progressive addition of SI diblock copolymer into the SIS/SI blends increased dangling PI ends in the rubbery matrix. Consequently, the enhanced dissipative properties and molecular mobility allowed more

efficient interfacial substrate adhesion.[4, 16] In contrast, the peel strength is heavily dependent upon nonlinear mechanical properties at large-strains.[3] Implementing rubbery PI bridging chains between hard PS domains increases the PSA cohesive strength, allowing for effective fibril formation and elongation during PSA debonding.[14-15] As a result, the primary debonding mechanism is adhesive failure, which is preferred over cohesive failure that generally leaves unwanted residue on the substrate. Optimizing the SIS/SI ratios in the blend enables convenient manipulation of the relative amounts of dangling PI ends and bridging PI chains in the rubbery matrix, which can be used to balance the interfacial adhesion and cohesive strength.

Unfortunately, styrenic block copolymers are petroleum-derived with poor degradability, primarily owing to their all carbon-carbon bond backbones, which contributes to an unsustainable life cycle and plastic waste accumulation.[17] Significant efforts have been devoted to develop more sustainable alternatives, such as aliphatic polyester block copolymers, with comparable performance in PSA formulations.[18-20] The unique advantages of aliphatic polyester block copolymers come from their degradability under various conditions and the fact that they can often be sourced from renewable feedstocks. For instance, the *γ*-methyl-*ε*-caprolactone and *L*-lactide monomers of poly(*L*-lactide)-*block*-poly(*γ*-methyl-*ε*-caprolactone)-*block*-poly(*L*-lactide) (LML) triblocks can be produced from renewable resources.[21-22] Moreover, LMLs can be readily degraded via enzymatic hydrolysis or under simulated industrial composting conditions.[23-24] Therefore, poly(lactide)-*block*-poly(menthide)-*block*-poly(lactide),[25] poly(lactide)-*block*-poly(*β*-methyl-*δ*-valerolactone)-*block*-poly(lactide),[5] poly(lactide)-*block*-poly(pentadecyl-caprolactone)-*block*-poly(lactide),[26] and other poly(alkyl-*δ*-lactone)-based polyester block copolymers[19] were successfully implemented in PSA applications, demonstrating promising adhesion properties with enhanced sustainability.

In our previous work,[27] tackified LML-based PSAs with semicrystalline poly(*L*-lactide) (PLLA) end blocks, showed competitive adhesion properties compared to commercial PSAs and are hydrolytic degradable. Inspired by previous efforts on SIS/SI blends and blends of poly(lactide-*co*-caprolactone) of different molar masses for improved adhesion performance,[28-29] we pursued tailored ratios of poly(*γ*-methyl-*ε*-caprolactone)-

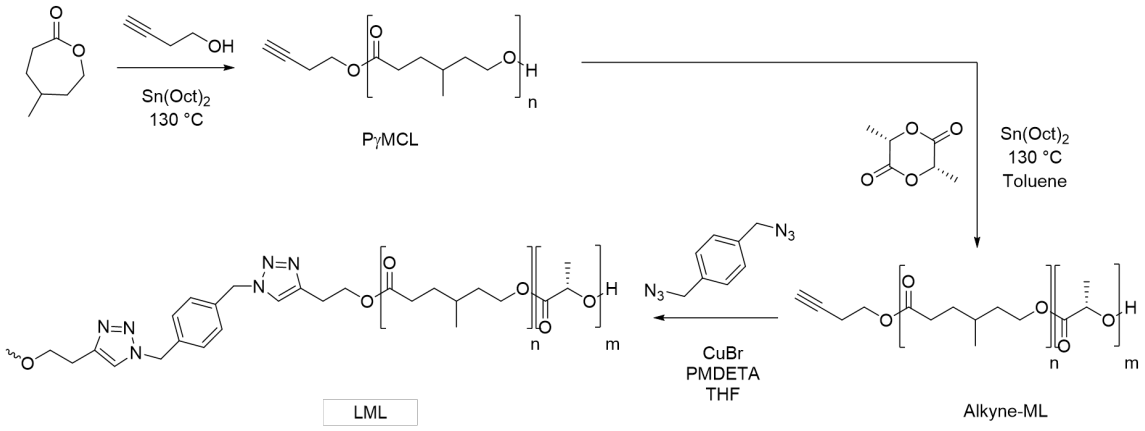
block-poly(*L*-lactide) (ML) diblocks and LML triblocks in tackified PSA formulations. We explored effects of blend composition on the thermal, microstructural, mechanical, and adhesion properties.

Here we report the synthesis of a set of LML/ML blends with tunable ratios by combining sequential ring-opening transesterification polymerization (ROTEP) and a copper-catalyzed alkyne-azido cycloaddition to produce the two components. The impacts of the LML wt% were probed by evaluating the thermal, microstructural, linear viscoelastic and tensile properties of blends after solvent-casting. The LML/ML blends were then mixed with a rosin ester tackifier to swell the poly(γ-methyl-ε-caprolactone) (PγMCL) rubbery matrix and evaluated as degradable PSAs. The formulated PSAs from tackified LML/ML blends with optimized LML wt% were also prepared by two different methods to demonstrate the generalizability of this approach. To further improve the adhesion properties, the PSAs with optimized formulations were subjected to a two-step annealing process after solvent casting. Compared to tackified LML-based PSAs, the tackified LML/ML blend-based PSAs exhibited tunable and substantially improved peel adhesion properties, with shear resistance values comparable to commercial products.

Results and Discussion

Synthesis and Molecular Characterizations

We synthesized end group functionalized ML by ROTEP (**Scheme 1**) and then coupled the reactive ML samples with a bifunctional linker to form LML/ML blends using a copper-catalyzed alkyne-azido cycloaddition reaction. Using literature procedures,[30-31] PγMCL was first synthesized by $Sn(Oct)_2$-catalyzed ROTEP in the melt at 130 °C for 90 min to reach high (>95%) monomer conversion using an alkyne-functionalized alcohol 3-



Scheme 1. Synthesis of alkyne-terminated PγMCL, alkyne-terminated poly(*L*-lactide)-*block*-poly(γ-methyl-ε-caprolactone) (Alkyne-ML), and LML.

butyn-1-ol as initiator. The as-prepared alkyne-terminated PγMCL had a total number average molar mass (M_n) of 33.1 kg mol^{-1}, determined by performing end-group analysis with proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The alkyne-terminated PγMCL with a hydroxyl end was used as a macroinitiator for the $Sn(Oct)_2$-catalyzed ROTEP of *L*-lactide at 130 °C for 90 min in toluene. The as-prepared alkyne-ML diblock copolymers were purified following previous work[31] and characterized by ^{1}H NMR spectroscopy (**Figure S1-S2**) and size exclusion chromatography (SEC) (**Figure S3**). The SEC trace of alkyne-ML showed a clear shift in the elution time compared to that of its PγMCL precursor, while the ^{1}H NMR spectra also indicated a shift of the methylene terminal resonance from 3.7 ppm of PγMCL to 4.4 ppm of PLLA,[31] supporting the successful preparation of ML diblock copolymers. The alkyne terminus of ML diblock copolymers was validated by the presence of a peak around 1.95 ppm in the ^{1}H NMR

spectra **(Figure 1**). The alkyne-terminated ML diblock copolymer, denoted alkyne-ML(38.8, 0.26), had a total M_n of 38.8 kg mol^{-1}, dispersity ($Đ$) of 1.56, and a PLLA volume fraction (f_{PLLA}) of 0.26, which is similar to that of PLLA or PS hard blocks in previously reported block copolymers used in PSAs.[6, 13, 32]

The copper-catalyzed alkyne-azido cycloaddition reaction has been shown to be useful for modifying the molecular architecture of polyesters.[33-35] Following a literature procedure,[36] a bifunctional linker, α,α'-diazido-*p*-xylene, was synthesized, characterized via ^{1}H NMR spectroscopy (**Figure S4**). The bifunctional α,α'-diazido-*p*-xylene can be used to link two alkyne-ML(38.8, 0.26) diblock copolymers and form a LML triblock. The alkyne-azido cycloaddition reactions were executed in tetrahydrofuran (THF) at room temperature without light exposure, and catalyzed by CuBr for 24 h. The ligand N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA) was used to improve the solubility and reactivity of CuBr in THF. After purification (details in *Electronic Supplementary Information*), ^{1}H NMR spectroscopic (**Figure 1**) and SEC analysis (**Figure 2**) corroborated the successful synthesis produced LML triblock architecture with commensurate arm length and f_{PLLA} as the ML diblock precursors.

All ^{1}H NMR spectra of LML/ML blends showed a substantial reduction in alkyne end group intensity (1.95 ppm) and emergence of new methylene hydrogens at 5.5 ppm and 2.8 ppm. The similar peak integration areas of these two distinctive methylene resonances indicated both azido ends on the linker had reacted with alkyne groups on ML(38.8, 0.26), suggesting successful LML formation. The LML wt% in the as-formed blends can be readily adjusted by tuning the alkyne-to-azido molar ratio. The LML wt% in the blends was determined by comparing peak integration areas of hydroxyl termination resonance at 2.65 ppm[37] and methylene resonances at 5.5 ppm. Full conversion of ML to LML would lead to a ratio of 1 to 2 and 100 wt% LML in the blend. For example, 50% conversion of alkyne groups would yield a 1 to 1 ratio of these two peaks (third trace from the bottom in **Figure 1**). Since the as-formed LMLs have approximately twice the molar mass of pristine alkyne-ML(38.8, 0.26), 50% conversion of alkyne-ML(38.8, 0.26) would produce an LML/ML blend with 50 wt% LML. Three LML/ML blends were prepared with

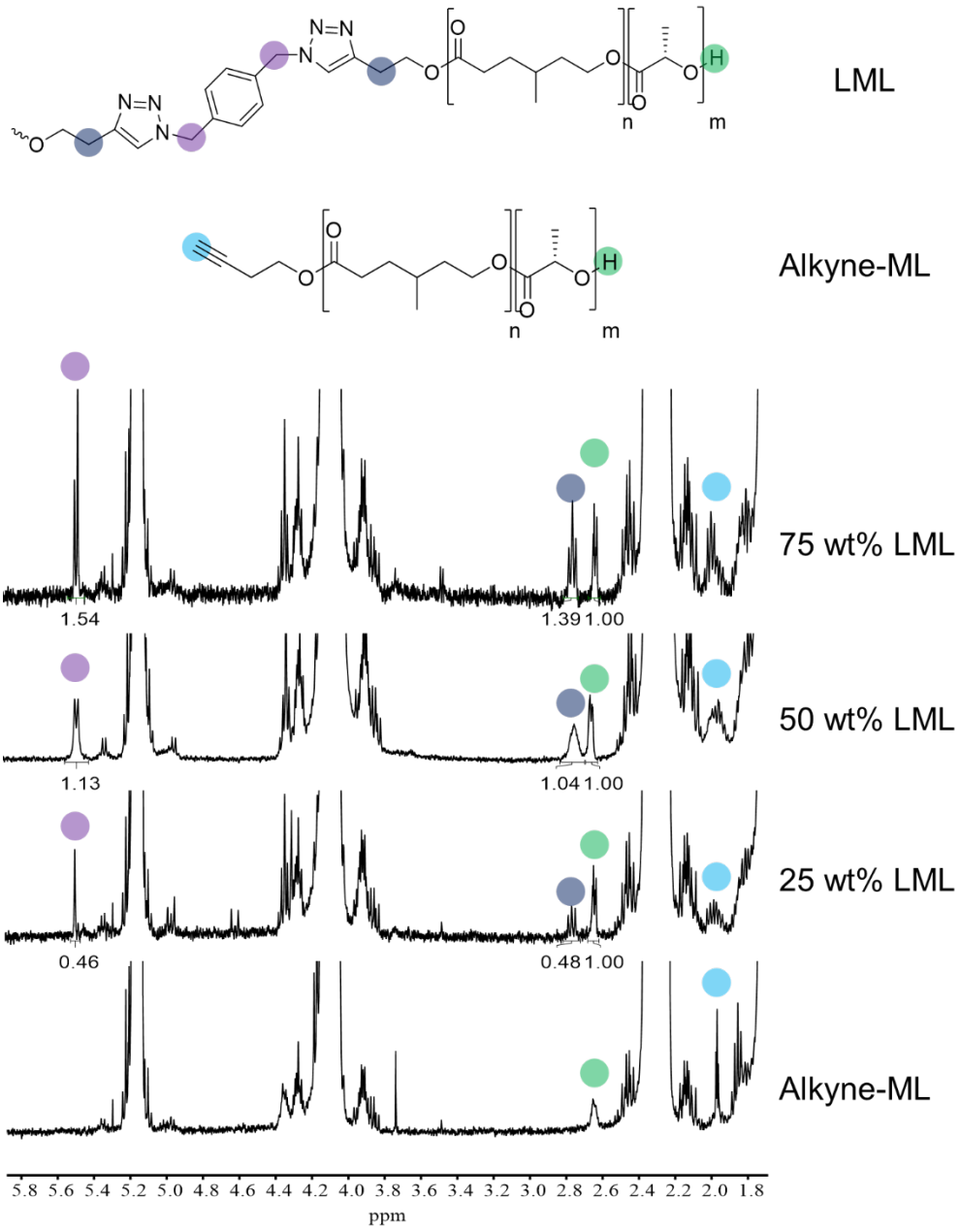


Figure 1. ^{1}H NMR spectra of alkyne-ML and LML/ML blends.

25 wt% (second trace from the bottom in **Figure 1**, denoted 25 wt% LML), 50 wt% (third trace from the bottom in **Figure 1**, denoted 50 wt% LML), and 75 wt% (top trace in **Figure 1**, denoted 75 wt% LML) LML, respectively. However, previous studies showed that the second ROTEP of *L*-lactide could also produce PLLA homopolymer alongside block copolymers if there is adventitious initiator present,[30, 37] which may result in some error in determining (and very likely underestimating) the reaction conversion and LML wt% in

the blends via ^{1}H NMR. The exchangeable protons on the hydroxyl terminations may also introduce errors in determining the LML to ML ratios. Theoretically, the methylene resonances at 5.5 ppm should be a singlet as shown in the pristine linker (**Figure S4**) and 25 wt% LML, rather than a doublet in 50 wt% and 75 wt% LML. The exact reason of this change of multiplicity is unknown, but may come from the formation of regioisomers.

Successful preparation of LML/ML blends was also confirmed via SEC analysis; all blends shifted to shorter elution times (**Figure 2**), indicating a molar mass increase after ML-linking reactions (**Table 1**). While a bimodal SEC trace from a sample containing both

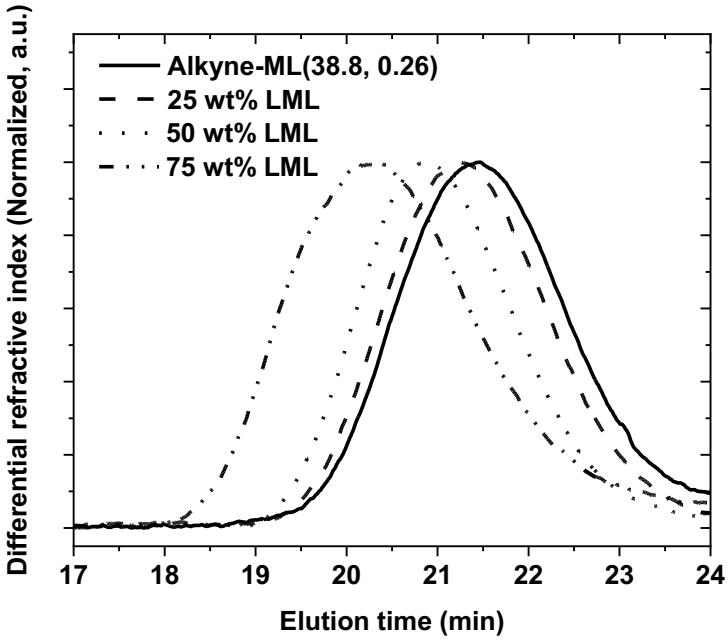


Figure 2. THF-SEC traces of alkyne-ML(38.8, 0.26) and LML/ML blends.

LML triblock and ML diblock copolymers may be expected, the high dispersity of the starting alkyne-ML(38.8, 0.26) ($Đ$ = 1.56) resulted in the observation of a unimodal but broad shape in the respective blend SEC traces. While the molar masses of 25 wt% LML and 50 wt% LML blends followed expectation based on coupling conversion, the 75 wt% LML blend yielded a molar mass (81.6 kg mol^{-1}), slightly higher than the theoretical molar mass of fully converted alkyne-ML(i.e., 77.6 kg mol^{-1}). While azido functionalized polyacrylates are known to cross-link and form networks via nitrene insertion into a C-H-

containing backbone under UV light irradiation,[38] a control polymer sample was prepared without alkyne functionalization and reacted under these conditions, which confirmed no detectable nitrene insertion side reaction occurred (details in **Table S1** and **Figure S5**). The slightly higher molar mass of 75 wt% LML blend and narrowed blend products compared to the alkyne-ML precursor may be a combined result from an underestimated amount of LML, error in SEC measurement, e.g., due to small amounts of column interactions, and/or high dispersity of starting alkyne-ML(38.8, 0.26).

In the ^{1}H NMR spectrum of the 25 wt% LML blend, the peak intensity of the alkyne endgroup in unreacted alkyne-ML diblock was much lower than expected based on the end-group analysis mentioned above. To verify if alkyne-ML(38.8, 0.26) with active alkyne endgroups remained in the blend, a small portion of 25 wt% LML blend was subjected to further reaction with excess α,α'-diazido-*p*-xylene bifunctional linker (molar ratio of azido to residual alkyne = 2:1) under the same conditions of initial copper-catalyzed alkyne-azido cycloaddition. Notably, SEC results (**Figure S6** and **Table S2**) showed the molar mass of the 25 wt% LML blend could be further increased to 77.8 kg mol^{-1}, which is comparable to the theoretical molar mass for 100 wt% LML (77.6 kg mol^{-1}). This result suggests the alkyne terminations remained active in the blends with high residual ML content and further confirmed that the excess azido group does not participate significantly in unfavorable nitrene insertion side reactions.

Table 1. Molar mass and dispersity of the as-prepared alkyne-ML block copolymers and LML/ML blends.

Sample ID ($M_{n,total}$, f_{PLA})	$M_{n,SEC,MALLS}$ (kg mol^{-1})[a]	$Đ$[b]
Alkyne-ML(38.8, 0.26)	36.4	1.56
25 wt% LML	45.5	1.41
50 wt% LML	57.2	1.40
75 wt% LML	81.6	1.71

[a]Determined using THF-SEC with multi-angle laser light scattering (MALLS) detector.
[b]Determined using THF-SEC with differential refractive index (RI) detector.

Microstructural, Thermal, Linear Viscoelastic and Tensile Properties

Before blending with tackifier and implementing as PSAs, to understand the impacts of LML contents, the alkyne-ML(38.8, 0.26) and three LML/ML blends were solvent-cast from chloroform into 400 μm films (details in *Electronic Supplementary Information*). Similar to previous work,[27] the small angle X-ray scattering (SAXS) patterns (**Figure 3**) of pristine alkyne-ML(38.8, 0.26) and three LML/ML blends showed broad principal scattering peaks and no higher-order peaks after solvent casting, suggesting some level of

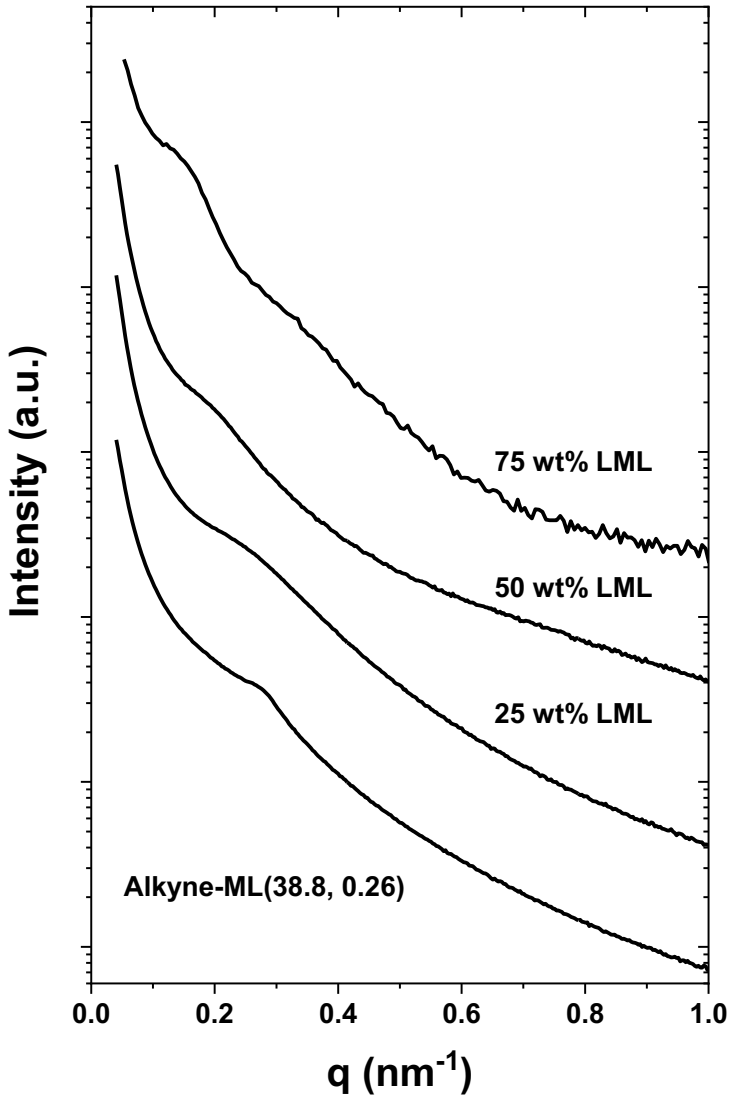


Figure 3. SAXS patterns of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting. (Vertically shifted for clarity)

microphase separation without long-range order. The rapid chloroform evaporation during the solvent casting and drying process likely trapped the blends in a non-equilibrium state.[39] Similar scattering patterns observed in the alkyne-ML(38.8, 0.26) and three LML/ML blends highlights that the introduction of molecular linkage and bridging PγMCL chains did not significantly impact the microphase separated morphology during solvent casting, which is similar to the case of poly(cyclohexylethylene)-*block*-poly(ethylene) multi-block polymer blends.[40] However, the principle domain spacing $D = 2\pi / q^*$ is 22.8 nm for alkyne-ML(38.8, 0.26) at room temperature, where q^* is the scattering vector at the primary peak. Since domain spacing scales with increasing molar mass,[41] we expected formation of LML triblocks to lead to larger domain spacings, evidenced by shifts to lower q^*-values. As expected, the formation of LML shifted q^* to lower values and increased domain spacing to 26.7 nm of 25 wt% LML blends, 31.9 nm of 50 wt% LML blends, and 38.8 nm of 75 wt% LML blends. These results corroborated the linking of alkyne-terminated ML diblock copolymers produced LML triblock architecture in the blends with higher molar mass and longer chain length, which may contribute to more bridging PγMCL chains in the rubbery PγMCL matrix that connect to two PLLA hard domains.

The thermal properties were investigated by differential scanning calorimetry (DSC) (**Figure 4**) and summarized in **Table 2**. After solvent casting, the first heating traces of alkyne-ML(38.8, 0.26) and LML/ML blends all showed a $T_{g,P\gamma MCL} \approx -60$ °C, a $T_{g,\ PLLA}$ around 54–59 °C, and a $T_{m,PLLA}$ (melting temperature of semicrystalline PLLA) centered around 160 °C, indicating the alkyne-ML(38.8, 0.26) and LML/ML blends shared similar thermal properties. The presence of T_g's for both block types supports microphase separation between PγMCL and PLLA blocks.[27, 30-31] The degree of PLLA crystallinity remained low (i.e., around 0.1 in **Table 2**) and was similar in all blends without a clear trend, which may be a result of formation of a non-equilibrium microstructure during rapid solvent evaporation. The appearance of an additional shoulder in the melting endotherms of alkyne-ML(38.8, 0.26) and 25 wt% LML traces may be attributed to the formation of smaller PLLA crystals or less-perfect α'-form of PLLA crystals, which normally have a lower melting temperature than the more stable α-form PLLA crystals.[42]

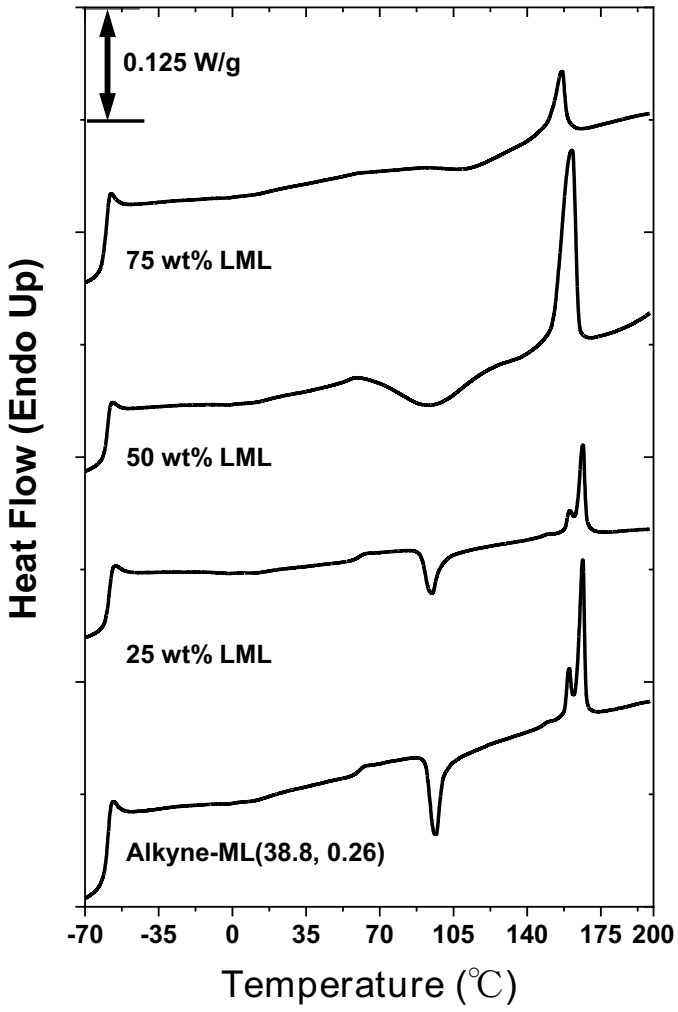


Figure 4. DSC traces of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting (first heating, 10 ℃ min^{-1}). (Vertically shifted for clarity)

The alkyne-ML(38.8, 0.26) and 25 wt% LML blend could cold crystallize around 95 ℃ (peak temperature of cold crystallization exotherm). The 50 wt% LML blend showed a similar peak temperature of cold crystallization exothermic transition at 94 ℃, but a broad cold crystallization peak, while 75 wt% LML blends only cold crystalized at 110 ℃ with a broad peak shape and smaller amplitude. In the case of poly(ethylene glycol)-*block*-poly(*L*-lactide) block copolymers (PEG-*b*-PLLA) with distinctive architectures, the increased arm number of PEG-*b*-PLLA with same molar masses of PLLA and PEG yielded reduced PLLA crystallinities, which was attributed to the reduced mobility of the star block copolymers.[43] The reduced cold crystallization kinetics have also been reported in poly(*L*-

lactide)-*block*-poly(ethylene-*co*-ethylethylene) polymers with multi-block architecture and restricted chain mobility of bridges and loops.[44] In this context, the increase of cold crystallization temperature and broadening of cold crystallization peaks may also reflect the presence of more LML triblocks with reduced mobility in the 50 wt% LML and 75 wt% LML blends.

Table 2. Thermal properties of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting.

Sample ID	$T_{g,\ P\gamma MCL}$ (°C)[a]	$T_{m,\ PLLA}$ (°C)[b]	$T_{g,\ PLLA}$ (°C)[a]	Degree of PLLA crystallinity[c]
Alkyne-ML(38.8, 0.26)	–60	160, 166	59	0.05
25 wt% LML	–59	160, 166	59	0.03
50 wt% LML	–60	160	54	0.12
75 wt% LML	–61	156	55	0.06

[a]Determined during DSC measurement of first heating at 10 °C min^{-1}. [b]Determined as the peak of melting endotherm during DSC measurement of first heating at 10 °C min^{-1}. [c]Determined using the equation for degree of crystallinity = $\Delta H_m/(w_{PLLA} \times \Delta H_m^{\infty})$, where ΔH_m is the enthalpy of melting taken as the area under the melting endotherm during the first heat at 10 °C min^{-1}, ΔH_m^{∞} = 93 J g^{-1}, and w_{PLLA} is the weight fraction of PLLA.

The linear viscoelastic properties of these blends were investigated using small amplitude oscillatory shear (SAOS) with frequency sweeps between –20 to 80 °C (**Figure 5** and **Figure S7**). Master curves were generated by horizontally shifting the data using a reference temperature of 20 °C. Effective PSAs should readily wet the substrate as a viscous liquid during a typical one-second bonding time, which requires the storage modulus (*G'*) to be less than 0.3 MPa at 1 rad s^{-1} (Dahlquist criteria).[45] Moreover, the tan(δ) (i.e., *G''*/*G'*, where *G''* is the loss modulus) should be 0.1-1.0 for sufficient cohesive strength and effective energy dissipation during debonding.[1]

The alkyne-ML(38.8, 0.26) and LML/ML blends showed similar plateau *G'* at high frequency range (i.e., 2.1 MPa of alkyne-ML(38.8, 0.26), 1.5 MPa of 25 wt% LML blend, 2.3 MPa of 50 wt% LML blend and 3.1 MPa of 75 wt% LML blend at 100 rad s^{-1},

respectively). The value of plateau modulus is dependent on the presence of entanglements in the rubbery matrix,[9-10] and PγMCL has a reported entanglement molar mass (M_e) of 2.9 kg mol^{-1}.[31] Therefore, alkyne-ML(38.8, 0.26) possesses a well-entangled rubbery matrix. While the formation of the LML triblock architecture does not increase the entanglement density in the blends, both LML and ML samples yielded similar plateau moduli in the high-frequency range (greater than 10^1 rad s^{-1}), akin to previous reports of SIS/SI blends.[10, 15]

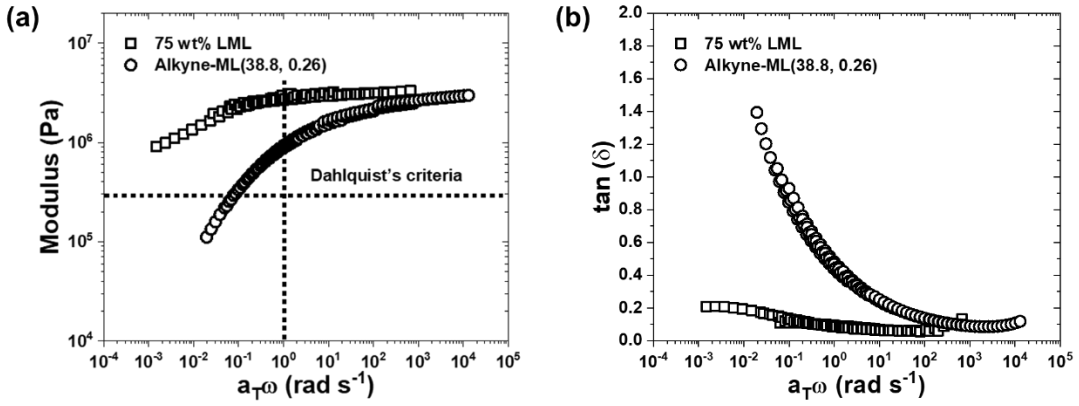


Figure 5. Master curves for the (a) storage modulus (*G'*) and (b) tan (δ) of alkyne-ML(38.8, 0.26) and 75 wt% LML blends after solvent casting. The Dahlquist criterion (*G'*=0.3 MPa at 1 rad s^{-1}) is marked by dashed lines.

After solvent casting, the alkyne-ML(38.8, 0.26) (**Figure 5**), 25 wt% LML (**Figure S7a**) and 50 wt% LML (**Figure S7b**) showed a relaxation at low frequencies that is more dissipative, evidenced by a high tan(δ). For instance, the tan(δ) at 1 rad s^{-1} for the ML diblock, 25 wt% LML blend, and 50 wt% LML blend were 0.47, 0.28, and 0.25, respectively. In contrast, the 75 wt% LML exhibited a low tan(δ) value of 0.09 at 1 rad s^{-1}, which is similar in magnitude to pure LML triblocks used as thermoplastic elastomers.[27, 31] The increase of LML content proportionally decreased the tan(δ) values and enhanced the elasticity of the blends, while dangling PγMCL ends of alkyne-ML(38.8, 0.26) could relax at long relaxation time facilitating the drop of *G'* in the low frequency range and produced liquid-like, viscoelastic behavior. By tuning the LML content in the blends, the *G'* at 1 rad s^{-1} increased from 0.91 MPa of alkyne-ML(38.8, 0.26) to 0.94 MPa (25 wt%

LML), 1.35 MPa (50 wt% LML), and 2.67 MPa (75 wt% LML). Therefore, these results indicate that tuning the molecular architecture in polyester block copolymer blends allows for convenient manipulation of their viscoelastic properties. However, the *G'* at 1 rad s^{-1} of alkyne-ML(38.8, 0.26) and all LML/ML blends are all higher than the aforementioned Dahlquist criteria (i.e., 0.3 MPa at 1 rad s^{-1}), highlighting the importance of adding tackifiers to enable more effective surface wetting for PSA applications.[1, 6, 11]

In addition to linear viscoelastic properties, the debonding of PSAs is impacted by their mechanical properties at large strain.[14-15] To understand the large-strain regime, nonlinear elastic behaviors of alkyne-ML(38.8, 0.26) and LML/ML blends during the PSA debonding process were examined; 3 replicate samples for each formulation were subjected to tensile testing at an extension rate of 305 mm min^{-1} which is the same to the PSA peeling rate in the following 180° peel tests. Representative tensile data is shown in **Figure 6** and **Table 3**.

Table 3. Tensile properties of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting.

Sample ID	δ_{Break}[a] (MPa)	ε_{Break}[a] (%)
Alkyne-ML(38.8, 0.26)	0.28 ± 0.05	77.2 ± 2.8
25 wt% LML	1.06 ± 0.05	853.3 ± 71.1
50 wt% LML	1.66 ± 0.09	649.3 ± 29.0
75 wt% LML	2.93 ± 0.12	457.0 ± 7.8

[a]Average values and standard deviations are calculated from tensile test of 3 replicates of each formulation extended at 305 mm min^{-1} until failure.

The pristine alkyne-ML(38.8, 0.26) contains no PγMCL bridging chains and accordingly is soft and has low ductility, with an average stress at break (δ_{Break}) of 0.28 ± 0.05 MPa and average strain at break (ε_{Break}) of 77.2% ± 2.8%. As a consequence, the lack of cohesive strength and ductility in the alkyne-ML(38.8, 0.26) is anticipated to compromise formation and extension of adhesive fibrils during the PSA debonding process, suggesting low peel strength and unfavorable cohesive failure (i.e., leaving PSA residue

on the substrate). The incorporation of 25 wt% LML in the blend significantly increased the tensile strength and ductility, produced an average δ_{Break} of 1.06 ± 0.05 MPa and an average ε_{Break} of 853.3% ± 71.1%. In the 25 and 50 wt% LML blends, strain softening was observed at intermediate strains, followed by strain hardening at high strain, which is similar to SIS/SI blends with a low SIS content.[14] Most SIS triblocks formed bridging PI midblocks without dangling ends, while the addition of SI diblocks of half molar mass linearly reduced the concentration of bridging PI chains in the SIS/SI blends.[46]

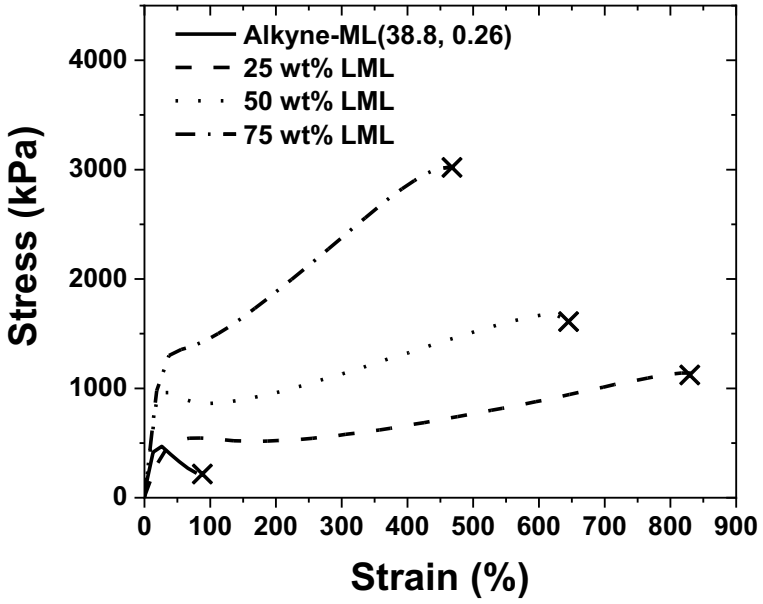


Figure 6. Representative tensile data for alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting. Extended at 305 mm min^{-1}, with the break point indicated by ×.

Further increase of LML content lead to continuous enhanced tensile strengths, and enhanced strain hardening effects with onsets at lower strain, and reduced ε_{Break} of 649.3% ± 29.0% of 50 wt% LML blends and 457% ± 7.8% of 75 wt% LML blends; these features resemble SIS/SI blends with high SIS triblock contents or pure SIS triblocks.[14-15] By systematically tuning the LML contents, the nonlinear mechanical properties of LML/ML blends were readily varied to suit PSA applications.

Adhesion Properties

A renewable rosin ester tackifier (Sylvalite RE 80HP, solid powder at room temperature) was blended with alkyne-ML(38.8, 0.26) and LML/ML blends to dilute the entanglements in the PγMCL rubbery matrix and promote interfacial adhesion with the substrate. The mass fraction of tackifier was kept at 20 wt% in the PSAs to avoid phase separation of the tackifier and PγMCL midblocks at high tackifier loading observed in a previous study.[27] The PSAs were prepared by blending all compounds in chloroform and solvent casting using a wire wound rod on poly(ethylene terephthalate) (PET) film (details in *Electronic Supplementary Information*) and drying, resulting in transparent PSA films with thickness around 80 μm. The adhesion properties of the PSAs were then characterized in terms of their peel strength, failure mode in peel adhesion tests and shear resistance time under an applied shear stress of about 15.2 kPa on stainless steel substrates (**Figure 7** and **Table 4**). Details of experimental conditions and parameters can be found in the *Electronic Supplementary Information*.

PSAs from tackified alkyne-ML(38.8, 0.26) showed a peel strength of 1.23 ± 0.15 N cm^{-1} and cohesive failure in the 180° peel adhesion test, leaving adhesive residue on the stainless-steel substrate (**Figure 7a**, leftmost image), leaving adhesive residue on the stainless-steel substrate (**Figure 7a**, leftmost image). With more LML, the peel adhesion failure mode shifted from cohesive failure to more preferred adhesive failure, without leaving any adhesive residue on the substrate after peeling (**Figure 7a**, middle and rightmost image). Without LML triblock bridging, alkyne-ML(38.8, 0.26)-based PSAs lacked cohesive strength to maintain their structural integrity during the debonding process; this is also reflected by the low shear resistance (i.e., 56 ± 10 min), highlighting an opportunity for improvement by addition of LML triblock. The addition of LML in the tackified PSAs increased the shear resistance (**Figure 7b** and **Table 4**) (e.g., 1497 ± 273 min of tackified PSA from 75 wt% LML in LML/ML blends). We posit the increased LML triblock content established an increased concentration of elastic interconnecting PγMCL midblock bridging segments, allowing the PSA to maintain microstructural integrity and ultimately led to enhanced shear resistance and change in peel adhesion failure mode.

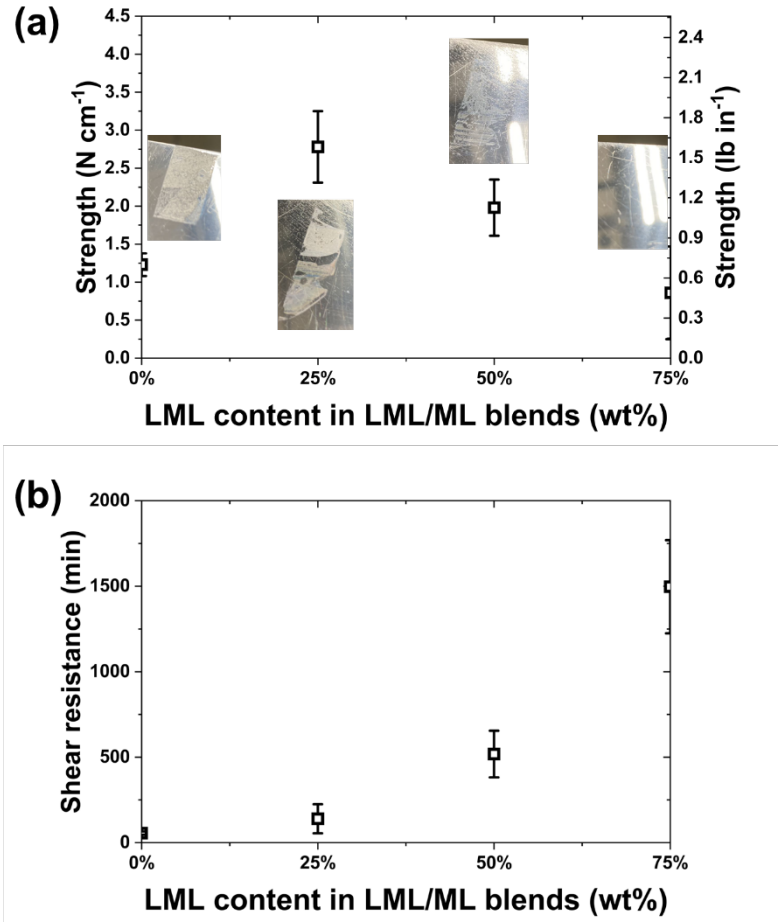


Figure 7. (a) 180° peel adhesion properties and (b) shear resistance properties on stainless steel substrates of alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting with additional 20 wt% tackifier. All of the 180° peel adhesion tests were performed at the rate of 305 mm min^{-1}. Inserted digital images in (a) showed the stainless steel substrates surface after the 180° peel adhesion tests.

The relationship between LML content in the PSA formulations and peel strength is shown in (**Figure 7a**). Compared to tackified PSA using pure ML, the tackified PSA with 25 wt% LML showed an increase in peel strength to 2.78 ± 0.47 N cm^{-1}. The peel strength then monotonically decreased with more LML (1.98 ± 0.37 N cm^{-1} of 50 wt% LML and 0.86 ± 0.61 N cm^{-1} of 75 wt% LML) as the PSA became more elastic and thus was less prone to wetting and establishing good contact with the substrate. At low LML contents, the LML/ML blends maintained dissipative characteristics from pure ML diblocks and possess low *G'* that promotes interfacial adhesion with the substrate during

PSA bonding. As indicated by the high ductility during tensile testing, the presence of LML triblocks enhanced the cohesive strength of the PSA and likely enabled effective fibril extension during PSA debonding. Collectively, the sufficient interfacial adhesion and enhanced cohesive strength contributed to improved peel strength and a transition to adhesive failure. However, in the case of 75 wt% LML, the high *G'* and low tan(δ) simultaneously reduced the interfacial adhesion likely due to poor wetting, leading to decreased peel strength, which is similar to the case of pure LML triblocks and 20 wt% tackifier in our previous study (i.e., 0.35 ± 0.02 N cm^{-1}).[27] Therefore, by systematically manipulating the LML triblock content in the blends, the adhesion properties of tackified PSA can be readily tuned.

Table 4. Adhesion properties of PSA from alkyne-ML(38.8, 0.26) and LML/ML blends after solvent casting with additional 20 wt% tackifier.

Sample ID	Peel strength (N cm^{-1})	Peel adhesion failure mode	Shear (min)
Alkyne-ML(38.8, 0.26)	1.23 ± 0.15	Cohesive failure	56 ± 10
25 wt% LML	2.78 ± 0.47	Cohesive failure	140 ± 85
50 wt% LML	1.98 ± 0.37	Cohesive/adhesive failure	518 ± 163
75 wt% LML	0.86 ± 0.61	Adhesive failure	1497 ± 273

To further evaluate the adhesion properties, the tackified PSAs were subjected to a two-step annealing process (i.e., first above the melting temperature of PLLA at 170 ℃ for 60 minutes and second at 100 ℃ to cold-crystallize the PLLA).[27] The shear resistance of the PSAs did not significantly change (**Figure S9** and **Table S3**). Similar to our previous results, formation of enhanced microphase separation and semicrystalline PLLA domains contributed to substantially enhanced peel strengths after annealing (**Figure S10** and **Table S3**). For instance, the peel strengths of tackified PSAs were increased to 2.37 ± 0.48 N cm^{-1} (alkyne-ML(38.8, 0.26)), 4.11 ± 0.16 N cm^{-1} (25 wt% LML), 3.66 ± 0.33 N cm^{-1} (50 wt% LML) and 1.53 ± 0.28 N cm^{-1} (75 wt% LML), which is comparable to commercial

products.[26] This demonstration is encouraging as it is more relevant to high speed accelerated solvent drying processes or hot melt PSA processing.

We explored the potential generalizability of this blending approach in a more polymer manufacturing friendly manner using two different methods to prepare LML/ML blends with 50 wt% LML. First, LML(74.0, 0.25) and ML(37.5, 0.22) were synthesized separately by sequential ROTEPs with similar compositions and arm length by using 1,4-benzenedimethanol and benzyl alcohol as initiator, respectively. Molecular characteristics of LML(74.0, 0.25) and ML(37.5, 0.22) can be found in **Table S2**. The separately as-prepared LML(74.0, 0.25) and ML(37.5, 0.22) were then dissolved in chloroform to form LML/ML blend of 50 wt% LML. In a separate experiment, a mixture of 1,4-benzenedimethanol and benzyl alcohol initiators were added together in a 1 to 2 molar ratio to form LML/ML blends of 50 wt% LML by simultaneous sequential ROTEP. This approach should theoretically yield ML and LML of similar compositions and arm length. The molar mass of PγMCL was controlled by the molar ratio of monomer to hydroxyl group of the initiators (250 to 1) and a conversion over 95%, producing roughly 30 kg mol^{-1} PγMCL, which is similar to the length of the PγMCL arm in the other two methods. The f_{PLLA} was controlled by the amount of *L*-lactide monomer added to the reaction, and running to high monomer conversion in the second ROTEP step. The molecular characteristics of LML/ML blends synthesized from the third method can be found in **Table S4**. However, the precise LML content in the blend could not be readily determined due to the unimodal peak shape in the SEC trace (**Figure S11**). The solvent-cast PSAs with additional 20 wt% tackifier of these LML/ML blends were prepared following the same procedure noted above and the 180° peel test results were summarized in **Table S5**.

Under the same processing conditions and with the same amount of tackifier, the peel strengths of PSAs from these two routes (i.e., 1.65 ± 0.25 N cm^{-1} from post-synthesis blending and 1.21 ± 0.52 N cm^{-1} from simultaneous polymerization) were not statistically different from that of PSAs prepared from LML/ML blends synthesized by azide-alkyne coupling synthetic strategy (**Table S5**), and all PSAs failed by adhesive failure. The small difference among different synthetic routes may originate from slightly different compositions and molar masses, and LML contents in the blends that are not exactly

equivalent. Nonetheless, regardless of preparation method, PSAs from LML/ML blends with optimized LML contents should manifest similar, improved adhesion properties compared to that of pure LML triblock or ML diblock copolymers.

Hydrolytic Degradation

The hydrolytic degradation of as-prepared PSAs was performed in 1 M NaOH aqueous solution at 45 °C and monitored by total organic carbon (TOC) analysis to quantify hydrolyzed products that leached into the aqueous media (**Figure 8** and **Figure S12**). Pristine LML triblocks were found to be completely degradable via hydrolytic degradation under the same conditions,[27] by enzymatic catalysis,[23] or under simulated industrial composting conditions.[24] Under basic conditions, all transparent PSAs turned opaque in 1 day and detached from the PET substrate after 10 days, forming white particles suspended in the solution. As shown in **Figure 8**, the hydrolytic degradation of tackified PSAs from LML/ML blends of 50 wt% LML led to a rapid increase in TOC values during the first 7 days and reached plateau values around 80% degradation after 15 days, affirming the excellent hydrolytic degradability of LML-based polyester block copolymer blends under basic conditions. Increasing the LML content in the blend did not change the TOC plateau values (**Figure S12**), but slightly reduced the degradation kinetics. Since all PSAs afforded similar compositions and were degraded under the same process, the slightly slower degradation kinetics were possibly a result of the longer time that the higher molar mass LML needed to be degraded into water-soluble or dispersible products. In a previous study, PSAs from tackified LML triblocks also experienced incomplete degradation under these conditions,[27] which was attributed to the lack of hydrolytic degradability of the rosin ester tackifier.[47] Clearly, the LML/ML blends studied here exhibited high levels of hydrolytic degradability while also affording enticing tunability through molecular architecture and blend composition for optimizing their adhesion properties.

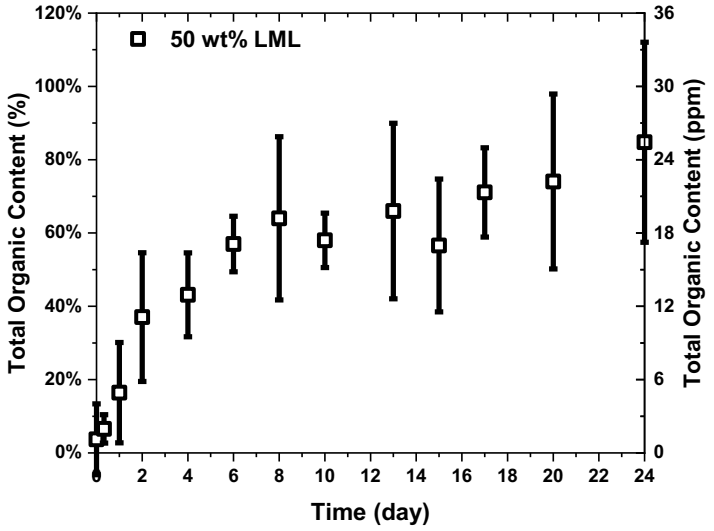


Figure 8. Hydrolytic degradation of solvent cast 20 wt% tackified LML/ML blend PSAs with 50 wt% LML in 1 M NaOH aqueous solution at 45 °C. The total organic carbon (TOC) content is the ratio of measured organic carbon in the aqueous solutions to the theoretical total carbon content of the blends with tackifier. The data points and error bars represent average and range for triplicate experiments, respectively.

Conclusion

LML/ML all-aliphatic polyester block copolymer blends were successfully prepared by combining sequential ROTEP to form ML diblock copolymers with a terminal alkyne and then coupling a fraction of the parent diblocks by copper-catalyzed alkyne-azido cycloaddition. The LML content in the blends after coupling could be tailored from 25 wt% to 75 wt% by tuning the stoichiometric ratio of bifunctional azido linker to alkyne ended ML diblock copolymer. This provided convenient strategy to prepare LML/ML blends with the same composition and arm length, but distinctive molecular architectures via azide-alkyne coupling. The effect of LML blend content on the microstructure, crystallinity, thermal and mechanical properties of the blends were systematically investigated. PSAs were formulated by blending with 20 wt% of a renewable tackifier, and the application of these LML/ML blends as PSAs showed widely tailorable adhesion properties that correlated to the LML content. With 50 wt% of LML in the LML/ML blends, the tackified PSAs exhibited simultaneously sufficient interfacial adhesion and improved

cohesive strength owing to the balance of dangling and bridging PγMCL chains in the rubbery matrix. After solvent casting, the PSA afforded a 1.98 ± 0.37 N cm^{-1} peel strength, desired adhesive failure mode in 180° peel test and a shear resistance of 518 ± 163 minutes. After an additional two-step annealing process, the peel strength of this tackified PSA of the same composition was further improved to 3.66 ± 0.33 N cm^{-1}, which is comparable to many commercial products, with no significant difference in shear strength. It was shown that this blending approach is potentially generalizable via other more polymer manufacturing friendly approaches, such as post-synthesis blending and simultaneous polymerization with different initiators. The high hydrolytic degradability of these LML/ML blends were demonstrated in 1 M NaOH aqueous solution at 45 °C suggesting promising sustainability prospects afforded by the ester linkages in the backbone. In summary, our results indicate the molecular architecture of polyester block copolymers allows for ready engineering of their properties for PSA applications with enticing renewability, degradability and competitive performance.

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Data Availability

The raw data files used in this manuscript are openly available in the Data Repository for University of Minnesota (DRUM) at

Electronic Supplementary Information

Materials**,** additional experimental details, supplementary characterization data (^{1}H NMR, SEC, and Rheology), adhesion test and hydrolytic degradation data.

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