Supporting Information for

Reactive Compatibilization of Poly(L-lactide) and Conjugated Soybean Oil

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Figure S1. General HEMI synthesis scheme. Procedure was adapted from Heath et al.¹



Figure S2. ¹H NMR spectrum of Furan-A (500 MHz, DMSO- d_6).

General procedure for synthesis of 4,10-Dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (Furan-A) All chemicals were purchased from Aldrich and used as received unless otherwise noted. Furan (92.5 g) and maleic anhydride (100 g) were added to a round bottom flask with ethyl acetate (125 mL). The reaction mixture was stirred for 24 hrs at room temperature, after which a colorless crystal was removed via suction filtration and dried under vacuum. The product (Furan-A) was used without further purification (yield 87.6%). Furan-A synthesis confirmed by ¹H NMR spectroscopy.¹ ¹H-NMR (500 MHz, DMSO-*d*₆) δ : 6.573 (s, 2H, –CHCH=CHCH–), 5.343 (s, 2H, –CHCH=CHCH–), 3.305 (s, 2H, O=CCH).



Figure S3. ¹H NMR spectrum of HEMI-A (500 MHz, DMSO- d_6).

General procedure for synthesis of 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (HEMI-A) Furan-A (100 g) and EtOH (150 mL) were added to a round bottom flask with a stir bar. A solution of MEA (37.4 mL) and EtOH (30 mL) was added drop wise to the Furan-A solution at a 1.03 molar excess of MEA to Furan-A. The resulting mixture was refluxed at 85 °C for 4 hrs, during which the solution turned a deep orange. After the reaction, the solution was cooled overnight and the crystallized product was removed via suction filtration. The collected crystals were dried under vacuum at room temperature. The colorless product (HEMI-A) was used without further purification (yield 49.3%). HEMI-A synthesis confirmed by ¹H NMR spectroscopy.¹ ¹H-NMR (500 MHz, DMSO-*d*₆) δ : 6.549 (s, 2H, – CHC*H*=C*H*CH–), 5.121 (s, 2H, –C*H*CH=CHC*H*–), 4.798 (br, 1H, NCH₂CH₂O*H*), 3.412 (m, 4H, NCH₂CH₂OH), 2.926 (s, 2H, O=CC*H*).



Figure S4. ¹H NMR spectrum of HEMI-A (500 MHz, DMSO-*d*₆).

General procedure for synthesis of 1-(2-Hydroxyethyl)-1*H*-pyrrole-2,5-dione (HEMI) HEMI-A (2.5 g) and toluene (50 mL) were added to a 3-neck round bottom flask with a stir bar. The reactor was continuously purged with nitrogen while the solution was refluxed at 110 °C for 5 hrs. Upon cooling at 0 °C for 2 hrs, a white solid (HEMI) was collected through suction filtration and washed with petroleum ether (yield 81.5%). The product was further purified (>99% purity) via sublimation under vacuum at 75 °C. HEMI synthesis confirmed by ¹H NMR spectroscopy.¹ ¹H NMR (500 MHz, DMSO-*d*₆) δ : 7.009 (s, O=CC*H*=C*H*C=O), 4.786 (s, 1H, NCH₂CH₂O*H*), 3.452 (m, 4H, NCH₂CH₂OH); (500 MHz, CDCl₃) δ : 6.736 (s, O=CC*H*=C*H*C=O), 3.782 (t, *J* = 4.9 Hz, 2H, NCH₂CH₂OH), 3.723 (t, *J* = 4.8 Hz, 2H, NCH₂CH₂OH), 2.090 (br, 1H, NCH₂CH₂OH).



Figure S5. ¹H NMR spectrum of HEMI-A (500 MHz, CDCl₃).



Figure S6. ¹H NMR spectrum with assignments for soybean oil (500 MHz, CDCl₃). Assignments made for linoleic acid residue in soybean oil triglyceride. R_1 and R_2 are any of the possible soybean fatty acid residues.² Assignment **g'** designates olefinic protons of the remaining unsaturated fatty acid residues present in soybean oil. * denotes H₂O present in solvent.



CDCl₃). Assignments made for conjugated linoleic acid residue in CS. Conjugated stereoisomers are produced: 9Z,11E (10E,12Z) and E,E during the conjugation of soybean oil. Peak assignments are made for the olefinic protons of each isomer.² Assignment **g'** designates olefinic protons of the remaining unsaturated fatty acids residues in soybean oil.



Figure S8. Assigned ¹H NMR spectra of (a) reaction product of HEMI-PLLA-1 and CS, (b) HEMI-PLLA-1, and (c) CS. The formation of new peaks observed in **Spectrum a** indicate that HEMI-PLLA-1 reacted with CS. Peak assignments indicate that HEMI-PLLA predominately reacts with the *E*,*E* isomers of CS. ¹H NMR spectra of other blends of HEMI-PLLA and CS show peaks at the same chemical shifts.



Figure S9. ¹H NMR spectrum for the methyl ester of conjugated linoleic acid (CLAME) that was purchased from Aldrich. Several stereoisomers of CLAME are present. The majority of the stereoisomers are (9*Z*,11*E*)-CLAME and (10*E*,12*Z*)-CLAME as indicated by the peaks belonging to vinyl protons labeled $f_{E,Z}$.² The *Z*,*E* and *E*,*Z* isomer peaks are indistinguishable. Minor isomers present include (*E*,*E*)-CLAME, indicated by peaks labeled $f_{E,E}$, and (*Z*,*Z*)-CLAME, indicated by peaks labeled $f_{z,z}$. Integration of the peak areas for each isomer was used to calculate the relative molar concentration of each isomer – 83 mol% *Z*,*E* (*E*,*Z*) isomers, 9 mol% *Z*,*Z* isomers, and 8 mol% *E*,*E* isomers. This CLAME molecule was used in model reactions with a model for HEMI-PLLA.



Figure S10. Synthesis scheme of trimethyl silane protected HEMI (TMSOEMI) and the ¹H NMR spectrum of TMSOEMI product (CDCl₃, 500 MHz) used as a model for HEMI-PLLA.

General Procedure for Synthesis of 1-(2-(trimethylsilyloxy)ethyl)-1*H*-pyrrole-2,5-dione (TMSOEMI) Using a modified procedure from Ahn et al.,³ HEMI (2.00 g) was dissolved in 350 mL of THF (dried over molecular sieves) in air. Once HEMI was in solution, one molar equivalent of Et₃N (1.98 mL, Aldrich) was added to the flask and allowed to activate. After 1 hr, 1.2 molar equivalents of TMSCl (2.17 mL, Aldrich) were added to the vessel upon which a white precipitate formed. After 4 hrs, the reaction mixture was passed through an alumina plug. Solvent was removed by rotary evaporation and the solid was dried under vacuum. The resulting solid was purified by sublimation (vacuum, 40 °C) to produce pure TMSOEMI (57% yield). ¹H NMR (500 MHz, CDCl₃): δ : 6.701 (s, 2H), 3.708 (t, 2H, *J* = 6.5 Hz), 3.661 (t, 2H, *J* = 5.3 Hz), 0.066 (s, 9H).



Figure S11. ¹H NMR spectrum of the reaction product of TMSOEMI and CLAME. Reaction carried out at 2 molar excess of TMSOEMI at 110 $^{\circ}$ C in toluene overnight. Resonances belonging to CLAME olefinic protons are no longer present, suggesting that the reaction proceeded to complete conversion of CLAME. Two diastereomers were formed as a result of a Diels-Alder reaction with the isomers of CLAME. **Product a** resulted from TMSOEMI reacting with the *E*,*Z* (*Z*,*E*) isomers. The six diastereotopic protons that exist on the reaction product are observed as six distinct resonances in the ¹H NMR spectrum. **Product b** resulted from TMSOEMI reacting with the *E*,*E* isomers and consequently has three sets of equivalent protons of which two sets appear as peaks distinct from **Product a**.⁴ The formation of the new peaks indicate that TMSOEMI and CLAME reacted by a Diels-Alder mechanism and strongly suggest that HEMI-PLLA and CS should behave in a similar manner.



Figure S12. Low resolution ESI-MS (Bruker BioTOF II) spectra of (a) CLAME, (b) TMSOEMI, and (c) the reaction product of TMSOEMI and CLAME (TMSOEMI + CLAME). In spectrum (a) the peak that corresponds to CLAME + Na^+ occurs at 317.4 m/z (317.5 calculated theoretical). In spectrum (b) two peaks are observed, the expected for TMSOEMI + Na^+ at 236.2 m/z (236.3 calculated theoretical) and a peak at 268.2 m/z that appears to correspond to TMSOEMI + Na^+ (268.3 calculated theoretical). In spectrum (c), the starting materials are observed along with an apparent reaction product at 530.6 m/z that corresponds to TMSOEMI + Na^+ (530.7 calculated). The formation of the higher molecular weight product corroborates the coupling of TMSOEMI and CLAME.

Table S1. Calculated probabilities for the number of fatty acid chains per CS molecule that contain a conjugated double bond. Fatty acids that have bis-allylic carbons (linoleic and linolenic) underwent the isomerization to produce the conjugated fatty acids present in CS. Linoleic and linolenic make up 53.8 mol% and 8.5 mol% of the fatty acids in soybean oil respectively.² The conversion of bis-allylic protons (96%) was used to correct the probability that a chain contained a conjugated double bond (59.8%).

| Number of Conjugated Fatty | Probability (%) | |
|----------------------------|-----------------|--|
| Acids in one CS Molecule | | |
| Zero | 6.5 | |
| One | 30.0 | |
| Two | 43.1 | |
| Three | 21.4 | |
| Multiple ^a | 64.5 | |

^aSummation of the probability of two and three fatty acid chains containing a conjugated double bond.



Figure S13. Representative ¹H NMR spectrum for HEMI-PLLA-67 blend with CS. Includes structural assignments. See Figure S8 for comparison of HEMI-PLLA and CS to the final product of the blend. Figure S13 is the ¹H NMR spectrum for 5 wt% CS melt blend with HEMI-PLLA-67. The fully expanded structure demonstrates the small mole percent of CS that is present in the blend.

| Matrix Polymer | $W_{CS0}{}^a(\%)$ | $T_{g}^{b}(\mathcal{C})$ | Crystallinity ^c (%) |
|---------------------------------------|-------------------|--------------------------|--------------------------------|
| PLLA-49 | | 59 | 19 |
| HEMI-PLLA-67 | | 57 | 39 |
| PLLA-49 | 15 | 59 | 40 |
| HEMI-PLLA-67 | 15 | 55 | 19 |
| PLLA-49 | 5 | 55 | 12 |
| HEMI-PLLA-67 | 5 | 54 | 19 |
| PLLA-49/HEMI- PLLA-67 ^d | 5 | 51 | 53 |
| PLLA-49 | 2 | 56 | 12 |
| HEMI-PLLA-67 | 2 | 55 | 18 |

Table S2: Crystallinity and glass transition temperatures of melt blends at 190 °C

^aWeight fraction of CS added to the mixer ^bGlass transition temperature of PLLA in blend ^cCrystallinity of PLLA homopolymer in blend

Thermal analysis was performed on a sample of tensile bar (5-10 mg). The samples was placed in a standard aluminum pan and was analyzed on a Texas Instruments TA Q1000 instrument with a scan rate of 10 °C/min from 0 °C to 220 °C. Blend T_g and crystallinity were determined from the initial heating curve. The heat of fusion used for an infinite crystal of PLLA was 94 J/g.⁵



Figure S14. Representative SEM images of tensile bar fracture surfaces for blends of CS with PLLA-49 (left column) and HEMI-PLLA-67 (right column) labeled by the amount of CS added to the mixer. After tensile testing (see Experimental Details), the fracture surfaces of select tensile bars were coated with 50 Å Pt by sputter coating and imaged on a JEOL 6700 microscope at 5.0 kV acceleration voltage. Shear yielding of the matrix is observed on several of the fracture surfaces. The HEMI-PLLA-67 blend with 5 wt% CS appeared to have the greatest degree of shear yielding as evidenced by the decreased CS particle size due to the deformation of the matrix. The CS debonded from all the fracture surfaces which suggests the compatibilizer formed at the interface does not improve the adhesion of the CS – it only reduces the interfacial tension, effecting morphology. This behavior is expected because of the liquid nature of CS and has been observed for polymerized soybean oil as well.⁶



Figure S15. SEC of tertiary 50/50 blend of HEMI-PLLA-67 and PLLA-49 with 5 wt% CS. SECs of the respective PLLA homopolymers are also given. The chromatogram suggests that the tertiary reactive blend has similar architecture of the binary blends as indicated by the shoulder off the main HEMI-PLLA-67 peak. The shoulder appears broader than the binary blend due to the broad distribution of PLLA-49 that is present in the mixture.

References

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