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

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ABSTRACT: Ring-opening bulk polymerization of L-lactide using *N*-2-hydroxyethylmaleimide (HEMI) as the initiator and tin(II) 2-ethylhexanoate as the catalyst produced a reactive end-functionalized poly(L-lactide) (HEMI-PLLA). Melt blends of HEMI-PLLA and conjugated soybean oil (CS) were prepared. HEMI-PLLA underwent a Diels−Alder reaction with the CS to high conversion, coupling the two immiscible components. Up to three HEMI-PLLA molecules reacted with one CS molecule to create products with varying architecture that acted as compatibilizers for the melt blend. Blends of HEMI-PLLA and 5 wt % CS resulted in a greater than 17-fold increase in elongation to break compared to PLLA homopolymer and more than doubled the elongation to break compared to a 5 wt % CS blend with unreactive PLLA. Analysis of the blend morphology indicated that the in situ formation of the compatibilizer decreased the CS droplet diameter compared to unreactive binary blends and that an optimum droplet diameter exists for toughening PLLA with CS.

Introduction

Renewable resource polymers have garnered a great deal of attention recently due to the rising cost and limited supply of petroleum.[1] Currently, most commodity polymers are derived from oil or other nonrenewable sources, while renewable resource polymers are created from annually renewable sources.[2] Moreover, these sustainable polymers are typically broken down into benign degradation products.[3] These features of renewable resource polymers make them desirable replacements for current commodity polymers.

One renewable resource polymer produced on a commercial scale is polylactide.[4,5] With mechanical properties similar to that of polystyrene (PS), polylactide is seen as a possible replacement for related petroleum based polymers. Accordingly, polylactide is available to the consumer in everyday products such as packaging and service ware.[5,7] However, polylactide is brittle and therefore enjoys a limited range of applications.[6,8,9] Thus, for polylactide to be suitable for the applications that require high elongation to break and impact strength, it must be toughened.

When attempting to toughen polylactide, research has focused on plasticization to lower the glass transition temperature of the amorphous component and polymer blending to provide stress dissipation mechanisms. Plasticization of polylactide has been accomplished through the addition of small molecules[4,10,11] and miscible polymers.[12−16] Typically, plasticized polylactide materials exhibit increased elongation to break, which is accompanied by decreased tensile stresses at break and elastic moduli.[17] Polymer blending offers a method to improve the toughness of polylactide with, generally, a smaller decrease in the stress at break and elastic modulus compared to the parent material. Typical polylactide blends consist of a minority component dispersed in a polylactide matrix. Polycaprolactone,[8,18−20] poly(vinyl alcohol),[21] poly(3-hydroxybutyrate),[22] and polyurethane[23] are examples of polymers that have been blended with polylactide and have resulted in mixed toughening effectiveness. Typically, binary blends of two polymers do not result in an improvement of mechanical properties due to poor interfacial adhesion between the two phases.[24] Compatibilization schemes have therefore been developed to lower the interfacial tension and improve the adhesion between the two immiscible phases.

Block copolymers containing blocks that preferentially segregate into the two polymer phases have been added to binary blends with polylactide to compatibilize the components.[8,25−28] In the case of a preformed block copolymer, diffusion of the hybrid macromolecule to the interface of the two phases reduces the interfacial tension and inhibits drop coalescence of the minor phase during mixing, resulting in a decreased droplet size and improved dispersion.[29−31] The block copolymers also improve transfer of stress between the two phases, which leads to tougher material compared to its binary counterpart.[32−34] Block copolymer compatibilization has been utilized in polylactide blends with polyethylene (PE)[25,26] and polycaprolactone (PCL),[8,27,28] among others,[9] to achieve increased toughness compared to binary blends. Most polylactide blending partners are nonrenewable and consequently research into developing a fully biorenewable blend is of current interest.

Soybean oil (SO) is one such renewable material that has been investigated as a blending partner for polyesters like polylactide. Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) has been blended with both SO and epoxidized soybean oil (ESO).[35] SO proved to be immiscible with PHBV and did not improve impact resistance without the addition of a compatibilizer. ESO appeared to plasticize the PHBV and resulted in an increase in toughness. The plasticization and subsequent increase of elongation at break of poly(L-lactide-*co*-polycaprolactone)[36] and poly(L-lactide)(PLLA)[37] by ESO has also been reported. Due to the immiscibility of SO and PLLA, a compatibilized SO/PLLA blend could possibly toughen polylactide without plasticization. Block copolymers of polylactide and polyisoprene have been used to affect the morphology of SO/PLLA blends, indicating that compatibilization of SO and PLLA is possible using preformed block copolymers.[38] Block copolymers have also been used to compatibilize blends of polymerized SO and PLLA.[39]

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Though preformed block copolymers have been successful in compatibilizing blends, their use can be limiting. The preformed block copolymer must diffuse to the interface of the immiscible components to compatibilize the blend, which does not happen with 100% efficiency as some block copolymer is wasted in the formation of micelles. Additionally, a preformed block copolymer that adequately compatibilizes the materials may be difficult to synthesize. To address these concerns, reactive blending schemes have been developed to produce compatibilizers in situ as opposed to adding preformed block copolymers.[24] The compatibilizers form at the interface of the immiscible components, eliminating the need for them to diffuse and simplifying their synthesis.

Reactive blending strategies have been employed for polylactide by blending with small molecules such as isocyanates, epoxides, and maleic anhydride that react to link two or more polymer chains.[40−42] Polylactide reactive blends have also been synthesized with another polymer such as a thermoplastic olefin backbone functionalized with maleic anhydride that is inherently reactive toward polylactide at the blend temperature.[43] Polylactide has been synthesized with reactive end-groups, but typically they are used in solution chemistry to end connect polylactide with another polymer.[44] Our aim is to develop these reactive end-functionalized polylactides that can be used in industrially relevant compounding strategies such as melt blending.

A reactive functional group of interest is maleimide, which has proven to be reactive toward several chemical groups including nitrones,[45] thiols,[44,46] conjugated dienes,[47,48] and amines.[49] For example, *N*-2-hydroxyethylmaleimide (HEMI) has been used as a hydroxyl-containing initiator for the ring-opening polymerization of lactide, producing a maleimide functionalized polylactide (HEMI-PLLA).[49] While typical SO does not contain functional groups reactive toward maleimide, conjugated dienes can be catalytically produced on the fatty acid chains to create conjugated soybean oil (CS).[50,51]

We have explored the reaction between HEMI-PLLA and CS both in solution and in the melt to produce coupled products with varying architecture. Melt blends of CS and either HEMI-PLLA or PLLA were prepared in a twin screw mixer to form blended materials with improved tensile toughness. In the HEMI-PLLA blends, in situ formation of compatibilizer during mixing decreased the CS droplet size, which resulted in a further enhancement of the tensile toughness compared to corresponding parent PLLA blends. An optimum CS particle size for toughening of PLLA was determined. Collectively, these results demonstrate that reactive compatibilization of PLLA and CS can lead to all renewable blends with enhanced toughness compared to the parent PLLA.

Results and Discussion

HEMI-PLLA Synthesis. HEMI-PLLA was synthesized using HEMI (see Supporting Information Figures S1−S5 for HEMI synthesis description) as an initiator for the melt ring-opening polymerization of L-lactide (Figure 1) with tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) as the catalyst. Three samples of HEMI-PLLA were prepared using different monomer to initiator ratios to control the average molar mass (Table 1). The polydispersity index (PDI) values of HEMI-PLLA samples were less than 1.25 at conversions greater than 90%, and lower PDI values were achieved at lower conversions (ca. 80%). Broadening of the molar mass distribution at higher monomer conversions is likely due to transesterfication reactions or depropagation; both are enhanced near the equilibrium monomer concentration.[52,53]

The ^{1}H NMR spectra of HEMI (Figure 2a) and precipitated HEMI-PLLA-1 (Figure 2b) indicate high initiation efficiencies. Resonances associated with protons in HEMI attached to PLLA shifted relative to free HEMI. Furthermore, the ^{1}H NMR spectrum of HEMI-PLLA agrees with that of previous syntheses using other catalysts.[46,49] We successfully carried out the HEMI-PLLA synthesis on a 100 g scale.

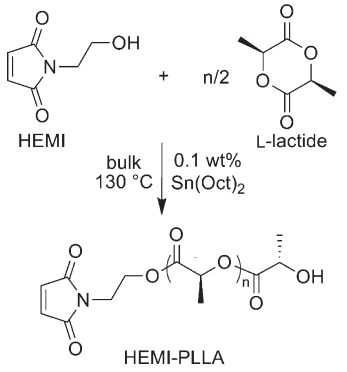

Figure 1. Synthesis scheme and chemical structure of HEMI-PLLA.

Table 1. Summary of PLLA Homopolymers

sample code	M_n[a] (kg/mol)	M_w[b] (kg/mol)	PDI[b]
PLLA-49[c]	49	138	1.85
HEMI-PLLA-1	1.1	2.0	1.24
HEMI-PLLA-20	20	37	1.05
HEMI-PLLA-67	67	129	1.24

[a] Determined using ^{1}H NMR spectroscopy end group analysis. [b] SEC using polystyrene standards. [c] Obtained from Toyota Motor Corporation.

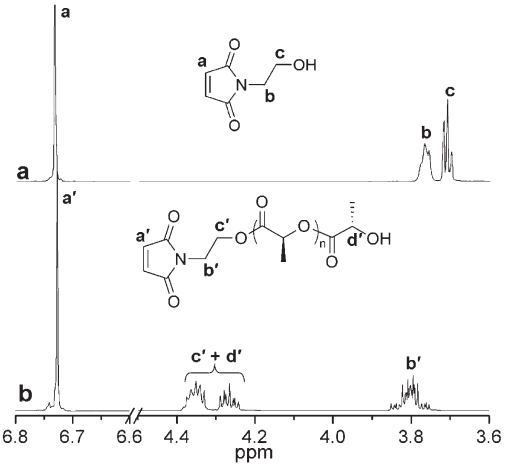

Figure 2. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of (a) HEMI and (b) HEMI-PLLA-1. Synthesis of HEMI-PLLA shifts the peak locations of protons on the HEMI end-group.

Synthesis of Conjugated Soy (CS). CS was prepared following the procedure of Larock et al. (Figure 3).[50] Both linoleic and linolenic fatty acid residues in soybean oil contain disubstituted olefins in the Z configuration separated by one (bis-allylic) carbon atom. Isomerization of the olefins by $RuHCl(CO)(PPh_3)_3$ gives dienes amendable to the Diels−Alder coupling with the HEMI group. After reaction of SO with $RuHCl(CO)(PPh_3)_3$, ^{1}H NMR spectroscopic analysis of the product indicated that 96% of the bis-allylic carbons were absent, indicating effective isomerization. Because of the isomerization mechanism, in the product diene a mixture of *E* and *Z* isomers are produced.[51] In our case, 64% of the conjugated dienes adopted the *E*,*E* configuration with the balance being *Z*,*E* and *E*,*Z* isomers as determined by ^{1}H

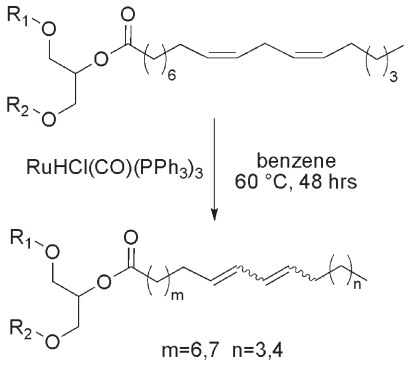

Figure 3. Reaction scheme of the conjugation of linoleic fatty acid residue in soybean oil. R_1 and R_2 represent the other fatty acid residues of the triglyceride, which may contain other conjugated chains in CS.

Table 2. Composition of Small Scale HEMI-PLLA and CS Blends

HEMI-PLLA	conditions[a]	[C=C−C=C]/[HEMI][b]	$X_{E,E}$ (%)[c]	$X_{E,Z}$ (%)[d]	X_{HP} (%)[e]
HEMI-PLLA-1	toluene	0.93	100	30	70
HEMI-PLLA-1	melt	0.89	100	38	94
HEMI-PLLA-20	toluene	25	21	10	100
HEMI-PLLA-20	melt	17	22	17	82

[a] Blends in toluene were synthesized at 110 °C, melt blends were prepared at 190 °C. [b] Molar ratio of conjugated double bonds to HEMI end-groups in each blend (see Experimental Details). [c] Conversion of all *E,E* isomers of CS, by ^{1}H NMR spectroscopy. [d] Conversion of all *E,Z* and *Z,E* isomers of CS, by ^{1}H NMR spectroscopy. [e] Conversion of HEMI end-groups of HEMI-PLLA, by ^{1}H NMR spectroscopy. All calculated conversions have an error of ±8% (see Experimental Details).

NMR spectroscopy (Supporting Information Figures S6−S7).

Exploratory Small Scale Reactive Blends. Small scale blends of CS and HEMI-PLLA were prepared to explore the reactivity of HEMI-PLLA toward CS under both melt and solution conditions (see Experimental Details). The composition and resulting conversion of the reactive species for these blends are given in Table 2. HEMI-PLLA-1 blends were prepared using an approximately 1:1 molar ratio of HEMI-PLLA to CS, while HEMI-PLLA-20 blends were synthesized using a molar excess of CS. Using ^{1}H NMR spectroscopy, conversions of the *E,E* ($X_{E,E}$) and *E,Z* (includes *Z,E*) isomers ($X_{E,Z}$) of CS were monitored along with the conversion of the HEMI end-group of HEMI-PLLA (X_{HP}). In all blends, $X_{E,E}$ of CS was greater than that of $X_{E,Z}$ consistent with decreased steric hindrance of the *E,E* isomer reaction site as compared to the *E,Z* (and *Z,E*) isomers as is typical for Diels−Alder reactions. The ^{1}H NMR spectrum (Supporting Information Figure S8) was consistent with the Diels−Alder reaction product between the *E,E* isomer of CS and HEMI-PLLA (Figure 4) as confirmed by model reactions (Supporting Information Figures S9−S12). Though the *E,Z* isomers of CS did react, resonances associated with the Diels−Alder adduct were not observed, presumably due to the smaller percentage of the *E*, *Z* (and *Z,E*) isomers initially present and their reduced conversion.

SEC data for the reactive blends with HEMI-PLLA-1 (Figure 5a) corroborate the reaction of HEMI-PLLA-1 with CS in both solution and the melt as evidenced by the shift of the products to lower elution volumes as compared to HEMI-PLLA-1. For the HEMI-PLLA-20 blend with CS (Figure 5b), the shift in elution volume are not surprisingly less pronounced. Interestingly, the melt blend of HEMI-PLLA-20 resulted in an SEC elution curve with several

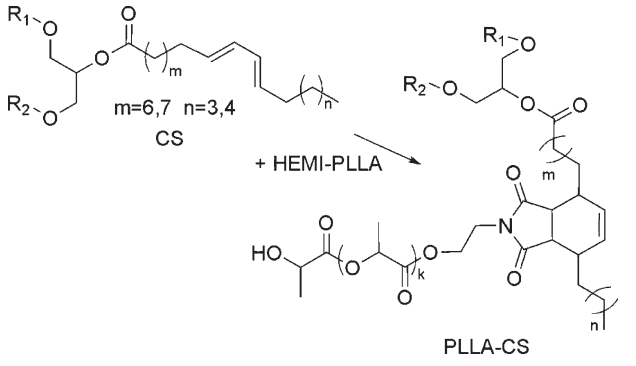

Figure 4. Diels−Alder reaction product of CS and HEMI-PLLA. The maleimide functionality of HEMI-PLLA reacts with the conjugated diene of CS by a Diels−Alder reaction mechanism to produce a PLLA grafted CS (PLLA-CS).

distinct peaks at apparent molar masses that are two (PLLA-CS-PLLA) and three (3-arm star-PLLA) times that of the HEMI-PLLA-20. The formation of these higher molecular weight products suggests that multiple reactions of HEMI-PLLA can occur with one CS molecule. Each of the three fatty acid residues in CS can contain conjugated double bonds, and the multiple additions of HEMI-PLLA to CS are likely responsible for the additional products observed in the SEC trace.[54] Heating either HEMI-PLLA-1 or HEMI-PLLA-20 without CS does not alter its SEC elution curve, confirming that the higher molecular weight products were not a result of HEMI-PLLA self-coupling.

Multiple peaks were not observed in the SEC data for the HEMI-PLLA-1 blends as they were observed in the melt blend for HEMI-PLLA-20. Statistically, a majority (65%) of the CS molecules have more than one set of conjugated double bonds (Supporting Information Table S1). Since most of the conjugated double bonds (>75%) reacted in both HEMI-PLLA-1 blends, we expect that multiple additions of HEMI-PLLA-1 should have occurred in both blends. Separate peaks that correspond to the multiple coupling products were likely not resolved due to the small difference in molecular weights that these products would have compared to the single addition of HEMI-PLLA-1 to CS.

The SEC of the HEMI-PLLA-20 blend in the melt signifies that multiple coupling occurred between the two molecules. A high molecular weight shoulder off the HEMI-PLLA-20 peak (Figure 5b) was present before blending, possibly due to transesterfication or radical coupling reactions during its synthesis. The shoulder is observed in the SEC of the HEMI-PLLA-20 blend in solution at a comparable relative height to the main peak, suggesting that multiple coupling reactions did not occur in solution. Conversely, the SEC of the HEMI-PLLA-20 blend in the melt indicates multiple additions to CS, even though the two blends have similar conversions. We attribute the distinct behaviors of the two HEMI-PLLA-20 blends as observed by SEC to inherit phase separation of the HEMI-PLLA-20 and CS in the melt and not in solution. In the melt, reactions between HEMI-PLLA-20 and CS occur at the interface of the two materials, resulting in the formation of the PLLA-CS compatibilizer. The coupled CS molecule remains at the interface where it would more likely react with another HEMI-PLLA-20, giving the multiple addition products observed. In solution, no interface exists so there is actually the opposite bias. Once a CS molecule has reacted the probability for a second addition is reduced due to steric arguments. Along with the steric effects, the large molar excess of CS molecules to HEMI-PLLA-20 molecules

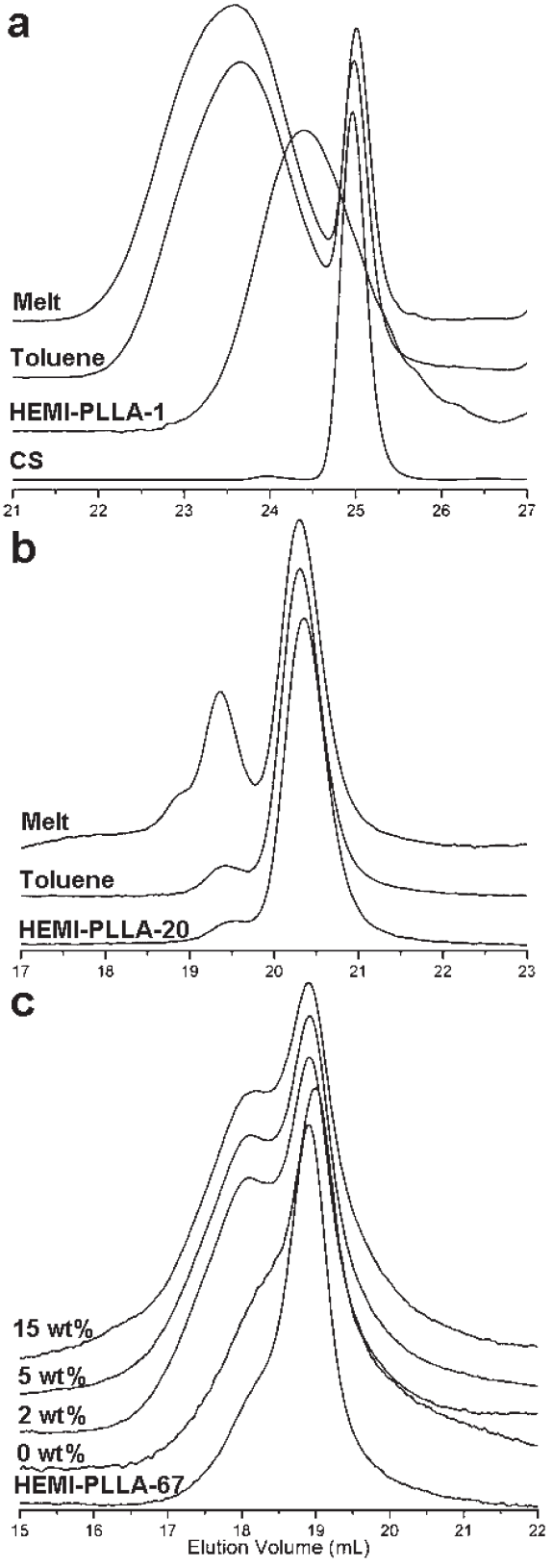

Figure 5. Normalized SEC elution curves for blends of HEMI-PLLA and CS. Blends of CS with (a) HEMI-PLLA-1 at a 1:1 molar ratio of HEMI-PLLA to CS and (b) HEMI-PLLA-20 at a molar excess of CS were conducted in both the melt (190 °C) and in toluene (110 °C) as indicated on the SEC chromatogram. Melt blends of (c) HEMI-PLLA-67 and CS were synthesized in the DACA melt mixer at varying weight fractions of CS as indicated on the chromatogram. In each chromatogram the HEMI-PLLA homopolymer elution curve is also given. The curves are offset from the baseline to improve clarity.

contributes to single additions of HEMI-PLLA-20 to CS in solution.

Melt Blends of HEMI-PLLA-67 and PLLA-49 with CS. Larger scale (4 g) melt blends of HEMI-PLLA-67 and CS were synthesized in a twin screw batch mixer. Blends of PLLA-49 and CS were also prepared as control groups for the reactive blends. CS blends with HEMI-PLLA-67 were compared to those of PLLA-49 due to their similar weight average molecular weight (Table 1). Components were compounded in the mixer at 190 °C for 10 min at which time blends were collected from the mixer for analysis and further processing. A summary of the blend analysis can be found in Table 3.

At high weight fractions of CS added (e.g., 15 wt %), excess CS pooled at the bottom of the mixer during compounding and was not fully incorporated. The unincorporated CS drained from the mixer when it was opened to remove the product. ^{1}H NMR spectroscopy was used to calculate the actual concentration of CS incorporated into the blends. Blends with 5 wt % or less added CS appeared to incorporate all the CS into the polylactide matrix. We determined that a maximum of 9 wt % CS could be incorporated into the blends, and this required addition of 15 wt % CS to the mixer. The incomplete incorporation of the oil is due to the large difference in viscosities between the polylactide and CS[55] and has been observed in previous blends of PLLA and soybean oil.[38,39]

The formation of compatibilizers by the Diels−Alder coupling of CS and HEMI-PLLA-67 during blending was also monitored by ^{1}H NMR spectroscopy. In blends containing a molar excess of CS (15 and 5 wt % added), over 90% of the HEMI end groups were converted (Table 3). As the molar excess of CS to HEMI-PLLA-67 was reduced the conversion of the HEMI end-groups (X_{HP}) decreased and the conversion of the CS *E*,*E* isomers (X_{CS}) increased as expected. The blend of HEMI-PLLA-67 and 2 wt % CS had a nearly one to one mole ratio of HEMI end groups to *E*,*E* isomers, which is reflected by the nearly equivalent X_{HP} and X_{CS} values. ^{1}H NMR spectroscopy (Supporting Information Figure S13) confirmed the formation of the Diels−Alder products between CS and HEMI-PLLA-67.

To probe the architecture of the products formed, the SEC chromatograms of HEMI-PLLA-67 blends with CS were compared to HEMI-PLLA-67 (Figure 5c). The HEMI-PLLA-67 homopolymer was heated at 190 °C in the mixer, mimicking the blending protocol. The SEC of the heated homopolymer broadened and increased in elution volume slightly as compared to the pure HEMI-PLLA-67. The small change is likely due to some thermal degradation of the polymer, which has been observed for PLLA at similar temperatures.[56] While no additional peak was observed after heating HEMI-PLLA-67, a new peak is observed in the chromatogram at 18 mL for all reactive blends, which corresponds to twice the molecular weight of the original polymer. The formation of the new peak suggests that not only PLLA-CS was synthesized but also PLLA-CS-PLLA. Whether or not 3-arm star-PLLA was formed is not clear since the predicted elution volume (17.4 mL) of such a product falls under the peak belonging to PLLA-CS-PLLA and therefore could be obscured.

Compression molded samples of the blends were utilized for tensile testing. Blends with more that 2 wt % CS resulted in an increase in elongation to break (ε_b) as compared to the corresponding polylactide homopolymer (Table 3). Blends with PLLA-49 resulted in 4−6 times the ε_b as compared to the PLLA-49 homopolymer. The ε_b values for blends with only 2 wt % percent CS were similar to that of the

Table 3. Physical Properties of Melt Blends of CS with PLLA-49 and HEMI-PLLA-67

matrix polymer	W_{CS0} (%)[a]	W_{CS} (%)[b]	E (GPa)[c]	σ_b (MPa)[d]	ε_b (%)[e]	X_{HP} (%)[f]	X_{CS} (%)[g]	d_{lm} (μm)[h]	σ_{lm} (μm)[i]	MLT (μm)[j]
PLLA-49			2.4 ± 0.3	58 ± 3	5 ± 2					
HEMI-PLLA-67			3.0 ± 0.2	67 ± 9	4 ± 1					
PLLA-49	15	9	2.4 ± 0.3	28 ± 4	22 ± 7			1.81	1.8	3.1
HEMI-PLLA-67	15	7	2.0 ± 0.5	34 ± 2	50 ± 30	100	14	0.91	2.0	2.2
PLLA-49	5	4	2.1 ± 0.3	38 ± 1	30 ± 10			1.17	2.0	3.6
HEMI-PLLA-67	5	7	2.5 ± 0.2	37 ± 2	70 ± 30	98	44	0.70	2.1	2.0
PLLA-49/HEMI-PLLA-67[k]	5	6	2.3 ± 0.3	36 ± 3	20 ± 10	96	39	0.96	1.8	2.1
PLLA-49	2	2	2.6 ± 0.1	51 ± 1	5 ± 2			0.30	2.0	1.3
HEMI-PLLA-67	2	3	2.5 ± 0.2	54 ± 5	4 ± 2	66	70	0.35	1.3	0.5

[a] Weight fraction of CS added to melt mixer. [b] Weight fraction of CS incorporated into blends, by ^{1}H NMR spectroscopy. [c] Elastic modulus. [d] Stress at break. [e] Elongation to break. [f] Conversion of HEMI end-groups for blends with HEMI-PLLA-67. [g] Conversion of *E,E* isomers of CS added to mixer. [h] Log-mean average CS droplet diameter. [i] Log-mean CS droplet size distribution parameter. [j] Matrix ligament thickness. [k] Matrix polymer was a 50/50 blend of PLLA-49 and HEMI-PLLA-67.

homopolymers, suggesting that there was a critical CS concentration for toughening. Using HEMI-PLLA-67 as the matrix component increased the ε_b further, presumably due to the in situ formation of compatibilizer. Blending 5 wt % CS into HEMI-PLLA-67 increased the elongation to break by a factor of more than 17 compared to homopolymer HEMI-PLLA-67 and more than doubled the elongation to break as compared to a similar blend with PLLA-49. The stress at break (σ_b) of the blends decreased with the addition of CS. The σ_b did not significantly vary between the blends with 15 and 5 wt % CS added, since all blends had similar amounts of CS incorporated (Table 3). The moduli of the blends decreased slightly as compared to the parent homopolymer, which is expected with the replacement of stiff material (polylactide) with the low modulus CS, but remained above 2.0 GPa for all blends.

To determine if the mechanism of toughening the blend was due to plasticization, differential scanning calorimetry (DSC) was performed on the tested tensile bars. The glass transition temperature (T_g) for the polylactide in the blends was not significantly different than the polylactide homopolymers. All blends and homopolymers had T_g's between 54 and 59 °C, indicating that significant plasticization did not occur. Generally, crystallinity of the PLLA in the blends ranged between 10 and 20%, similar to the homopolymers (see Supporting Information Table S2).

The morphology of the CS particles dispersed in the polylactide matrix was investigated with scanning electron microscopy (SEM). Samples were polished by cryo-microtomy prior to imaging to give a smooth surface suitable for image analysis. Representative SEM micrographs of PLLA-49 and HEMI-PLLA-67 blends with CS are shown in Figure 6. Reactive HEMI-PLLA-67 blends qualitatively appear to have smaller CS domains compared to the unreactive blends with PLLA-49. The log-mean CS particle diameter (d_{lm}) and the log-mean particle distribution parameter (σ_{lm}) were calculated from the SEM images for each blend (Table 3). As observed qualitatively in the SEM micrographs, analysis indicates the reactive blends with HEMI-PLLA-67 resulted in smaller d_{lm} as compared to the corresponding PLLA-49 blends, presumably due to the formation of compatibilizer at the interface. Compatibilizers in melt blends have been known to reduce the particle size of the minor phase by decreasing the interfacial tension between the two phases and inhibiting droplet coalescence.[57,58] Since compatibilizer formed during blending, the interfacial tension between the two phases decreased, resulting in smaller droplets in the blends. The matrix ligament thickness (MLT), a measure of the interparticle distance, was also calculated for all blends (Table 3). The MLT was reduced for all reactive blends compared to their unreactive counterparts as expected for blends with the same amount of CS, but with smaller particles.

In previous PLLA toughening schemes, a critical particle diameter and MLT for toughening were determined.[25,26] For the CS blends, as the diameter of the CS domains decreases (Figure 7), ε_b increases until a maximum is achieved at an optimal particle diameter. The MLT (Figure 7) also has a similar trend where the elongation to break sharply drops off around an MLT of 2 μm. For many brittle polymers, an optimal particle diameter is required for toughening.[59] Rubber toughening in brittle polymers relies heavily on the particles acting as craze terminators. More particles can provide sites for craze termination, but as the number of particles increase their size decreases at fixed dispersed phase content. Smaller particles are less efficient at terminating crazes, leading to a balance between number of particles and toughening efficiency. For the polylactide and CS blends, the optimal particle diameter appears to occur somewhere between 0.5 and 0.9 μm.

As discussed previously, varying amounts of CS were incorporated into the blends (Table 3). The amount of CS present can affect both the d_{lm} and MLT so it should be considered in the analysis. Generally, the HEMI-PLLA-67 blends with CS had similar amounts of CS incorporated as compared to the respective PLLA-49 blends. The comparable amounts of CS present suggest that a change in d_{lm} or MLT is mostly due to the reactive compatibilization that occurred and not a difference in CS content. Since the HEMI-PLLA-67 blends with 5 and 15 wt % added to the mixer had the same amount of CS incorporated, their particle diameters were included in the range for the optimum particle diameter. Presumably, the two blends are nearly identical in composition, though the blend with 15 wt % CS added would initially have a greater concentration of CS with which HEMI-PLLA-67 could react and therefore may have a slightly different amount of compatibilizers present at the particle interface. Variation in the relative amount of compatibilizer affects the degree of compatibilization and subsequently the CS particle diameter. The small variation in the average ε_b values for the HEMI-PLLA-67 blends with 5 and 15 wt % CS added (both exhibiting 7 wt % incorporation) likely results from this difference in the particle diameters.

SEM images of the tensile bar fracture surfaces (Supporting Information Figure S14) indicate that matrix yielding occurred in samples with improved elongation to break. Typically, blends toughened by energy dissipation mechanisms such as shear yielding and cavitation have a critical MLT.[60,61] The MLT appears to have an optimal value around 2 μm, which contradicts previous results where a critical MLT for rubber toughening PLLA was

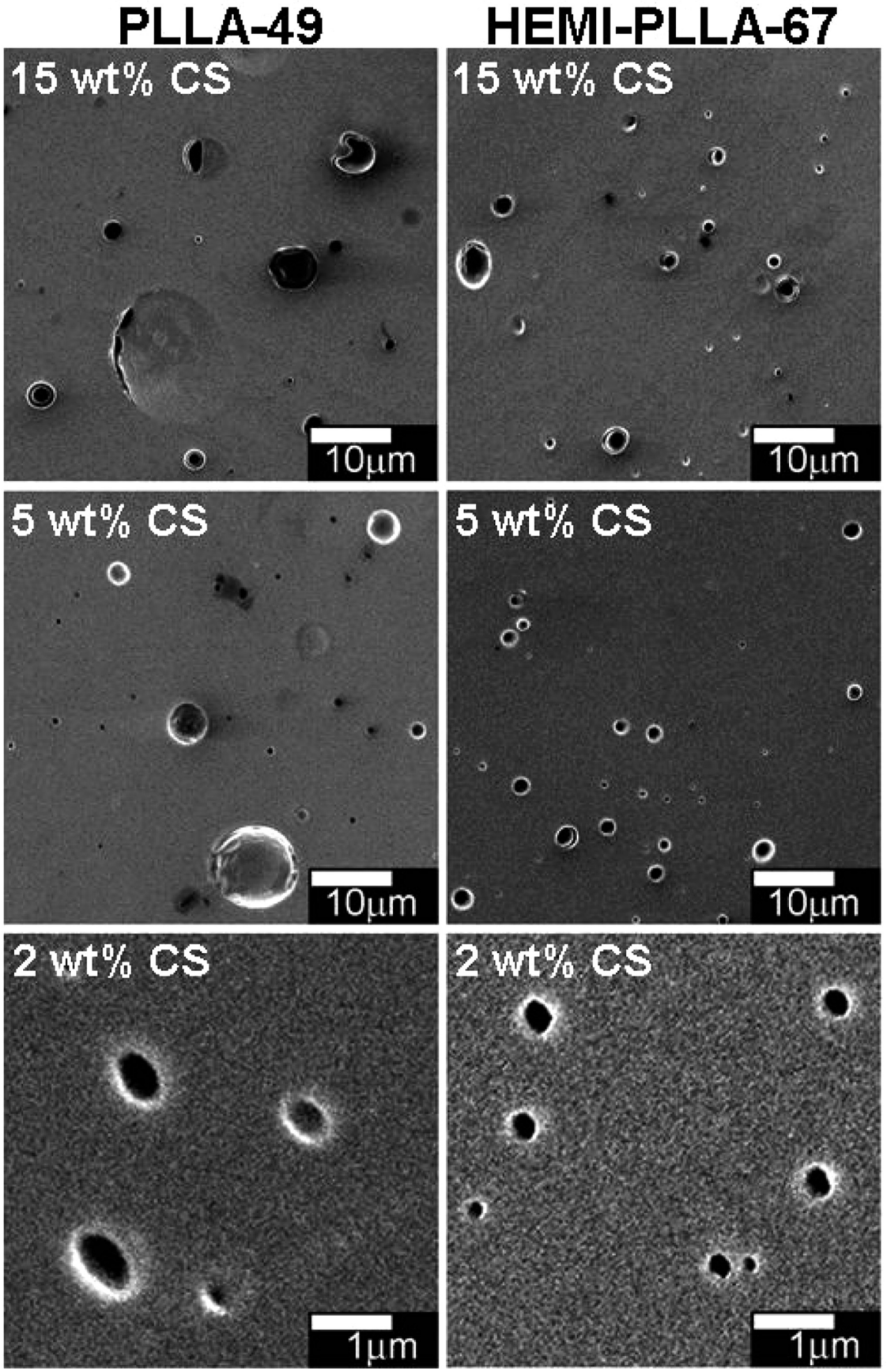

Figure 6. Representative SEM images of cryo-microtomed surfaces of CS binary blends with PLLA-49 (left column) and HEMI-PLLA-67 (right column). Samples are labeled by the amount of CS initially added to the mixer. See Table 3 for amount of CS incorporated. Microtomy of the samples removed CS at the surface creating the dark holes seen in the images.

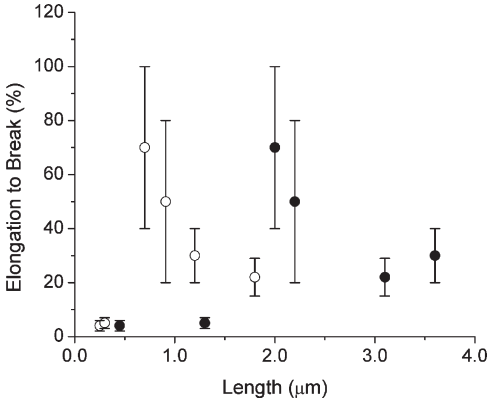

Figure 7. Correlation of average elongation to break with d_{lm} (open circles) and MLT (closed circles) for binary blends of CS with PLLA-49 and HEMI-PLLA-67. Error bars indicate standard deviation of elongation to break.

observed.[25,26,39] Corté et al. have theorized that the critical MLT for a particular polymer matrix is a function of particle diameter in semicrystalline polymers.[61] According to their theory, the blends with smaller particles (2 wt % CS) should have a smaller critical MLT than the blends with larger CS particles (5 and 15 wt % added). Perhaps, in these blends the critical MLT for the "small" particles was not reached while the critical MLT for the "large" particles was, qualitatively explaining the apparent optimum MLT value. Consequently, the data suggest that both crazing and shear yielding could be acting as energy dissipation mechanisms that give the observed improvement in elongation to break at an apparent optimal particle diameter.

To reduce the amount of reactive PLLA added, a ternary blend was synthesized in the melt mixer that contained a matrix phase composed of half HEMI-PLLA-67 and half PLLA-49 and 5 wt % CS. Interestingly, the blend had mechanical properties similar to the PLLA-49 and 5 wt % CS blend despite containing HEMI-PLLA-67. ^{1}H NMR spectroscopy confirms that the HEMI-PLLA-67 reacted to form compatibilizer and SEC (Supporting Information Figure S15) indicates that the architecture of the compatibilizer formed was similar to that of the other reactive blends. Because of the decreased loading of HEMI-PLLA-67, the number of compatibilizer molecules in the blend did decrease which could reduce the overall compatibilization of the blend. The d_{lm} of the blend (0.96 μm) was slightly less than the d_{lm} of the corresponding PLLA-49 blend (1.17 μm), indicating that the reaction products were compatibilizing the blend. While the MLT looked close to optimal (2.1 μm), the ternary blend d_{lm} was somewhat greater than that of the apparent optimum particle diameter and consequently the ε_b of the blend did not increase beyond that of the unreactive binary blend. The results of the ternary blend further suggest that an optimal d_{lm} exists for the blends as opposed to an optimal MLT. A majority of the matrix polymer should be HEMI-PLLA to achieve the required d_{lm} and subsequent increase to the elongation to break.

Conclusions

Reactive melt blends of HEMI-PLLA and CS were investigated. End-functionalized reactive PLLA (HEMI-PLLA) samples with controlled molar mass were synthesized in the bulk using $Sn(Oct)_2$ as the catalyst. Small scale blends of HEMI-PLLA and CS, in solution and in the bulk, demonstrated that the two components can react by a Diels−Alder mechanism to give a PLLA coupled to CS. Multiple HEMI-PLLA molecules could react with one CS molecule to give three different architectures of coupled products. Melt binary blends of with greater than 2 wt % CS and with either HEMI-PLLA or PLLA resulted in materials with an increased elongation to break compared to polylactide homopolymers. Reactive blends of CS with HEMI-PLLA doubled the elongation to break compared to similar blends with unreactive PLLA. The reactively formed compatibilizer at the HEMI-PLLA/CS interface reduced the CS droplet diameter to an optimal value, resulting in the increase in elongation to break compared to the unreactive blends.

Experimental Details

Materials and General Methods. All chemicals were purchased from Aldrich and used without further purification unless otherwise stated. L-lactide (Purac) was purified through recrystallization in ethyl acetate and then dried under vacuum at room temperature. *N*-2-hydroxyethylmaleimide (HEMI) was synthesized using a modified literature procedure (Figure Supporting Information S1).[62] Dry toluene (HPLC grade) was purified by passing it through a home-built solvent purification system with activated alumina column and a supported copper catalyst. Commercial grade poly(L-lactide) homopolymer (PLLA-49) was provided by the Toyota Motor Corporation. All other polymers were synthesized using the techniques given below. An overview of all polymers used can be found in Table 1.

^{1}H NMR spectroscopy was performed on a Varian Inova 500 MHz spectrometer in $CDCl_3$ unless otherwise noted. Size exclusion chromatography was performed on an Agilent 1100 high-pressure liquid chromatograph at 35 °C equipped with a PLgel (Varian) 5 μm guard column followed by three PLgel columns with varying pore sizes with HPLC grade chloroform as the mobile phase. Molecular weights and polydispersity index (PDI) were measured by a Hewlett-Packard P1047A refractometer calibrated with polystyrene standards (Polymer Laboratories).

General Procedure for Synthesis of HEMI-PLLA Using Tin(II) 2-Ethylhexoate [Sn(Oct)$_2$] as the Catalyst. Purified L-lactide (10 g) was added to a dry 48 mL pressure vessel along with HEMI (1.410 g) and 0.1 wt % $Sn(Oct)_2$ (10 mg) in air. After addition of a magnetic stir bar, the vessel was sealed and placed in an oil bath at 130 °C. After 2 h, the vessel was removed and cooled in an ice bath to quench the polymerization. The resulting solid was dissolved in CH_2Cl_2 and precipitated in 10× excess hexanes. The resulting polymer suspension was centrifuged to collect the material. Upon drying under vacuum, a 1.1 kg/mol HEMI-PLLA (HEMI-PLLA-1) was recovered (96% lactide conversion, 90% HEMI-PLLA yield). HEMI-PLLA polymers with higher molecular weights and at larger scales were precipitated in 10× excess of methanol. HEMI-PLLA at 100 g scale was removed from the reaction vessel without dissolution and pressed into pellets before melt mixing. Additional molecular weights were achieved by varying the monomer to initiator molar ratio and the L-lactide conversion. See Table 1 for a summary of HEMI-PLLA polymers synthesized. ^{1}H NMR spectroscopy chemical shifts of HEMI-PLLA end-group protons (500 MHz, $CDCl_3$) δ: 6.720 (s, −C*H*=C*H*−), 4.344 (m, HO−C*H*− and N−CH$_2$−C*H*H−O), 4.259 (m, N−CH$_2$−CH*H*−O), 3.788 (m, N−C*H*$_2$−CH$_2$−O), 2.671 (br, *H*O−CH−). ^{1}H NMR spectroscopy chemical shifts of HEMI-PLLA repeat unit protons (500 MHz, $CDCl_3$) δ: 5.157 (q, J = 6.9 Hz, O−C*H*−CH$_3$), 1.576 (d, J = 7.8 MHz, O−CH−C*H*$_3$).

Synthesis of Conjugated Soybean Oil (CS). Following the procedure of Larock et al.,[50] Wesson soybean oil purchased from a local grocery store (23 g) was dissolved in 75 mL of benzene with 0.5 mol % $RuHCl(CO)(PPh_3)_3$ (0.39 g) in an air-free flask. The solution was degassed and heated at 60 °C for 48 h under an argon atmosphere. After cooling, the benzene was removed by evaporation and the crude product dried under

vacuum at 35 °C. The crude product was then dissolved in CH_2Cl_2 (200 mL) in a nitrogen drybox and $P(CH_2OH)_3$ (0.5 g) was then added. The solution was stirred for 48 h at room temperature at which point the mixture was passed through a silica gel column with 1.5 L CH_2Cl_2 to remove the catalyst.[63] The solvent was removed by rotary evaporation and dried under vacuum to collect CS (89.7% yield). Conjugation of bis-allylic double bonds was 96%. ^{1}H NMR spectroscopy (500 MHz, $CDCl_3$) δ: 6.286 (m, 0.4 H, *Z*- =CH−C*H*=CH−), 5.974 (m, 1.9 H, *E*- =CH−C*H*=CH−), 5.654 (m, 0.4 H, *Z*,*E*- =CH−CH=C*H*−), 5.552 (m, 1.6 H, *E*,*E*- =CH−CH=C*H*−), 5.376 (m, 3.6 H, *Z*- =CH−CH=C*H*− and =C*H*−), 5.261 (m, 1 H, OCH_2CHCH_2O), 4.289 (dd, J = 11.8 Hz, J = 5.0 Hz, 2 H, $OCH_aH_bCHCH_aH_bO$), 4.14 (dd, J = 12.7 Hz, J = 5.8 Hz, 2 H, $OCH_aH_bCHCH_aH_bO$), 2.305 (t, J = 7.9 Hz, 6 H, CH_2C=O), 2.20−1.90 (m, 12H, =CHCH_2), 1.602 (s, 6.6 H, CH_2CH=O), 1.40−1.20 (br m, 52.8 H, CH_2), 0.877 (t, J = 6.9 Hz, 9H, CH_2CH_3).

Synthesis of Exploratory Small Scale Reactive Blends of CS and HEMI-PLLA. CS and HEMI-PLLA were blended in both solution and the melt. As an example solution blend, HEMI-PLLA (350 mg) was dissolved in 3 mL of dry toluene in a 10 mL round-bottom flask with a magnetic stir bar. CS (200 mg) was added to the solution which was placed in an oil bath at 110 °C to reflux for 18 h. Melt blends were performed as follows. HEMI-PLLA and CS were added to a glass test tube in the same proportions as in the solution blend. The glass test tube was lowered into an oil bath at 190 °C and an overhead mechanical stirrer was used to mix the components for 10 min after which the test tube was removed from the oil bath. Upon cooling in ice water, the reaction mixtures (both solution and melt) were analyzed by ^{1}H NMR spectroscopy and SEC. The concentration ratios of conjugated dienes to HEMI-PLLA ([C=C−C=C]/[HEMI]) initially present in blends were calculated by using the molecular weights of CS (872 g/mol) and the HEMI-PLLA polymers, the average number of conjugated dienes per molecule of CS (1.2, as determined by ^{1}H NMR spectroscopy), and the known mass of each component. Control blends were synthesized by heating the individual components following the protocols described above. ^{1}H NMR spectra and SEC of the heated components were compared against the original material. Analysis of the ^{1}H NMR spectra for the control blends indicated that the maximum error for the measured conversions was ±8%, which was determined by comparing the original spectra of the homopolymers and CS to their spectra after heating.

Synthesis Melt Blends of HEMI-PLLA-67 and PLLA-49 with CS. All larger scale blends were made in a twin screw batch mixer (DACA Instruments) at 190 °C and 100 rpm screw speed. Prior to mixing, HEMI-PLLA and PLLA were dried overnight at 60 °C to remove moisture and CS was heated slightly above room temperature so that it would be a liquid and easier to work with. To the 190 °C mixer, the matrix polymer was added first and allowed to mix for 5 min prior to the addition of CS, allowing for complete melting of the polymer. CS was added dropwise to the mixer at the desired ratio (total blend mass of 4 g) over 1 min of mixing. After the polymer and CS were compounded for 10 min, the blend was collected from the mixer. The blends were cooled in liquid nitrogen upon being removed from the mixer and were stored in a −20 °C freezer until the samples could be further processed.

Characterization of Melt Blends of HEMI-PLLA-67 and PLLA-49 with CS. Blends were analyzed by SEC and ^{1}H NMR spectroscopy. In addition, the blends were compression molded at 190 °C into "dog bone" tensile bars (gap dimensions, 15 mm × 3 mm × 0.4 mm) and cooled to room temperature in press. It should be noted that though the bar dimensions do not follow any testing standard, literature values for the mechanical properties of PLLA were obtained.[6] A minimum of 3 bars were tested for each blend on a Rheometrics Instruments MINIMAT tensile tester at a cross head speed of 10 mm/min. Differential scanning calorimetry was performed on the blends after tensile testing. A sample of tensile bar (5−10 mg) 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 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.[64]

Scanning electron microscopy images for particle analysis were taken on JEOL 6500 and 6700 microscopes. Samples were taken from the middle section of a piece of extrudate from the mixer. Prior to imaging, the surface of each sample was polished by cryo-microtomy (Reichert Ultracut S) with a glass knife at −120 °C to provide a smooth surface for image analysis. The microtomed surfaces were coated with 5−10 nm of Pt via sputtering and imaged at a 5.0 kV acceleration voltage. Microtomy of the samples resulted in the CS being pulled from the matrix, creating dark holes that were used for particle analysis. Image analysis was performed with ImageJ software to calculate the area of each CS particle. The area of the particle was used to calculate the diameter of the equivalent circle. A log-mean diameter (d_{lm}) and distribution parameter (σ_{lm}), a measure of the dispersion of the particle diameters, were calculated.[65] The MLT was calculated using eq 1

$$\mathrm{MLT} = d_{lm}\left[\left(\frac{\pi}{6\phi}\right)^{1/3}\exp(1.5\ln^2\sigma_{lm}) - \exp(0.5\ln^2\sigma_{lm})\right] \quad (1)$$

where ϕ is the volume fraction of CS incorporated into the blend (found by ^{1}H NMR spectroscopy).[65]

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Supporting Information Available: Synthesis details and ^{1}H NMR spectra for HEMI and its intermediates. ^{1}H NMR spectra of CS and the reaction products of HEMI-PLLA and CS from solution and melt blends. Detailed analysis of the number of conjugated double bonds present in one CS molecule. Synthesis details of model compounds and their blends used for HEMI-PLLA/CS reaction product structure elucidation (^{1}H NMR and ESI-MS spectra). DSC thermal characterization of melt blends (crystallinity and glass transition temperature). SEC of the ternary blend and its components. This material is available free of charge via the Internet at http://pubs.acs.org.

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