# Polylactide Vitrimers

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S *Supporting Information*

ABSTRACT: While much research has been aimed at new approaches to the healing of cross-linked polymers, there is a dearth of effort in the healing of renewable cross-linked polymers. In this study, the healing ability of renewable polylactide-based vitrimers containing $Sn(Oct)_2$ was investigated. The vitrimers were prepared from hydroxyl-terminated star-shaped poly(($\pm$)-lactide) samples that were cross-linked with methylenediphenyl diisocyanate. Cross-linked samples were prepared with isocyanate:hydroxyl (IC:OH) ratios of 0.6:1 to 1.1:1 and initial catalyst:hydroxyl ($Sn(Oct)_2$:OH) ratios ranging from 0.013:1 to 0.050:1. The plateau modulus and T_g values for the cross-linked samples decreased with decreasing IC:OH ratio. The materials were subjected to stress relaxation analyses, which confirmed that the materials not only were vitrimeric in nature but also exhibited remarkably short characteristic relaxation times of less than 50 s at 140 °C. Finally, vitrimers fractured in uniaxial tensile testing were healed by compression molding and exhibited up to 67% recovery of ultimate elongation, up to 102% recovery of tensile strength, and up to 133% recovery of tensile modulus values.
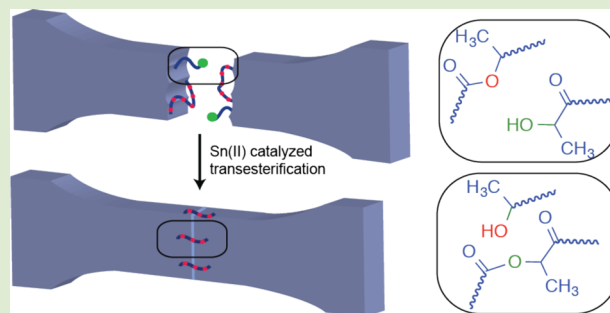
Cross-linked thermosets are a class of polymers that result from a typically irreversible bonding process and are materials that can no longer flow or dissolve, rendering them practical for both high-temperature and solvent-intensive applications. Unfortunately, thermosets cannot be reprocessed by traditional means such as melt processing. Numerous methods involving thermally reversible physical cross-links, such as Diels−Alder cycloadducts, have been utilized to create reprocessable cross-linked polymers.[1−5] However, these reactions do not conserve the number of cross-links in the network structure (i.e., the cross-link density is reduced in such nondegenerative bond cleaving processes), and thus the materials exhibit a loss in structural integrity upon heating.

Vitrimers, a new class of healing materials pioneered by Leibler and co-workers, are cross-linked polymers whose flow dynamics are reliant on the transient nature of their network structure.[6−8] The intrinsic properties of vitrimers were originally demonstrated using polyester epoxy resins that incorporated a Zn(II) transesterification catalyst. Extraordinarily, interchain transesterification occurs upon heating, and when stress is applied to the material, the bonds rearrange such that the stress is completely dissipated. Because transesterification is an isodesmic reaction, the materials do not exhibit a loss in structural integrity, even at elevated temperatures in solvents. The flow behavior of vitrimers relies on the rate of a chemical reaction in the melt state, and the viscosity (η) of vitrimers follows an Arrhenius relationship with temperature dependences similar to silica-based glasses, rather than the more typical Williams−Landel−Ferry (WLF) behavior.[6,8] A freezing transition temperature, T_v, in vitrimers is defined as the temperature above which a reversible network

topology can be achieved through bond exchange. In more quantitative terms, T_v is the temperature at which $\eta = 10^{12}$ Pa·s, the traditionally defined solid to liquid transition viscosity.[6,8−11] Since their discovery, vitrimers have been shown to be useful in a variety of practical applications, including adhesives and liquid-crystalline elastomers,[12,13] and hold tremendous promise for a range of advanced material technologies. Vitrimers have also been produced utilizing olefin metathesis, and those materials exhibited healing properties at room temperature.[14,15]

Recently, Altuna et al. developed a renewable vitrimer based on epoxidized soybean oil and citric acid.[16] These vitrimeric materials were effective without the use of an extrinsic catalyst based on using low carboxylic acid:epoxide ratios, thus achieving a high concentration of hydroxyl (OH) moieties within the cross-linked system. These β-hydroxyester networks exhibited almost complete recovery in the mechanical properties after healing fractured samples at 150 °C. In these systems, the authors could achieve characteristic relaxation times (τ^*) as small as 5.5 h at 150 °C. In comparison, Leibler et al. achieved a τ^* of approximately 1 h at 150 °C in the Zn(II)-catalyzed transesterification reaction of the polyester epoxy resins, showing that the use of a catalyst, even at low concentrations, can significantly shorten the healing times.[8]

Poly(lactide) (PLA), arguably the most studied bioderived thermoplastic, has a high tensile modulus and strength, making it a promising replacement for petroleum-based polymers such as poly(styrene) and poly(ethylene terephthalate).[17,18] A

variety of strategies have been adopted to broaden the range of PLA applicability. In particular, cross-linking has been used to create evenly degrading scaffolding for tissue regeneration applications and materials with significantly higher thermal stability as well as improved tensile and impact strengths.[19−23]

Given the importance of PLA as a commercially viable sustainable thermoplastic, we sought to develop PLA vitrimers to achieve a system that is both easily processed (e.g., as in two-part thermosets) and reprocessed or healed post use or damage. Here we use a cross-linking reaction between hydroxyl-terminated 4-arm star-shaped poly((±)-lactide) (HTSPLA) and methylenediphenyl diisocyanate (MDI), with stannous(II) octoate [Sn(Oct)$_2$] as both the cross-linking and trans-esterification catalyst. We reasoned that the concentration of ester groups in the resulting material would be much higher (one ester group per three backbone atoms) than the vitrimers previously developed, and thus the materials should exhibit even faster relaxation rates and, consequently, faster healing characteristics. As the hydroxyl functionality will be consumed in the cross-linking reaction and some remaining hydroxyl groups are necessary for the thermal and stress-activated transesterification healing process, a range of isocyanate:hydroxyl (IC:OH) ratios were evaluated. Furthermore, Sn(Oct)$_2$ was selected as the catalyst due to its high catalytic activity in transesterification reactions,[24] high stability in most media,[25] low toxicity (FDA approved),[26,27] and commercial relevance (Scheme 1).

Scheme 1. Synthesis of HTSPLA and ICSPLA
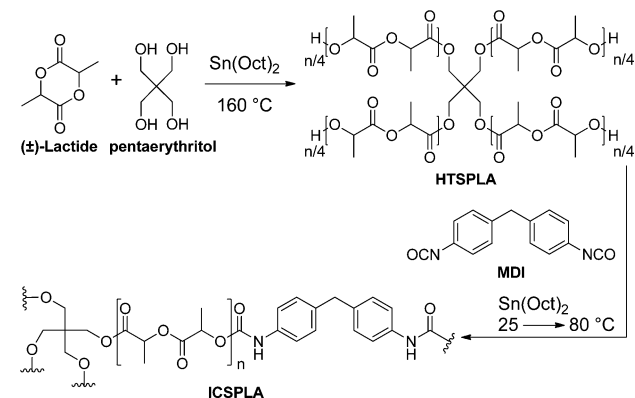
Two sets of isocyanate cross-linked star-shaped poly((±)-lactide) (ICSPLA) materials were produced. In set A, the IC:OH ratio was varied from 0.6:1 to 1.1:1 while maintaining a constant initial Sn(Oct)$_2$:OH loading of 0.025:1. In set B, the initial Sn(Oct)$_2$:OH loading was varied from 0.013:1 to 0.05:1 while maintaining a constant 0.75:1 IC:OH ratio (set B also included a control sample with no Sn(Oct)$_2$). All materials were then subjected to uniaxial tensile testing and exhibited mechanical properties similar to the previously reported and related tolylene diisocyanate cross-linked polylactide samples (σ_{TS} = 55 MPa, ε_b = 5%, and E = 1.7 GPa; Table S2, Supporting Information).[20] The gel fractions (≥0.94) of all samples were determined by room-temperature swelling tests (Table S2, Supporting Information).

Dynamic mechanical thermal analysis (DMTA) experiments were performed on set A. Figure 1a demonstrates a drop in modulus of more than 2 orders of magnitude while heating through the glass transition temperature (T_g). The subsequent appearance of a relatively constant plateau modulus (80−120
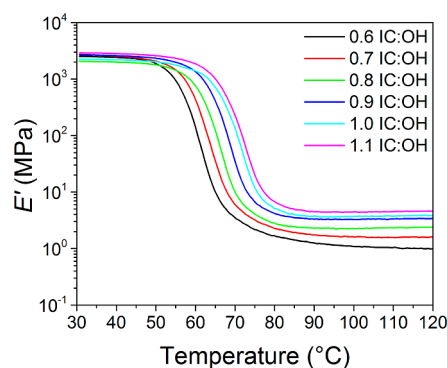
Figure 1. DMTA analysis: storage modulus of ICSPLA with respect to IC:OH ratio (set A). DMTA data for varying catalyst loading are given in Figure S1 (Supporting Information). Data acquired in uniaxial tension deformation (30 to 120 °C at 5 °C min^{-1}, ω = 6.28 rad s^{-1}, and γ = 0.05%) with a rectangular sample geometry.

°C) was consistent with having a network structure. As the amount of MDI was increased from 0.6 to 1.1 IC:OH, the plateau modulus (at 100 °C), cross-linking density (ν_e), and the T_g of the materials increased from 1.1 to 4.5 MPa, 1.2 to 4.8 × 10^{-4} mol cm^{-3}, and 55 to 65 °C, respectively (Figure 1 and Figure S1c and Table S1, Supporting Information). Conversely, the molar mass between cross-links (M_x) decreased with increasing cross-link density, all indicative of a more constrained network as the result of an increase in the equivalents of MDI utilized. DSC analysis showed a similar trend in T_g values (Table S1, Supporting Information).

The samples comprising set B with varying catalyst concentrations were also subjected to DMTA. The concentration of Sn(Oct)$_2$ in the system did not significantly affect the cross-link density. This analysis indicated that there was a negligible difference in the plateau modulus (1.1−1.3 MPa) with respect to the amount of Sn(Oct)$_2$ (Figure S1a, Table S1, Supporting Information). Similarly, the calculated values of ν_e (1.2−1.4 × 10^{-4} mol cm^{-3}) and M_x (9.0−11 kg mol^{-1}) did not change significantly with catalyst loading.

Stress relaxation analyses (SRA) were then performed on all of the materials in the linear viscoelastic regime until the samples had relaxed to 1/e of the initial stress relaxation modulus (i.e., after one mean lifetime, τ^*) [Figure 2].[8] The control sample with negligible amount of Sn(Oct)$_2$ relaxed only about 3% of its initial relaxation modulus over 5000 s (the black curve in Figure 2b). Indeed, it has been shown previously that while thermally activated transesterification in polyesters can occur, it does so at a much slower rate.[7,16] The materials containing catalyst relaxed significantly faster, despite their high degree of cross-linking, giving evidence to their vitrimeric nature. Reduction in IC:OH ratios resulted in shorter relaxation times, likely due to an increase in number of unreacted hydroxyl groups (Figure 2a). Furthermore, materials with lower IC:OH ratios have lower plateau moduli, allowing for the reactive dangling chain ends to move more freely in the material. Indeed, Altuna et al. attributed faster relaxation of their materials to this phenomenon.[16]

At IC:OH ratios of 0.9:1 and above, the rate of stress relaxation no longer began to decrease but remained essentially constant. We suggest that at a perfect 1:1 IC:OH ratio there would be little to no stress relaxation observed due to full consumption of hydroxyl groups. However, stress relaxation was observed in these materials and could be attributed to an
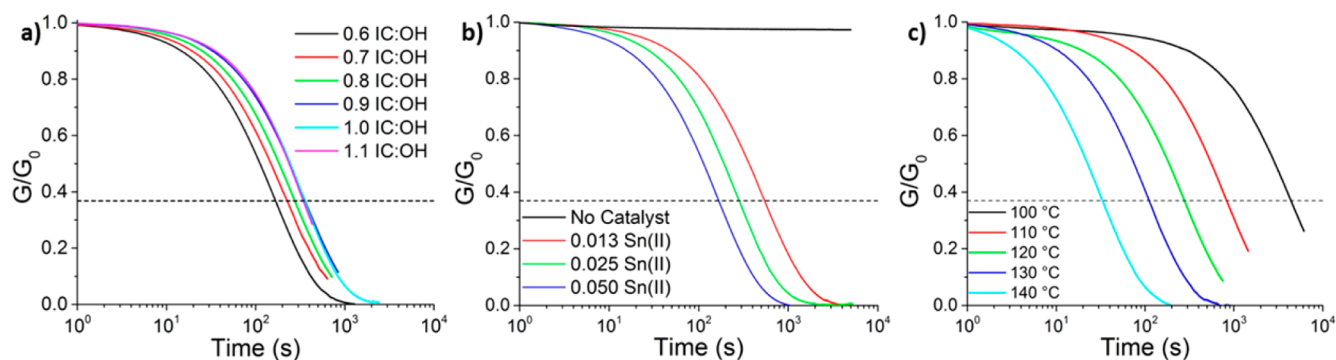
Figure 2. Stress relaxation analysis with respect to (a) varying IC:OH ratio (set A) at 120 °C, (b) varying initial mol ratio of $Sn(Oct)_2$:OH (set B) at 120 °C, and (c) temperature with 0.75:1 IC:OH and initial 0.025:1 $Sn(Oct)_2$:OH ratios. The dashed line indicates 37% of the G_0. Data normalized and acquired at 9.3% strain.

incomplete conversion of the isocyanates in MDI. These remaining isocyanates would rapidly react with any moisture, releasing CO_2 and forming amines. The resulting amines can also react with esters, forming amides and releasing hydroxyls capable of further transesterification.

Increasing the catalyst loading also accelerated the relaxation rate with a decrease in τ^* from 410 s to only 154 s at 120 °C (Figure 2c). An increase in the temperature also showed a direct correlation with the stress relaxation rate in agreement with Leibler and co-workers.[6,8] For example, τ^* for a sample with a 0.75:1 IC:OH ratio and an initial mol ratio of 0.025:1 $Sn(Oct)_2$:OH decreased from 4055 s at 100 °C to 33 s at 140 °C. In fact, at 140 °C, all nine of the materials containing catalyst exhibited τ^* values below 50 s. These results are significant when compared to previous work[6,8] where the polyester epoxy resins containing 5 mol % Zn(II) to initial OH exhibited $\tau^* \approx 26$ s at 280 °C, while the ICSPLA material with an initial mol ratio of 0.050:1 Sn(II):OH (approximately 5 mol % Sn(II) to initial OH) achieved an average $\tau^* = 22 \pm 2$ s at a temperature 140 °C lower. We attribute this phenomenon to the high concentration of ester moieties in PLA-based materials and the high activity of Sn(II) catalysts, leading to an increase in the rate of transesterification.

To determine T_v for ICSPLA samples, the Maxwell equation (eq S3, Supporting Information) was used to relate τ^* to T_v.[8] The average plateau modulus of these materials was approximately 2.2 MPa (see Figure 1) and $\eta = 10^{12}$ Pa·s at the solid to liquid transition temperature (T_v for vitrimers), thus giving a $\tau^* = 1.4 \times 10^6$ s at T_v. The experimental τ^* values were then plotted vs $1000/T$ and fit to the Arrhenius relationship (eq S2) in Figure S2 (Supporting Information). The curves in Figure S2 were then extrapolated to $\tau^* = 1.4 \times 10^6$ s, which gave T_v for the ICSPLA materials (Table S1, Supporting Information).[8] Remarkably, all of the systems had a T_v within a few degrees of their T_g values, indicating that as soon as the materials reach the rubbery state, they are capable of transesterification and thus flowing. Furthermore, as the IC:OH ratio was decreased and the catalyst loading was increased, T_v decreased in agreement with the literature.[8,16]

An activation energy, E_a, of 150 ± 3 kJ mol^{-1} was extracted from the Arrhenius relationship (eq S3, Supporting Information). The literature value of E_a for transesterification catalyzed by $Sn(Oct)_2$ in the polylactide melt was reported as approximately 83 kJ mol^{-1},[24] almost half of what was determined by stress relaxation. The inconsistency between these two values could be attributed to the presence of

tris(nonylphenyl)phosphite (TNPP), which was added to thwart oxidative degradation, as it is an effective inhibitor of some transesterification catalysts.[28−32] However, the same E_a was obtained for a sample similar to ICSPLA-0.025−0.75 with no TNPP (Figure S2, Supporting Information). Further investigation is ongoing to explain this discrepancy.

All the materials broken by uniaxial tensile testing were healed via compression molding at 140 °C and 4 MPa for 30 min [or approximately 35 to 85τ^*] (Figure 3). Remarkably, all
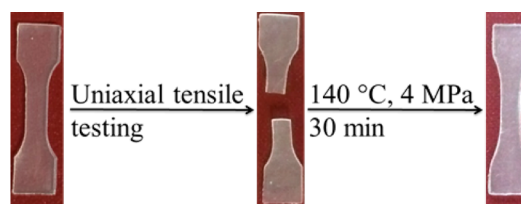

Figure 3. Representative ICSPLA material subjected to uniaxial tensile testing and then healed. Sample shown has an initial mol ratio of 0.013:1 $Sn(Oct)_2$:OH and a 0.75:1 IC:OH ratio. Also see Figure S4 (Supporting Information).

of the samples with catalyst showed healing capability under these conditions (Figure S4, Supporting Information). In stark contrast, the control sample showed a clear interface where it had been broken and, upon removal from the mold, broke into two separate pieces. Uniaxial tensile testing revealed a trend similar to that of SRA; samples containing lower IC:OH ratios and higher catalyst loadings showed a greater recovery of tensile properties (Figure 4 and Table S3, Supporting Information). In particular, samples containing a 0.75:1 IC:OH ratio or lower and an initial mol ratio of 0.025:1 $Sn(Oct)_2$:OH or higher showed remarkable healing characteristics.

Thus, these PLA-based vitrimers were capable of relaxing stress at significantly higher rates than any other polyester-based vitrimer systems at moderate temperatures. DMTA evidenced that at temperatures well above the T_g and T_v, under low stress and strain, the materials will also maintain their structural integrity. Furthermore, we demonstrated that by tuning the hydroxyl functionality and catalyst loading an array of material properties can be achieved. Additionally, the T_v of all the materials was within a few degrees of the T_g, and many of the materials were capable of a full recovery in their tensile strength.
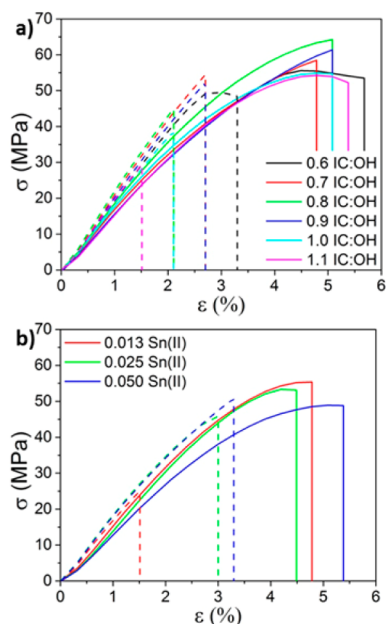
Figure 4. Uniaxial tensile testing of fresh ICSPLA materials (solid lines) and after healing (dashed lines) with respect to (a) varying the IC:OH ratio (set A) and (b) varying the initial mol ratio of Sn(Oct)$_2$:OH (set B).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and all characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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