

Effect of multi-branched PDLA additives on the mechanical and thermomechanical properties of blends with PLLA

Lennard Torres,¹ Colleen McMahan,² Lucas Ramadan,² Kevin M. Holtman,² Gustavo H. D. Tonoli,^{2,3} Allison Flynn,¹ William J. Orts²

¹Lapol, LLC, Santa Barbara, California 93105

²ARS US Department of Agriculture, Bioproducts Research Unit, WRRRC, Albany, California 94710

³Department of Forest Science (DCF), Universidade Federal De Lavras, C.P. 3037, Lavras, MG 37200-000, Brazil

Correspondence to: W. J. Orts (E-mail: bill.orts@ars.usda.gov)

ABSTRACT: Stereocomplex formation between poly(L-lactic acid) (PLLA) and poly(D-lactic acid) (PDLA) in the melt state was investigated and altered via the addition of multi-branched poly(D-lactide) (PDLA) additives. Two different multi-branched PDLA additives, a 3-arm and 4-arm star-shaped polymeric structure, were synthesized as potential heat resistance modifiers and incorporated into PLLA at 5, 10, and 20 (w/w) through melt blending. Mechanical and thermomechanical properties of these blends were compared with linear poly(L-lactide) (PLLA) as well as with blends formed by the addition of two linear PDLA analogs that had similar molecular weights to their branched counterparts. Blends with linear PDLA additives exhibited two distinct melting peaks at 170–180°C and 200–250°C which implied that two distinct crystalline domains were present, that of the homopolymer and that of the stereocomplex, the more stable crystalline structure formed by the co-crystallization of both D- and L-lactide enantiomers. In contrast, blends of PLLA with multi-branched PDLA formed a single broad melting peak indicative of mainly formation of the stereocomplex, behavior which was confirmed by X-ray diffraction (XRD) analysis. The heat deflection temperature determined by thermal mechanical analysis was improved for all blends compared to neat PLLA, with increases of up to 180°C for 20% addition of the 3-arm PLLA additive. Rheological properties of the blends, as characterized by complex viscosity (η^*), remained stable over a wide temperature range. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42858.

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INTRODUCTION

Poly(lactic acid) (PLA) is fast becoming a viable alternative to petroleum-based plastics in the market since it is biodegradable,^{1,2} it is generated from renewable resources,² and like most thermoplastics, it can be easily formed into different products using standard industrial processes such as injection molding or thermoforming.³ Mechanical properties of PLA-based products are also comparable to petroleum-based plastics. For these reasons, PLA is found in many drop-in applications such as packaging, single-use utensils, mulch-films, and cold liquid containers. Still, it is difficult for PLA to be used for long term, high performance applications such as injection molded automotive parts, textiles or hot liquid (microwaveable) containers due to its high cost, inherent brittleness, and poor heat resistance.^{4–8}

The inherent brittleness of industrialized PLA can be improved by melt blending with various plasticizers,^{2,9,10} including low

molecular weight citrate esters¹¹ or poly(ethylene glycol), which decrease the glass transition and can improve both elongation and impact resistance.^{9–14} The poor heat resistance of PLA can be improved by adding nucleating agents^{9,15–20} sometimes in combination with plasticizers⁹ to increase the rate of crystallization. Talc,^{15–17} phosphates,¹⁹ and organoclays²⁰ have all been applied as nucleating agents to increase the relatively slow crystallization rate of PLA. All of these additives, though, add cost to manufacturing and, more importantly, they rely on nonequilibrium modifications to the final product. As a result changes in processing and/or changes in thermal history (including storage in the sun) can readily reverse their effect either through recrystallization or through immiscibility; i.e. migration of these small-molecule additives out of the product. Long-term modifications of PLA properties are required to improve its shelf-life and thus its commercial appeal.

Stereocomplexation^{21–32} of PLA holds the promise of improving thermo-mechanical properties on a more stable basis. The lactic

acid monomer exists in two enantiomeric forms, L-lactic acid and D-lactic acid. During polymerization, the ratio and distribution of D- and L-enantiomers can be varied, resulting in an array of properties ranging from completely amorphous to semicrystalline.^{21,22} The L-rich homopolymer, termed PLLA, is the most widely commercialized PLA and is often produced as a semicrystalline thermoplastic. One unique property of PLA is that the D-rich and L-rich chains, termed PDLA and PLLA, respectively, can cocrystallize to form a stereocomplex resulting in polymers with more robust mechanical properties. The stereocomplex provides a higher melting temperature, higher heat deflection point, and, with optimal thermal processing,²³ improved ductility. Thus, end-use properties of semicrystalline PLA can be varied and even “tailored” by changing the ratio and distribution of D- and L-lactic acid enantiomeric units along the polymer chains.

Increasing evidence shows that the stereocomplex is the more favored equilibrium structure for semicrystalline PLA.^{22,26,29–32} Interestingly, the presence of stereocomplexed crystallites appears to result in multiple crystalline morphologies. Saeidlou *et al.*,²⁶ for example, presented clear evidence that melt-processed stereocomplexation resulted in a crystalline structure with dual morphologies for the stereocomplex, consisting of distinct spherulites surrounded by a less-ordered crystalline network. These multiple morphologies were shown directly via optical microscopy and has implications in the final end-use properties of the PLA product. One can hypothesize that this is similar to reinforced polymer/polymer composites in which the highly crystalline spherulitic structures act as stiffening agents within the more flexible network structure.

Stereocomplexation of PDLA and PLLA is also an effective method of increasing the crystallization rate of PLA-based materials. Schmidt and Hillmyer²³ investigated the non-isothermal crystallization of PLLA and discovered that formation of the stereocomplex, even at very low concentrations of additive, acts as a significant nucleating agent, with crystallization rates for racemic mixtures of PLLA and PDLA higher than for talc. Yamane and Sasai²⁴ discovered that the addition of high molecular weight PLLA to PDLA increased, not only the stability of the crystal, but also crystallization rate during cooling from the melt. Several groups^{33,34} have shown that stereocomplex formation can be used to change the hydrolytic degradation rate of PLA by introducing new crystalline morphologies.

One drawback of stereocomplexing, though, is that it can lead to brittleness, which could reduce industrial applications. In a recent study to increase heat resistance of PLA, Torres *et al.* [2014, unpublished data] discovered that increasingly higher levels of stereocomplexing resulted in materials that were unsuitably brittle for commercial products. More research is needed to meet the challenge of improving, simultaneously, the heat deflection and toughness of PLA by striking a balance between improved toughness and higher heat resistance.

The purpose of this study was to determine the effect of the addition of short-chain, branched PDLA additives on the thermal, mechanical, and heat resistance of linear PLLA. It was hypothesized that the incorporation of branched PDLA addi-

tives into linear PLLA would form stereocomplex crystallites in which branching points would impart ductility, while short-chain arms of D-enantiomers would promote stereocomplex formation. Short chain-branched additives have been applied commercially to commodity polymers to add ductility to highly crystalline morphologies.^{35,36}

The overarching target of this research is to have enough control of the stereocomplex crystalline morphology of PLA polymers to ultimately tailor commercial properties. This study was carried out via melt blending. Solution blending studies that mix linear PLLA with branched PDLA^{25,27–31} provide important data to the field, although melt blending was undertaken here because it is far more practical in industrial applications. In this report, 3-arm and 4-arm PDLA additives, along with their linear analogs, were synthesized and melt blended with PLLA to promote formation of the PDLA-PLLA stereocomplex. Blends were then characterized using DSC, thermal mechanical analysis, X-ray diffraction analysis, flexural mechanical testing, and rheology with the goal of introducing a commercially viable means to increase heat resistance in PLA-based biomaterials without inducing significant brittleness.

EXPERIMENTAL

Materials

PLA 4032D was kindly supplied by NatureWorks, LLC (Minnetonka, MN) and D-lactide kindly supplied by PURAC (Netherlands). All other chemicals including the solvents were purchased from Sigma–Aldrich (St. Louis, MO) and used without purification.

Synthesis of PDLA Additives

Linear and multi-branched PDLA additives were synthesized via ring-opening polymerization of D-lactide using different initiators, as outlined in Figure 1. The 1-propanol and 1,3-propanediol were used as the initiators to prepare linear PDLA additives. To prepare the 3-arm and 4-arm star-shaped PDLA additives, 1,1,1-tris(hydroxymethyl)ethane and pentaerythritol were used, respectively.

Typically, a round-bottom flask was flame-dried and then charged with predetermined amounts of D-lactide and initiator (see Table I). The flask was then immersed in an oil-bath at 175°C. Once the D-lactide melted, a small amount of stannous octoate was added dropwise. The reaction mixture was periodically sampled and monitored by GPC. After reaching a certain monomer conversion, the reaction mixture was dissolved in chloroform and precipitated in an excess amount of cold methanol. The white solid was then washed several times with cold methanol and then dried at 70°C in a vacuum oven for several hours prior to further characterization and blending. Proton-NMR confirmed the structure of the PDLA additives and provided number average molecular weights (M_n) which corresponded with the same trends in M_n as the GPC (data not shown).

Sample Preparation

PLLA resins were dried in an oven at 80°C overnight prior to melt blending to prevent hydrolysis. From PLA previous work with these type samples (data not shown) we anticipated about

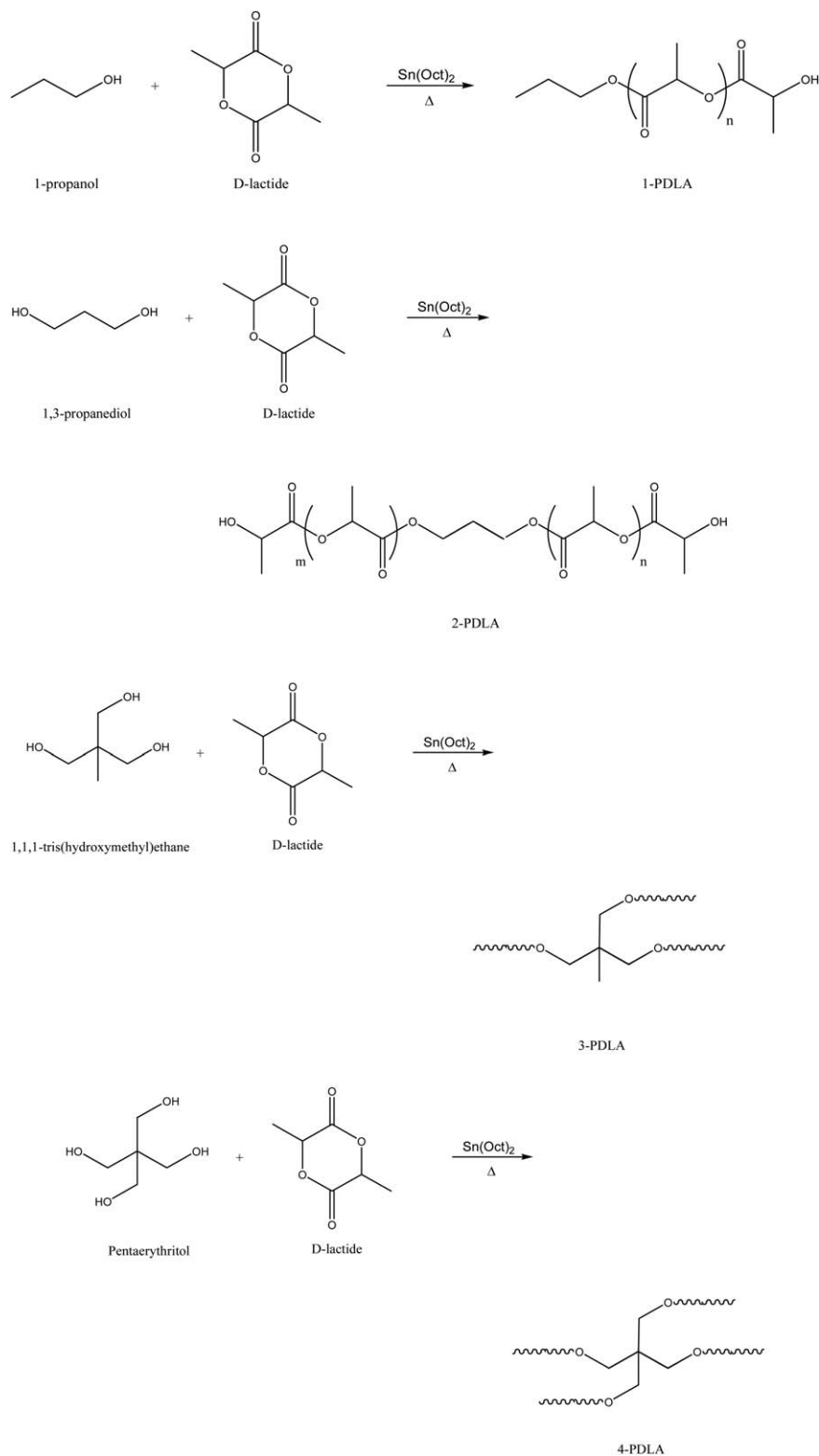


Figure 1. Synthesis scheme for the preparation of linear and branched PDLA additives.

2–5% decrease in M_w due to hydrolysis, which likely does not have a significant impact on the final results. The PLLA and PDLA were first dry mixed (at PDLA loadings ranging from 5 to 20 wt %) and then fed into a 60 cm³ capacity Haake Rheo-

mix 6000 (Thermo Scientific, Waltham, MA) laboratory scale melt mixer, which was operated at the temperature of 170–175°C with a screw speed of 45 rpm. The residence time in the melt mixer was five minutes. Blends with linear and branched

Table I. Molecular Weight Data of Neat PLLA and PDLA Additives

Samples	mmol initiator	mmol monomer	Architecture	M_n	M_w	PDI
PLLA	–	–	Linear	123,000	218,000	1.77
1-PDLA	20	673	Linear	5349	7303	1.37
2-PDLA	20	673	2-Arm linear	6237	7928	1.27
3-PDLA	20	673	3-Arm star	6333	7767	1.23
4-PDLA	20	673	4-Arm star	3908	5206	1.33

PDLA were mixed at 175 and 170°C, respectively. Resulting blends were then compression molded into 6-in. diameter \times 1.5-mm-thick discs using a heated Carver press at 165–180°C, depending on the composition of the blends. The compression molded samples were removed from the heated press to solidify in air for \sim 1 min, the time to reach room temperature. Prior to mechanical and thermomechanical testing, the discs were stored for 24 h in a desiccator to avoid moisture absorption.

Gel Permeation Chromatography (GPC)

Molecular weights of the PLLA and PDLA homopolymers were determined on a Waters (Milford, MA) liquid chromatograph equipped with a refractive index detector, three Waters Styragel columns HR1, HR2, and HR4 THF 7.8 \times 300 mm, and a Styragel guard. The mobile phase was tetrahydrofuran. Columns were calibrated using monodisperse polystyrene standards. Because PDLA homopolymers are insoluble in THF, samples were first dissolved in a small amount of chloroform and then diluted with THF. The diluted samples were then injected into the GPC for molecular weight determination.

Differential Scanning Calorimetry (DSC)

Thermal properties of neat PLA and resulting blends were characterized using a Perkin Elmer (Santa Clara, CA) DSC 8000 differential scanning calorimeter calibrated for melting temperature and enthalpy with indium. Samples (\sim 10 mg) were placed into stainless steel pressure pans, heated from 25 to 250°C at 10°C min⁻¹. The heats of fusion, ΔH_{m1} and ΔH_{m2} , were calculated as the area under melting endotherms, T_{m1} and T_{m2} , respectively using the machine software.

Thermomechanical Analysis (TMA)

The heat deflection temperature (indicative of heat resistance) of each blend sample was determined using a TA Instruments (New Castle, DE) thermomechanical analyzer TMA 2940. Test bars were cut at 19-mm length, 4.9-mm width, and 1.5 mm thickness. Again, samples were equilibrated at room humidity and temperature for 24 h. During TMA analysis, samples were held at 30°C for 1 min before ramping temperature to 200°C at 10°C min⁻¹.

X-ray Diffraction (XRD)

XRD patterns were obtained for the PLA blend samples using a Philips PANalytical X'Pert XRD System (PANalytical, Westborough, MA) with Cu K α radiation at 45 kV and 40 mA with a wave length, $\lambda = 0.154$ nm. Scattered radiation was detected from ground powders in the range of $2\theta = 5$ –40°, at a scan rate of 2° min⁻¹. Samples were blended in the melt mixer at 170–175°C, compression-molded into 1.5-mm-thick discs using a

heated Carver press at 175°C, quenched quickly and then ground (several weeks after molding) into a uniform powder for XRD analysis.

Mechanical Test

Flexural properties of each sample were measured using an Instron (Canton, MA) 5500R universal testing system equipped with a 1 kN load cell and operated at an extension rate of 25.4 mm min⁻¹. Samples were cut into rectangular test bars measuring 63.5 \times 12 mm, with a thickness of 1.5 mm. Prior to testing, each sample was conditioned at room temperature (\sim 25°C) and relative humidity (near 50%) for 24 h.

Rheology

Shear moduli (G') and complex viscosities (η^*) were measured as a function of temperature using an APA 2000 oscillating rheometer from Alpha Technologies (Akron, OH) configured in parallel plate geometry and with sample thickness \sim 0.9 mm. A thermal equilibration time of 2 min at the specified starting test temperature of 180°C was applied. Small deformation (less than 2%) dynamic oscillatory motion was imposed on the sample at a frequency of 1 Hz over a temperature range from 40 to 180°C.

RESULTS AND DISCUSSION

PDLA Additives and Thermal Properties of the Blends

Molecular weights of the synthesized PDLA additives used to prepare blends are outlined in Table I and ranged between 4000 and 8000. According to their GPC chromatograms, molecular weight distribution for most additives was fairly monomodal with polydispersity indexes near 1. Low molecular weight additives were chosen for this study because it was believed that short chain branching would produce significant improvements in toughness and ductility while still imparting significant positive effects on heat resistance via formation of the stereocomplex crystalline structure.

Table II summarizes the composition of blends prepared by melt mixing of PDLA additives with linear PLLA in a laboratory scale melt mixer, while Table III outlines their thermal properties as measured by DSC. Processing temperatures of the blends were in the range, 170–175°C, which is above the melt point for linear PLLA but below the melt point for the stereocomplex polymorph. This thermal treatment was chosen to “encourage” formation of the more stable crystal; specifically, to ensure that the relatively stable stereocomplex that did form *in situ* would have a chance to stabilize, not melt. Thus the stereocomplex would presumably act as a heterogeneous nucleating agent for the rest of the PLLA matrix.²³ Also, this temperature regime is

Table II. Composition of Blends (% by Weight) and Corresponding Nomenclature

Blend nomenclature	%PLLA	%PDLA	Additive	Architecture
100L	100	-	-	Linear
95L-05M	95	5	1-PDLA	1-Arm linear
90L-10M	90	10	1-PDLA	1-Arm linear
80L-20M	80	20	1-PDLA	1-Arm linear
95L-10D	95	5	2-PDLA	2-Arm linear
90L-20D	90	10	2-PDLA	2-Arm linear
80L-20D	80	20	2-PDLA	2-Arm linear
95L-10T	95	5	3-PDLA	3-Arm branched
90L-20T	90	10	3-PDLA	3-Arm branched
80L-20T	80	20	3-PDLA	3-Arm branched
95L-10Q	95	5	4-PDLA	4-Arm branched
90L-20Q	90	10	4-PDLA	4-Arm branched
80L-20Q	80	20	4-PDLA	4-Arm branched

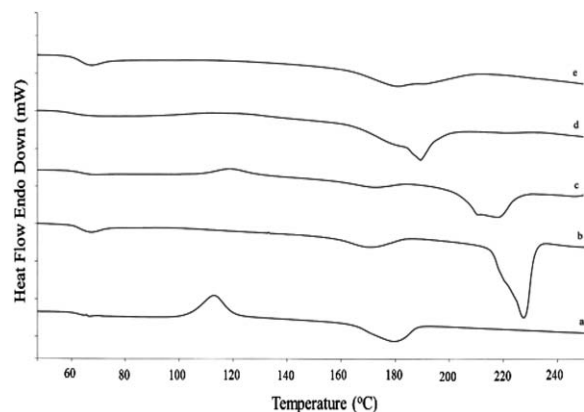
not inconsistent with viable processing conditions that would be applied in a commercial setting. Note also that for consistency the neat PLLA was also processed in the melt mixer using the same parameters as the blends.

DSC data for all of the blends created in this study are summarized in Table III while Figure 2 shows representative DSC traces of PLLA blends derived from each of the additives at 20% loading. Each sample exhibits a glass transition, T_g , a crystallization peak, T_c , and an additional first melting temperature, T_{m1} . The crystallization temperature, T_c , and the first melting temperature, T_{m1} , remained similar to neat PLLA for all samples, with T_c ranging from 105 to 115°C and T_{m1} roughly between 170–180°C. For most of the additive blends, a secondary melting

Table III. Thermal Properties of Neat PLLA and Melt Blends with PDLA Additives Heated from 30 to 250°C at a Rate of 10°C min⁻¹

Blend	T_g (°C)	T_c (°C)	T_{m1} (°C)	ΔH_{m1} (J g ⁻¹)	T_{m2} (°C)	ΔH_{m2} (J g ⁻¹)
100L	61	110	176	21	-	-
95L-05M	63	106	180	29	222	5
90L-10M	68	108	177	23	222	15
80L-20M	63	101	173	7	229	50
95L-05D	67	110	180	20	211	9
90L-10D	66	106	179	16	214	22
80L-20D	60	111	169	6	208	32
95L-05T	59	-	178	30	196	7
90L-10T	63	105	172	12	192	9
80L-20T	61	121	-	-	196 ^a	24
95L-05Q	60	101	174	32	-	-
90L-10Q	62	100	172	26	-	-
80L-20Q	60	-	181	24	-	-

^a A broad melting curve was observed.

**Figure 2.** DSC thermographs of PLLA and melt blends derived by additions of linear and branched PDLA additives at 20% loading.

temperature, T_{m2} , was also observed, ranging from 192 to 229°C (Table III). T_{m2} has been ascribed to correspond with melting of the stereocomplex, with a temperature range that is in broad agreement with previous literature reports.^{18,21–24,35–39}

The highest T_{m2} melting temperatures were from blends prepared with the unbranched monofunctional-PDLA (1-PDLA), followed by the difunctional PDLA (2-PDLA) additive. Although both 1-PDLA and 2-PDLA are linear, 2-PDLA contains propanediol units within its backbone that could presumably disrupt crystallinity. One can hypothesize that non-crystallizable units within the 2-PDLA chain would result in differences in crystalline morphology and/or defects relative to the crystallites formed between 1-PDLA and PLLA. Defects would lead to a slight depression of the melting temperature. For example, McKee³⁹ reported that increased flexibility in a polymer backbone led to a larger number of chain conformations in the melt, which resulted in a depression of T_m . Lower stereocomplex melting temperatures were also observed in the 3-arm star polymer blends 95L-05T and 90L-10T, probably for similar reasons.

All blends containing the 4-arm star PDLA polymers and the blend with 20% 3-arm PDLA (Figure 2) exhibited such broad melting curves at T_{m2} that it was difficult to report a distinct T_{m2} value. A similar trend was reported by Biela *et al.*²⁵ for equimolar PLLA and PDLA 6-, 13-, 32-arm star-shaped stereocomplexes, all of which exhibited broadened T_{m2} melting endotherms as the number of branches increased.^{25,26} It was hypothesized²⁶ that increased chain entanglement for the branched PDLA arms hindered the crystallization process, preventing crystallizable chain segments from reaching the growing crystal front.²⁷ This resulted in smaller, less perfect stereocomplex crystallites with a wide range of melting points.

One goal of this study was to alter the heat resistance of PLA-based biomaterials through formation of stable stereocomplex crystalline domains. Figure 3 shows the deflection-temperature curves, as determined by TMA, of neat PLLA (the control) compared with the blends outlined in Tables II and III. The addition of all of the additives at 5, 10, and 20% [Figure 3(a–c), respectively] increased the heat deflection temperatures (HDT)

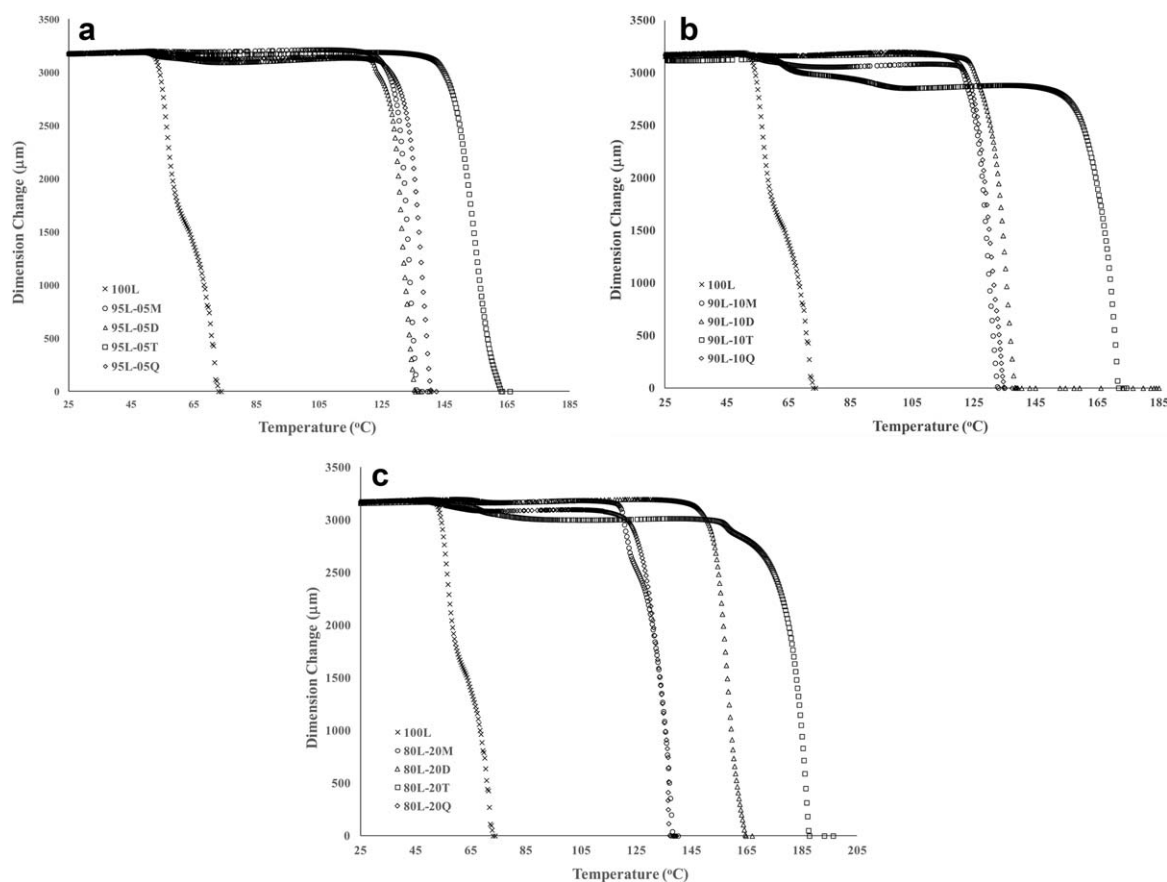


Figure 3. Heat deflection temperature (HDT) curves from TMA analysis of neat PLLA and melt blends with PDLA additives at (a) 5% (w/w), (b) 10% (w/w), and (c) 20% (w/w) concentrations.

significantly, with increases ranging from 60 to 120°C. Neat PLLA exhibited a deflection near its glass transition temperature of ~60°C. Blends made with the 3-arm star PDLA polymer were the most heat resistant with additions of 5% [Figure 3(a)] and 10% [Figure 3(b)] resulting in HDT of roughly 157°C, while a 20% loading [Figure 3(c)] resulted in HTD of 182°C. Similarly, the M, D, and Q blends all resulted in higher HDTs than for PLLA with roughly the same HDT of ~130°C at 5 and 10% loading. Interestingly, the Di-block sample at 20% loading (80L-20D) exhibited significantly better heat resistance than either the Mono- or Quaternary-block. It is interesting to note that the trend in HDT does not correspond exactly with the trend in DSC melting point, T_{m2} ; i.e., 80L-20M, the blend with the 1-arm PDLA additive exhibited the highest T_{m2} , while 80L-20T, the 3-arm PDLA additive resulted in the highest HDT. The reason for the enhanced HDT of 80L-20T is not yet well-understood. One possibility may be related to the different ways the stereocomplexes behave as they melt. Linear stereocomplexes (in blends with 1- and 2-PDLA) most likely “unzip” from one end (or both ends), separating L- and D-components. Branched PDLAs, however, (as in blends with 3- and 4-PDLA) are tethered to multiple PLLA chains, making the “unzipping” process difficult. Because of lower degrees of freedom, some arms may reform stereocomplexes with nearby PLLA chains. This may be reflected in enhanced melt stability and thus ultimately, improved HDT.

Closer inspection of the curves in Figure 3(a–c) reveals bimodal heat deflection behavior for multiple samples, especially at 20% loading. For example in Figure 3(c), sample 80L-20T, the 3-arm additive at 20%, begins to exhibit heat deflection at ~70°C, then more sharply at 170°C and then its most significant deflection at ~185°C. Likely, the first HDT is due to glass transition²⁶ while the higher deflection points indicate disruption of the stereocomplex morphology within the sample. Similarly, the 3-arm additive at 10% loading [90L-10T in Figure 2(b)] exhibits a range of heat deflection points. This likely indicates that more than one morphological domain is present in these samples,²⁶ as will be explored via X-ray diffraction analysis.

X-ray Diffraction: Multiple Crystalline Domains

Figure 4 presents the XRD patterns for samples containing 20% of each of the PDLA additives. It is noteworthy that all samples, despite undergoing the same thermal history (compression molded at 175°C, quenched, and ground into powder), resulted in differing XRD patterns. The XRD pattern for PLLA (bottom curve, Figure 4) confirms that the homopolymer remained completely amorphous as a result of this thermal history, likely due to quick quenching. In contrast, the XRD patterns from all of the samples with PDLA additives show distinct crystalline structure.

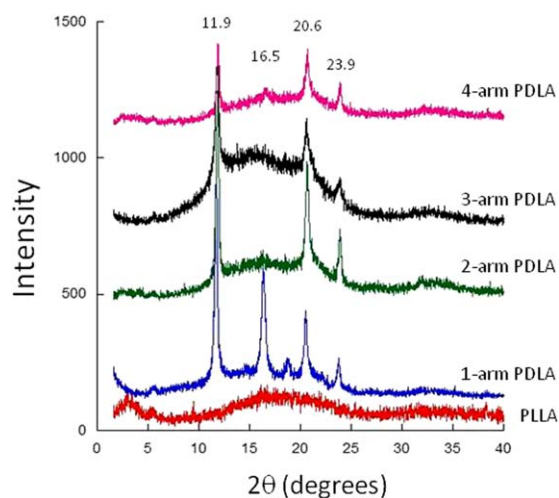


Figure 4. XRD diffractograms of PLLA and melt blends derived by additions of linear and branched PDLA additives at 20% loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Two distinct crystalline structures are indicated by the XRD reflections. Peaks at $2\theta = 11.9^\circ$, 20.6° , and 23.9° correspond to the stereocomplex, while those at $2\theta = 15^\circ$, 16.5° , and 18.5° are associated with homopolymer crystals.²² The XRD trace for the 1-arm PDLA additive (Fig. 4, 2nd from bottom curve) exhibited all of these peaks clearly, with a strong peak at 16.5° corre-

sponding to the homopolymer and strong peaks at both $2\theta = 11.9^\circ$, 20.6° , and 23.9° corresponding to the stereocomplex. Interestingly, the 1-arm PDLA additive, which clearly formed a stereocomplex with PLLA, is potentially acting as a nucleating agent for PLLA chains^{38–42} considering how distinctly sharp the peaks are, implying relatively high crystallinity. Maintaining the temperature between 170 and 175°C would ensure that the stereocomplex would not melt, while other chains may be more mobile, thus allowing the additive to act as a nucleating agent for PLLA chains. In contrast, the branched structures exhibited weak peaks corresponding to the homopolymer, yet relatively strong peaks corresponding to the stereocomplex.

Flexural Properties

Figure 5 shows the relationship of flexural properties with the concentration of PDLA additives in the blends. The blends generally exhibited higher flex modulus than that of neat PLLA [denoted by X and a dashed line in Figure 5(a)]. Tsuji *et al.*⁴¹ found similar results (trends in Young's modulus) in 1:1 equimolar blends of PLLA/PDLA. In the present study, flex modulus dropped at higher PDLA additive concentrations, suggesting an optimum concentration around 10% additive. In contrast, Petchsuk *et al.*²⁷ created solution-cast blends of PLLA with branched PDLA having longer branch segments than the additives being reported here. Their tensile modulus increased as a function of chain branching.²⁷ Perhaps the chain segments between branch points were long enough to avoid the steric hindrance caused

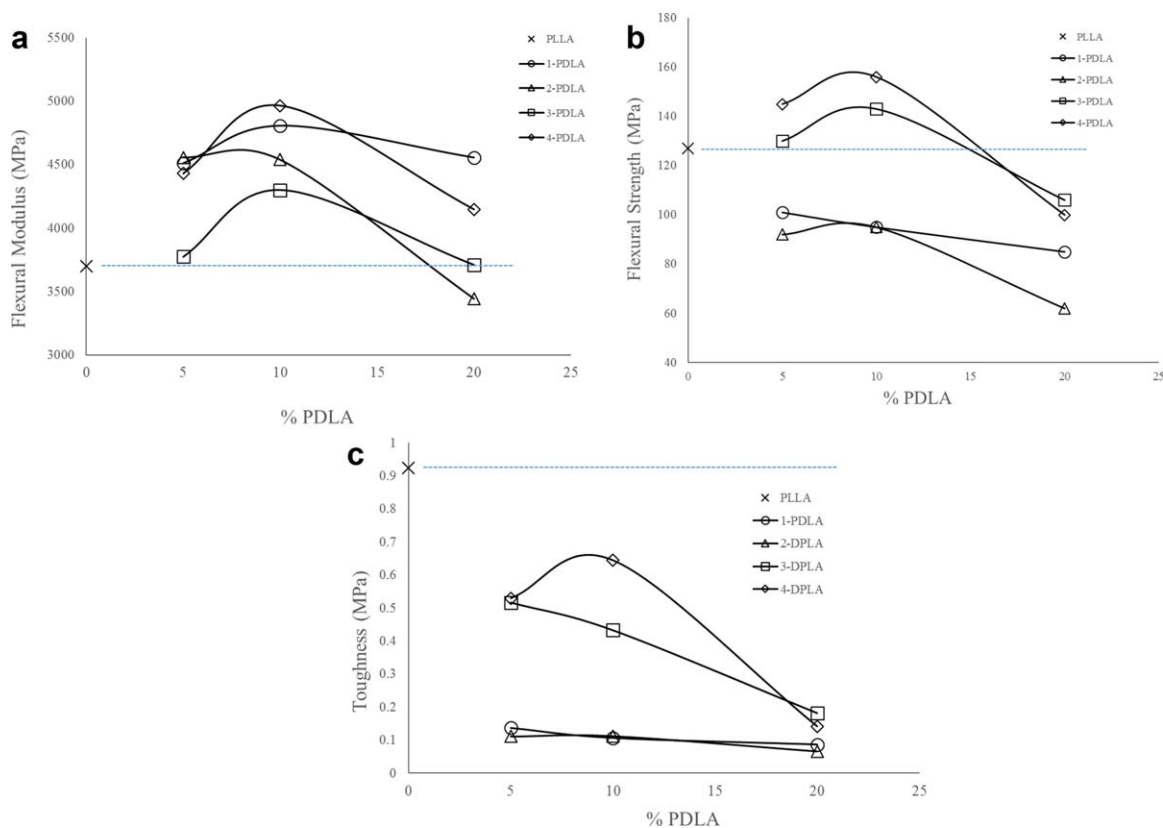


Figure 5. Effect of PDLA additives on (a) flexural modulus (MPa), (b) flexural strength (MPa), and (c) toughness (MPa). Dashed-lines are the values with no PDLA additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

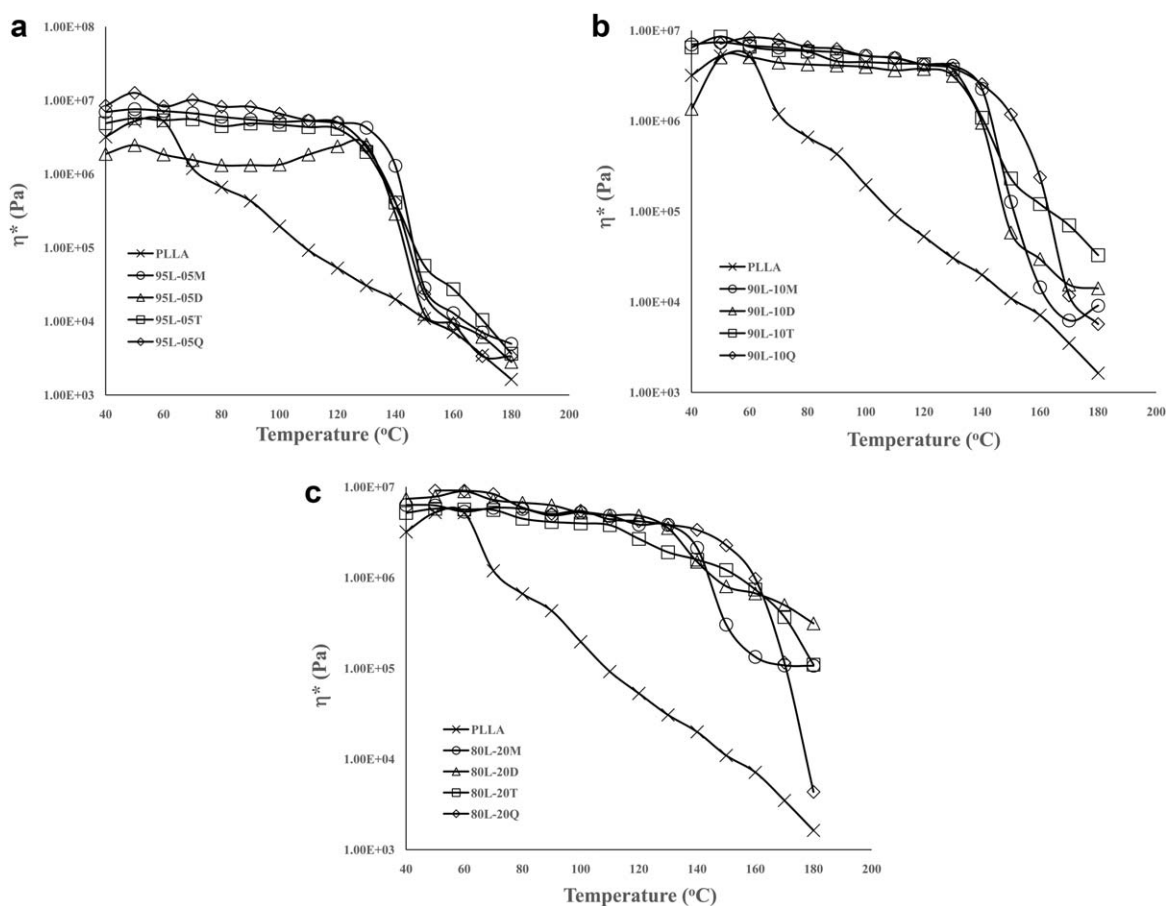


Figure 6. Effect of linear and branched additives on complex viscosity (η^*) (a) 5, (b) 10, and (c) 20% (w/w).

here by having more tethering points. Interestingly, Sakamoto and Tsuji²⁹ in a study of multi-branched PDLA additives showed that the end-use properties, especially glass transition and melting temperatures, were highly dependent on the length of side chains, which adds segment mobility, without necessarily changing the branching structure.

Figure 5(b) shows the relationship of flexural strength with increasing PDLA content. In contrast to flexural modulus [Figure 5(a)], the flexural strength of the blends with branched PDLA additives was higher than their linear counterparts. It was also interesting to note that the blends with the linear PDLA additives had slightly lower strength values than neat PLLA [X and dashed line in Figure 5(b)]. Figure 5(c) shows the dependence of the toughness on the different PDLA additives. Toughness of the sample is measured as the area under the stress-strain curves. In this case, neat PLLA had the highest value, at ~ 0.9 MPa. The toughness values for blends with 3-arm and 4-arm PDLA additives were next highest, higher than the blends with their linear analogs. In fact, they are nearly two to three times greater. As mentioned above, it can be hypothesized that the addition of branching units within the stereocomplexes produces a reinforcing effect whereby relatively stiff stereocomplex crystallites, “reinforcing agents,” would impart stiffness while imbedded in a less organized matrix would impart ductility. This structure would prevent crazing and prop-

agation of cracks during flexural testing. At the highest loading levels (20% by weight) all of the PDLA additives exhibited similar toughness values. Perhaps the presence of too many stereo-complex crystallites caused brittleness, a similar result implied by Tsuji *et al.*³⁸

Rheological Properties

Melt rheology as a function of temperature is a critical factor in industrial melt blending. As outlined in Figure 6, the addition of branched additives had an effect on the complex viscosity (η^*) of PLLA and PDLA-PLLA blends. For the homopolymer PLLA, η^* falls rapidly above $\sim 70^\circ\text{C}$; i.e., the material softens above T_g , presumably as the amorphous chains begin to mobilize. The addition of the PDLA additives imparted higher complex viscosity compared with neat PLLA in the temperature range from 40 to 140°C . As the temperature approached the onset melting temperature of the stereocomplex crystallites, the complex viscosity dropped quickly, as the material entered the melt state. At 5 and 10% by weight of PDLA additives, the viscosity decreased three orders of magnitude between 140 and 180°C [Figure 6(a,b)], which thus defines a temperature window for “good processability.” At 20% loading [Figure 6(c)], the complex viscosity was observed at roughly half its original value, perhaps due to formation of stronger interactions between the PLLA matrix and PDLA additives. Only the blends made with the quaternary 4-arm star PDLA deviated from this

trend. One possible reason is due to incomplete formation of the stereocomplex between the 4-arm PDLA additive and the linear PLLA, a result supported by the very broad T_{m2} melting peak seen for this sample.

CONCLUSION

The effect of the addition of low molecular weight branched poly(D-lactide) (PDLA) additives on the thermal, mechanical, and heat resistance of blends with linear poly(L-lactide) (PLLA) was examined. Unlike previous studies performed from solution blending, this study relied on PDLA additives that were melt blended with PLLA, a process that is more economically viable for commercial applications. The addition of branched PDLA additives generally resulted in significant increase in heat deflection temperature with a range of thermomechanical properties that are notably different from neat PLLA. Specifically, all blends had heat deflection temperatures (HDT) well over 120°C and ranged as high as 185°C, compared with HDT of ~65°C for typical linear PLLA. Especially interesting was the behavior of the 3-arm PDLA additive, which resulted in a heat deflection temperature of >180°C and potentially interesting flexural properties for commercial applications. At higher PDLA additive loadings, mechanical properties implied increasing brittleness and a loss of toughness, probably because they had formed “too many” stereocomplex crystallites within the less-ordered PLA matrix. Nevertheless, throughout the range of additives studied, the branched PDLA additives imparted good heat resistance without sacrificing too much toughness. These data, especially the multiple X-ray reflections from the PLLA-PDLA complexes, clearly show the presence of multiple crystalline morphologies. Accordingly, it would be very useful to be able to determine the way in which the different branched additives affected and even “tailored” these morphologies. Saeidlou *et al.*²⁶, for example, presented clear evidence via optical microscopy that melt-processed stereocomplexation resulted in distinct spherulites surrounded by a less-ordered crystalline network. Considering that morphology and molecular size^{42,43} would surely impact final end-use properties of the PLA product, this type of knowledge will be the target of future studies.

Another significant consideration for commercialization is the cost of stereocomplex formation. Under present market conditions D-lactic acid monomer is more expensive than the L-enantiomer. Addition of these short-chain branched PDLA additives at minimal loadings of 10% results in good processability at moderate temperatures, expanding the application of PLA biomaterials toward more heat-sensitive applications.

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