Preparation and properties of multi-branched poly(D-lactide) derived from polyglycidol and its stereocomplex blends

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Abstract. Multi-branched poly(D-lactide)s (*mbPDLAs*) with various structures are synthesized *via* ring-opening polymerization by using polyglycidol (PG) macro-initiators. Their chemical structures and thermal properties are controlled by adjusting feed ratios of D-lactide (DLA) and PG. The materials are blended with commercial linear poly(L-lactide) (*l*-PLLA) to form a stereocomplex structure. Effects of *mbPDLAs* structures and *l*-PLLA/*mbPDLA* ratios on the blends' thermal, mechanical, and rheological properties are evaluated. Mechanical properties of the stereocomplex blends, especially elongation at break and toughness, are dependent on the blend compositions, in which a 90:10 ratio exhibits the most desirable properties. The material also exhibits the lowest complex viscosity, which provides easy processing conditions. This is achieved by the incorporation of copolymers with multi-branched structures and an ability to form a much stronger stereocomplex structure.

Keywords: polymer blends and alloys, polylactide, stereocomplex, multi-branched, polyglycidol

1. Introduction

Poly(lactide) or polylactic acid (PLA) is a degradable polymer that is widely used in many applications, especially packaging, biomedical, agricultural, and environmental fields, due to its biodegradability, biocompatibility, and its renewable monomer resources. Despite these excellent characteristics, its thermal stability, durability, impact strength, and heat deformation temperature are significantly low, which limit its use in certain applications [1, 2]. Various physical and chemical modifications have been employed to improve these properties, *e.g.* copolymerization with other monomers [3–11], or blending with other (co)polymers [5, 9, 10, 12–15].

Stereocomplexation is a promising technique to enhance PLA properties, by utilizing the strong interaction between its helical stereo-conformations, *i.e.*, poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA). This PLLA/PDLA stereocomplex exhibits a unique crystalline structure and morphology [2, 10, 12, 16], which has a melting temperature (T_m) 50°C higher than its homopolymer counterparts. The stereocomplex structure has high potential to improve heat resistivity and mechanical properties (tensile strength, Young's modulus, and elongation at break) of the materials [17]. The structure can be obtained by either solution or melt blending methods. Recently, supercritical fluids

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[18], microwave [19], and nano-processing techniques [20–22] have been employed in the stereocomplex formation. Preparation, structures, properties, and applications of this structure have been extensively studied [17, 23–27]. Formation of stereocomplex structure is usually accompanied by homo-crystallization, predominantly when high molecular weight PLAs are employed [2, 10]. A complete stereocomplexation, without homo-crystallite, is obtained from an equimolar mixture of sufficiently-low molecular weight PLLA and PDLA.

Stereocomplexation is also observed in block copolymers of L-lactide (LLA) and D-lactide (DLA) during polymerization, or during solid state polymerization of small-sized PLLA and PDLA [24, 28–30]. Stereoblock PLA copolymers have been used as compatibilizers in an enhancement of stereocomplexation efficiency, by suppressing the homo-crystallite formation of large-sized PLLA and PDLA [24]. However, these stereoblock copolymers cannot be processed into fibers or films, because of their relatively low molecular weight. Recently, a preparation of high-molecular weight stereoblock copolymers by employing non-equimolar LLA/DLA ratios was reported [31]. A complete stereocomplex without homo-crystallite was obtained when PDLA compositions of at least 15% was employed. An effective but rather expensive process of radiation-induced crosslinking was also employed to enhance the stereocomplex formation and to lower processing temperatures of its low molecular weight blends [32]. Although various structural formation mechanisms and analyses of PLA stereocomplex have been proposed, insights into the improvement of their toughness and rheological properties have not been presented.

Inclusion of branch-structured polymers into brittle plastics leads to improvement in their mechanical properties, especially toughness. Multi-branched polymers possess lower chain entanglements, lower solution and melt viscosity, but higher thermal stability, compared to their linear-structured counterparts. Other unique characteristics, *i.e.*, their globular shape, and their large number of functional groups within a molecule, make these polymers suitable for various applications. The number and types of functional groups on these polymers can be

modified to control their properties for specific applications [33]. Recently, multi-branched PLAs have been developed, and their possible applications have been assessed [34–38].

In this work, multi-branched poly(D-lactide)s (*mbPDLAs*), with different structures and properties, are prepared by employing polyglycidol (PG) as a macro-initiator. Depending on *mbPDLAs* structures, the stereocomplex can be achieved by blending with linear poly(L-lactide) (*l*-PLLA). The major advantages of these stereocomplex mixtures derived from the branched constituents are an enhancement in the blend's mechanical properties and a decrease in melt viscosity. The resulting blends have high potential for use as high performance materials with easy fabrication processes.

2. Experimental

2.1. Materials

l-PLLA ($\bar{M}_w = 178\,000$ g/mol) and D-lactide monomer (DLA) were supplied by PURAC (Netherlands). Tin(II) octoate catalyst, Sn(Oct)₂, was purchased from Wako (Japan). Glycidol was purchased from Aldrich (USA) and used as received. Ethyl acetate, chloroform, ethanol, and toluene solvents were purchased from Lab Scan (Thailand).

2.2. Synthesis of *mbPDLAs*

Polyglycidol (PG) is employed as a macro-initiator in the synthesis of *mbPDLAs*. PG was prepared by a ring-opening polymerization of glycidol under an inert atmosphere, using Sn(Oct)₂ catalyst at a polymerization temperature and time of 110°C and 3 h. Effect of catalyst contents on structures of PG was examined by varying the contents from 0.25–1.0 mol%. *mbPDLAs* were then synthesized *via* a ring-opening polymerization of DLA in a presence of Sn(Oct)₂ catalyst and PG macro-initiator, under an inert atmosphere at 120°C for 24 h [39, 40]. The products were purified by dissolving in chloroform and precipitating in an ethanol/hexane mixture, and then dried under vacuum at 50°C for 24 h. The DLA/PG molar ratios were varied from 5/1 to 50/1, to produce *mbPDLAs* with different structures. The resulting copolymers were coded according to the feed DLA/PG ratios, *e.g.*, *mbPDLA051* was synthesized from a 5/1 ratio.

2.3. Stereocomplexation of *l*-PLLA and *mb*PDLAs

Stereocomplex blends of *l*-PLLA/*mb*PDLA were prepared by mixing THF solutions of the constituents at various weight ratios, *i.e.*, 90/10, 80/20, 70/30 and 50/50. The mixtures were then casted on a glass surface, in which the solvent was removed by evaporation in a vacuum oven at room temperature for 48 h. The resulting films were cut into rectangular shape with 50 mm gauge length and 15 mm width, according to ASTM D882, for mechanical tests.

2.4. Characterizations

Average molecular weights ($\bar{M}_n$, $\bar{M}_w$) and polydispersity (PDI) of *mb*PDLAs were measured using a Gel Permeation Chromatography (GPC), Waters e2695 with dual detectors: Viscotek Model 3580 Reflective Index detector and Model 270 differential viscometer detector comparative to mono-disperse polystyrene standards (4490–1 112 000 g/mol). The measurement was performed on PL gel 10 micron mixed B2 columns (Polymer Laboratories), at 35°C, using tetrahydrofuran eluent with a flow rate of 1.0 mL/min. The glass transition (T_g) and melting (T_m) temperatures of the copolymers were determined by Differential Scanning Calorimeter (DSC) on a DSC822e Mettler Toledo. The samples were scanned twice from –60 to 250°C with a heating and cooling rate of 20.0°C/min. Chemical structures of *mb*PDLAs were examined using an AVANCE^{III} 500 MHz digital Nuclear Magnetic Resonance spectrometer (AV-500, Bruker Biospin;), using CDCl₃ (for *mb*PDLAs) and D₂O (for PG) solvents.

Tensile properties of blend samples were measured at room temperature on a universal testing machine (Instron model 55R4502, Instron Corp., USA) with a 100 N load cell and a crosshead speed of 50 mm/min. The specimens were prepared as rectangular specimens (prepared by solvent casting) with 50 mm gauge length and 15 mm width, according to ASTM D882. Each reported value is an average of measurements carried out on at least 4 specimens. Rheological properties, *i.e.*, elastic modulus (G'), loss modulus (G''), and complex viscosity (η^*), were measured on a strain-controlled rheometer (ARES, TA Inc., New Castle, USA) with a torque transducer capable of measurement over the range of 2–200 g·cm. Disc samples with a diameter of

25 mm and 1 mm thickness were prepared by hot-pressing. The strain amplitude for dynamic measurements was fixed at 5%. The measurements were conducted in a temperature range of 190–250°C, with a heating rate of 10°C/min at a frequency of 1 rad/s. Complex viscosity (η^*) changes of the melts as a function of shear rate were conducted at a constant temperature of 230°C.

3. Results and discussion

3.1. Chemical structures and properties of *mb*PDLAs

PG macro-initiators are synthesized by varying the catalyst contents from 0.25–1.0 wt%. Figure 1a shows ¹H NMR spectrum of a PG sample, whose hydroxyl number is 340 mg KOH/g sample (according to standard test method D4274-05, test method C). Complex signals, appeared in the range of 3.3–3.8 ppm, correspond to methylene and methine protons, while a resonance located at 4.7 ppm is assigned to hydroxyl terminals. The integral ratio of methylene and methine/hydroxyl of 9/1 is observed. Detailed information on chemical structure of PG can be derived from ¹³C NMR Inverse Gated spectra, in which complicated patterns of perfect dendritic (*D*), linear (*L*), and terminal (*T*) units can be identified. The assignments have been applied to

Figure 1. ¹H NMR (a), ¹³C NMR (b), and ¹³C NMR DEPT (c) spectra of PG synthesized from tin catalyst

the spectra of PG synthesized from anionic polymerization [41–44]. Similar spectral characteristics are observed in this study, in which a tin catalyst is employed, as shown in a ^{13}C NMR and a distortionless enhancement by polarization transfer (DEPT) spectra in Figure 1b and 1c, respectively. This reflects a formation of similar products. The advantage of this synthesis route is, however, its one-step process, in which branching structures of PG products can be manipulated by varying the catalyst contents. GPC chromatograms of PG synthesized from various catalyst contents are compared in Figure 2. At 1.0 mol%, a mono-modal size distribution is observed with a molecular weight at peak (M_p) of 2100 g/mol. As the catalyst content decreases to 0.5 and 0.25 mol%, the results show bi-modal distribution with similar M_{p1} of 2000 g/mol, and a variation in M_{p2} from 11 500 to 24 800 g/mol, respectively. The relative intensity of the high-molecular weight fraction increases with the decrease in the catalyst contents. Although the polydispersity value (~ 3.4) is significantly high, compared to that obtained from anionic polymerization [41–44], this synthesis route is considered as an alternative approach when structural perfection may not be a strict requirement for most applications.

Figure 2. GPC chromatograms of PG synthesized at different catalyst contents: 0.25 (a), 0.5 (b), and 1.0 mol% (c)

The relatively larger-sized PG prepared from a catalyst content of 0.25 mol% is employed as a macro-initiator in the synthesis of *mbPDLAs*. ^1H NMR spectra of the resulting copolymers obtained from various PG/DLA ratios are shown in Figure 3. Characteristic signals of PG appear at 3.5–3.7 ppm (d, e), corresponding to methylene protons ($-\text{CH}_2-\text{CH}-\text{O}$) and methine proton ($-\text{CH}_2-\text{CH}-\text{O}$). The signal at 5.1–5.2 ppm (b) is assigned to methine $[\text{O}=\text{C}-\text{CH}(\text{CH}_3)-\text{O}-]$ of lactate units. This confirms the presence of PDLA chains on the PG core. The integral ratios of the signals at 3.5–3.7 and 5.1–5.2 ppm reflect the PG/PDLA compositions in the copolymer chains. Average DLA length/branch (DLA_n) is calculated from the integral ratio of $^b\text{H}/^c\text{H}$. Results on chain compositions and molecular weight of the copolymers are summarized in Table 1. Copolymers with $\bar{M}_w$ ranging from 35 000–80 000 g/mol are obtained. The chain compositions are significantly similar to the corresponding feed ratios, reflecting a high incorporation efficiency of lactate units. DLA compositions and molecular weight of the copolymers increase with an increase of the DLA/PG feed contents. DLA_n value increases with an increase in the feed ratios from 5/1 to 20/1. Although *mbPDLA201* and *mbPDLA501* show

Figure 3. ^1H NMR spectra and signal assignments of *mbPDLAs*

Table 1. Synthesis conditions and properties of *mbPDLAs*

Samples	DLA/PG compositions		DLA_n	$\bar{M}_n^b$ [g/mol]	$\bar{M}_w^b$ [g/mol]	PDI
	in feed	in chain ^a				
<i>l</i> -PLLA	—	—	—	88 800	178 100	2.01
<i>mbPDLA051</i>	5/1	83/17	4	6 700	35 200	5.25
<i>mbPDLA101</i>	10/1	92/8	7	20 600	48 900	2.37
<i>mbPDLA201</i>	20/1	96/4	17	19 100	64 400	3.38
<i>mbPDLA501</i>	50/1	98/2	17	23 000	81 500	3.54

^a ^1H NMR, ^bGPC, DLA_n = average DLA length/branch, PDI = polydispersity index

Table 2. Thermal properties of *mbPDLAs* derived from DSC thermograms

Samples	1 st scan			2 nd scan		
	T_g [°C]	T_m [°C]	ΔH_m [J/g]	T_g [°C]	T_m [°C]	ΔH_m [J/g]
<i>l</i> -PLLA	–	179	44.7	58	174	45.4
<i>mbPDLA</i> 051	18	–	–	29	–	–
<i>mbPDLA</i> 101	36	90	11.9	37	–	–
<i>mbPDLA</i> 201	50	125	32.5	49	–	–
<i>mbPDLA</i> 501	46	140	36.2	44	135	14.1

similar DLA_n values, a difference in their average molecular weights reflects different numbers of lactate branches per molecule. This, in turn, imposes strong effect on physical and mechanical properties of the copolymers, discussed later.

DSC thermograms of *mbPDLAs* are compared with *l*-PLLA in Figure 4. Their thermal properties derived from 1st heating scans are summarized in Table 2. *l*-PLLA exhibits cold crystallization in both of its 1st and 2nd heating scans, indicating that its crystallization is not complete at the applied DSC cooling rate, due to its long-chain structure. From the 1st heating cycles, all *mbPDLAs* exhibit melting characteristics

without cold crystallization. This is likely because these samples are prepared from a solvent-casting technique, which allows high freedom of crystallization. T_m 's of *mbPDLAs* shift toward higher temperatures, whose heat of fusion values (ΔH_m) also increases, with an increase in DLA block lengths and DLA contents of the chains. This indicates a strong influence of DLA sequences on crystalline structure of the copolymers.

In the 2nd heating scans, however, cold crystallization and melting characteristics of *mbPDLAs* are not observed, except *mbPDLA*501. This reflects the influences of the samples structures and their thermal history, in which the multi-branched structure retards crystallizability of molten *mbPDLAs* during DSC cooling and re-heating cycles. For the largest copolymer in the series (*mbPDLA*501), however, its sufficiently-long DLA sequences enable formation of crystalline domains upon re-heating. The results from both heating scans show that the copolymers have lower T_g than *l*-PLLA, due to their shorter DLA sequences. The T_g values increase with the copolymer's molecular weights.

Figure 4. DSC thermograms of *mbPDLAs* synthesized at various DLA/PG molar ratios: (a) 5/1, (b) 10/1, (c) 20/1, (d) 50/1, and (e) *l*-PLLA

3.2. Thermal properties of *l*-PLLA/*mbPDLA* stereocomplex blends

Effects of *mbPDLA* structures and the blend compositions on properties of *l*-PLLA/*mbPDLA* stereocomplex are investigated. Figure 5 shows DSC thermograms (2nd heating scan) of blends (prepared at a 90/10 ratio) consisting of various *mbPDLAs*. This non-equimolar blend composition is employed to investigate interplay between crystallization behaviors of homo-crystallite and stereocomplex. Ther-

Figure 5. DSC thermograms of (a) *l*-PLLA and *l*-PLLA/*mbPDLA*501 stereocomplex blends (prepared at a 90/10 blend ratio) containing: (b) *mbPDLA*051, (c) *mbPDLA*101, (d) *mbPDLA*201, and (e) *mbPDLA*501

Table 3. Thermal properties (2nd heating scan) of *l*-PLLA and *l*-PLLA/*mb*PDLA501 stereocomplex blends containing various *mb*PDLAs at a 90/10 blend ratio.

Blend component	T_g [°C]	T_c [°C]	ΔH_c [J/g]	Homo-crystallite		Stereocomplex	
				T_m [°C]	ΔH_m [J/g]	T_m [°C]	ΔH_m [J/g]
<i>l</i> -PLLA	58	117	45.3	174	45.4	–	–
<i>l</i> -PLLA/ <i>mb</i> PDLA051	55	113	35.3	174	39.4	–	–
<i>l</i> -PLLA/ <i>mb</i> PDLA101	58	120	33.2	173	40.1	–	–
<i>l</i> -PLLA/ <i>mb</i> PDLA201	59	120	36.2	172	34.6	186	6.6
<i>l</i> -PLLA/ <i>mb</i> PDLA501	56	113	34.5	173	33.2	202	10.2

mal properties of all blends are summarized in Table 3. The glass transition and homo-crystallite melting characteristics are clearly observed in all samples, which remain unchanged regardless of size of *mb*PDLA components. Blends containing *mb*PDLAs with $\bar{M}_w$ higher than 60 000 g/mol, *i.e.*, *mb*PDLA201 and *mb*PDLA501, show an additional T_m of the stereocomplex structure at 186 and 210°C, respectively. This indicates that a critical length of DLA sequences is required to form the stereocomplex structure, whose structural strength is dependent on the copolymer sizes.

Cold crystallization is observed in *l*-PLLA and all blends. The heat of cold crystallization (ΔH_c) value of *l*-PLLA is similar to ΔH_m of its homo-crystallite, indicating an absence of melt crystallization, *i.e.*, the crystalline domains are mainly formed during the reheating process. The corresponding values for blends of small-sized *mb*PDLAs are lower than ΔH_m , despite the absence of the stereocomplex melting peak. This reflects that the DLA short sequences act as nucleating species promoting the formation of homo-crystallite during melt crystallization [45, 46]. In contrast, ΔH_c values of the blends containing large-sized *mb*PDLAs, which show stereocomplex peak, are slightly higher than ΔH_m of their homo-crystallite. This is likely because stereocomplex formation occurs rapidly during the melt crystallization, but the crystallization is not complete at the applied cooling rate as the blends contain high *l*-PLLA content. When the sample is reheated higher than T_g , chain rearrangements take place, resulting in the formation of homo-crystallites and additional stereocomplex structures.

In blends containing large-sized *mb*PDLAs, ΔH_m values of their stereocomplex endotherm increase with molecular weight of the *mb*PDLA component, whereas the corresponding values of the homo-crystallites significantly decrease. This is likely due to the suppression of homo-crystallization by the

formation of the stronger stereocomplex structure. For blends consisting of small-sized *mb*PDLAs, however, ΔH_m remains constant as the suppression effect from the stereocomplex is negligible. All samples show a single T_g ranging from 55–59°C, indicating miscible blends.

Effect of blend compositions on thermal properties of the stereocomplex blends is examined. DSC thermograms (2nd heating scan) of blends containing *mb*PDLA501 at various blend ratios are compared in Figure 6. Cold crystallization is clearly observed in *l*-PLLA and *l*-PLLA-rich blends, along with the melting characteristic of homo-crystallite and stereocomplex. This reflects that the stereocomplex structure is formed at a much faster rate during the DSC cooling cycle, which retards formation of homo-crystallite in *l*-PLLA-rich blends [12]. In contrast, a 50:50 blend shows only the stereocomplex melting peak, with no cold crystallization, reflecting that no homo-crystallite domains are formed for an equimolar blend. Thermal properties of the blends are summarized in Table 4. T_m of homo-crystallite shifts to lower temperatures, whereas that of the stereocomplex slightly shifts toward higher temperatures, with

Figure 6. DSC thermograms (2nd heating scan) of (a) *l*-PLLA, and *l*-PLLA/*mb*-PDLA501 stereocomplex blends at various compositions: (b) 90/10, (c) 80/20, (d) 70/30 and (e) 50/50

Table 4. Thermal properties of *l*-PLLA/*mb*PDLA501 stereocomplex at various blend compositions

Blend ratios	T_g [°C]	T_c [°C]	ΔH_c [J/g]	Homo-crystallite		Stereocomplex	
				T_m [°C]	ΔH_m [J/g]	T_m [°C]	ΔH_m [J/g]
<i>l</i> -PLLA	58	117	45.3	174	45.2	—	—
90/10	56	113	34.5	173	33.2	202	10.2
80/20	55	99	25.8	169	24.5	204	20.4
70/30	53	100	11.1	162	18.2	205	28.6
50/50	54	—	—	—	—	206	54.3

an increase in the *mb*PDLA501 contents. The heat of fusion (ΔH_m) values also exhibit a similar trend, reflecting lower quality and contents of homo-crystallite, and vice versa for the stereocomplex. Single T_g is also observed in all blend samples, which decreases with an increase in the *mb*PDLA501 contents, reflecting a complete miscibility at all compositions. ΔH_c values of *l*-PLLA-rich blends are similar to that of ΔH_m values, also indicating that a cold crystallization mainly corresponds to homo-crystallite formation, whereas the stereocomplex is generated very fast during the melt crystallization.

3.3. Mechanical properties of *l*-PLLA/*mb*PDLA stereocomplex blends

Mechanical properties of the stereocomplex blends are evaluated in terms of tensile strength, modulus, and elongation at break, in which examples of stress-strain curves (4 replicates) of a *l*-PLLA/*mb*PDLA101 blend (90/10) are shown in Figure 7. Toughness is calculated from the area under the curves, which only represent the samples behaviors at low deformation rates, but not impact toughness. Table 5 summarizes mechanical properties of blends containing *mb*PDLA101, as a function of the

Figure 7. Stress-strain curves of *l*-PLLA/*mb*PDLA101 stereocomplex blend at a 90/10 composition (4 replicates)**Table 5.** Mechanical properties of *l*-PLLA/*mb*PDLA101 stereocomplex blends, as a function of blend ratios

Blend ratios	Tensile strength [MPa]	Young's modulus [MPa]	Elongation at break [%]	Toughness [mJ/mm ³]
100/0	22.4±1.3	1269±69	13.8±2.1	1.7±0.5
95/5	17.2±1.6	1065±131	16.9±3.2	1.7±0.6
90/10	19.8±2.4	1134±58	144.9±29.1	19.0±5.1
80/20	18.2±2.1	1004±99	13.1±4.1	1.4±0.6
70/30	17.7±0.9	964±41	16.2±1.0	1.9±0.4

Table 6. Mechanical properties of *l*-PLLA and *l*-PLLA/*mb*PDLA (90/10) stereocomplex blends consisting of different *mb*PDLAs

Blend component	Tensile strength [MPa]	Young's modulus [MPa]	Elongation at break [%]	Toughness [mJ/mm ³]
<i>l</i> -PLLA	22.4±1.3	1269±69	13.8±2.1	1.7±0.5
<i>mb</i> PDLA051	16.9±1.0	998±83	63.4±22.1	8.6±2.9
<i>mb</i> PDLA101	19.8±2.4	1134±58	144.9±29.1	19.0±5.1
<i>mb</i> PDLA201	32.1±2.2	1120±62	76.3±17.0	13.3±2.8
<i>mb</i> PDLA501	30.3±0.9	1631±189	97.7±28.4	26.1±7.7

blend contents. Slight decreases in all properties are observed with an inclusion of *mb*PDLA101, except those of the 90/10 blend, whose elongation at break and toughness are largely increased without sacrificing much of the tensile strength and modulus. This reflects a strong influence of an optimum blend ratio on the improvement of the blends mechanical properties.

Enhancements in tensile strength and modulus of the blends are also feasible by varying *mb*PDLAs sizes. Table 6 summarizes mechanical properties of stereocomplex blends of different *mb*PDLAs, prepared at the same composition (90/10). The blend consisting of *mb*PDLA501 exhibits higher tensile strength and modulus than those of *l*-PLLA, whereas those of smaller *mb*PDLAs show slight drops in the values. This reflects that a critical molecular weight value of *mb*PDLA is required in the formation of appropriate stereocomplex structure, which in turns imposes a large influence on the enhancement of their mechanical properties.

3.4. Rheological properties of *l*-PLLA/*mb*PDLA stereocomplex blends

Rheology behaviors of stereocomplex blends containing different *mb*PDLAs, prepared at a 90/10 ratio, are examined at a fixed strain of 5%. Figure 8 shows results on complex viscosity (η^*), storage modulus (G'), loss modulus (G''), and $\tan \delta$ of the

Figure 8. Temperature dependence of complex viscosity (η^*) (a), storage moduli (G') (b) and loss moduli (G'') (c) of stereocomplex blends containing different *mbPDLAs*

blends, as a function of temperature. At temperatures below their stereocomplex's T_m , the blends consisting of *mbPDLA501* and *mbPDLA201* show high η^* , G' and G'' values, due to the presence of the stereocomplex structure in a glassy state. An incorporation of small-sized *mbPDLA101* leads to a reduction in the values, compared to *l*-PLLA, as this acts as a plasticizer. When the chain length of *mbPDLAs* increases, the value sharply increases, where an increase of 1 and 2 orders of magnitude is observed in *mbPDLA201* and *mbPDLA501*, respectively. This reflects a formation of stronger interaction, *i.e.*, hydrogen bonding, between the 2 stereo-constituents [2, 47, 48]. A sharp decrease in the values is observed when the structure melts. This

Figure 9. Steady shear viscosity of stereocomplex blends containing different *mbPDLAs* at a 90:10 blend composition

behavior is not seen in blends consisting of smaller *mbPDLAs*, due to the absence (or low content) of stereocomplex structure, as previously discussed. The steady shear rheology behaviors, as a function of shear rate, of blends containing different *mbPDLAs* (90/10 blend compositions) are shown in Figure 9. The experiments are conducted at 230°C, above T_m of the stereocomplex. Typical non-Newtonian behavior is observed in all samples. At low shear rates, the shear viscosity of stereocomplex blends are comparable to that of *l*-PLLA, except that of *mbPDLA501*, which is about 1 order of magnitude lower. This is due to the influence of its branched component, which possesses the required arm length. At higher shear rates (>200 1/s), the shear thinning behavior is clearly evidenced, except for that of *mbPDLA501*. The results also indicate that this behavior of the blends is observed earlier (at lower shear rates) than that of *l*-PLLA, in which the inclusion of *mbPDLAs* with shorter arm lengths shows a sudden drop in the viscosity at lower rates. Interestingly, the stereocomplex blend of *mbPDLA501* does not exhibit shear-thinning characteristics in this shear rate range ($<10,000$ 1/s), probably because of its sufficiently-long arm lengths that enable effective chain entanglements, and its strong interaction between the 2 enantiomeric structures. Given its excellent mechanical property, the *l*-PLLA/*mbPDLA501* blend show high potential for industrial use, as this rheological property also leads to easy processing conditions.

4. Conclusions

Multi-branched PDLAs (*mbPDLAs*) derived from polyglycidol (PG) core are successfully used to

enhance mechanical properties and processing conditions of commercial linear-structured PLLA (*l*-PLLA). Chemical structures of *mb*PDLAs are controlled by adjusting the feed ratio of DLA monomer to the PG macro-initiator, which in turns leads to a variation in the copolymers thermal and physical properties. The *mb*PDLAs structures and blend compositions impose strong effects on physical and mechanical properties, *i.e.*, T_g , T_m , toughness, tensile strength, modulus, and elongation at break, of the *l*-PLLA/*mb*PDLAs stereocomplex blends. The stereocomplex with a blend ratio of 90/10 exhibits the most desirable properties, in which the highest elongation at break value is gained whereas tensile strength and moduli are comparable to *l*-PLLA. The material also exhibits the lowest complex viscosity, which provides easy processing conditions. This is achieved by the incorporation of copolymers with multi-branched structures and an ability to form a much stronger stereocomplex structure.

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