

Article

Maintaining Structural Stability of Poly(lactic acid): Effects of Multifunctional Epoxy based Reactive Oligomers

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Abstract: In order to reduce the effects of hydrolytic degradation and to maintain sufficient viscosity during processing of biomass based poly(L-lactic acid) (PLLA), various epoxy functional reactive oligomers have been characterized and incorporated into the degraded fragments as chain extenders. The molecular weight of PLLA increased with the increase in functionality of the reactive oligomers. No further increase in molecular weight was observed for oligomers with functionality of greater than five. Under our experimental conditions, no gelation was found even when the highest functionality reactive oligomers were used. This is attributed to the preferential reaction of the carboxylic acid *versus* the negligible reactivity of the hydroxyl groups, present at the two ends of the degraded PLLA chains, with the epoxy groups. The study provides a clear understanding of the degradation and chain extension reaction of poly(lactic acid) (PLA) with epoxy functional reactive oligomers. It is also shown that a higher functionality and concentration of the reactive oligomers is needed, to bring about a sufficient increase in the molecular weight and hence the hydrolytic stability in circumstances when PLA chains suffer significant degradation during processing.

Keywords: poly(lactic acid); degradation; epoxy; multifunctional

1. Introduction

Poly(lactic acid) (PLA) is one of the few bio-based polymers currently being produced on a commercial scale with an attractive cost structure [1,2]. This linear, aliphatic thermoplastic polyester possesses many attractive characteristics, including biocompatibility, high modulus and the ability to be melt processed using conventional processing techniques such as extrusion and injection molding [3,4]. Despite all of its advantages, there are limitations such as its inherent brittleness, poor melt strength, narrow processing window and low thermal stability [4]. It is also well known that thermal processing of PLA is a challenge because of hydrolytic degradation during processing at elevated temperatures. The drop in the molecular weight adversely affects the rheological properties, mechanical properties and durability of the PLA based materials [5].

In order to overcome these limitations, the use of plasticizers, blends, copolymerization, micro and nanocomposites have been investigated [6–11]. It has been shown that these modifications result in PLA based materials with improved elongation at break, impact strength, toughness and barrier properties. However, similar to unmodified PLA, hydrolytic degradation remains a concern [12–14]. In fact depending on the hydrophilicity of the modifier used, the degradation rate of PLA has been found to increase in modified materials significantly affecting their processability [11,14].

By introducing a polymer consisting of all D isomer (PDLA) based triblock copolymer it is possible to convert PLLA from a stiff, brittle material to a soft, flexible rubbery material [15–17]. In these blends the slow quiescent crystallization of poly(L-lactic acid) (PLLA) and the preferential crystallization of the PLA stereocomplex resulted in the formation of a morphology that can be described as stereocomplex crystals dispersed in a soft continuous amorphous phase when the softblock used in the triblock copolymer was miscible with PLLA [15]. In addition it was found that on addition of a molecular plasticizer to these blends, further improvement in the rubbery property of the blend was obtained [17]. Despite the attractive mechanical properties achieved, it was found that because of the hydrophilic nature of the soft mid-block used in the triblock copolymer, the degradation of PLLA was accelerated in these blends during melt processing leading to a significant drop in the molecular weight of PLLA. This negatively affected the rheological properties and durability of these blends.

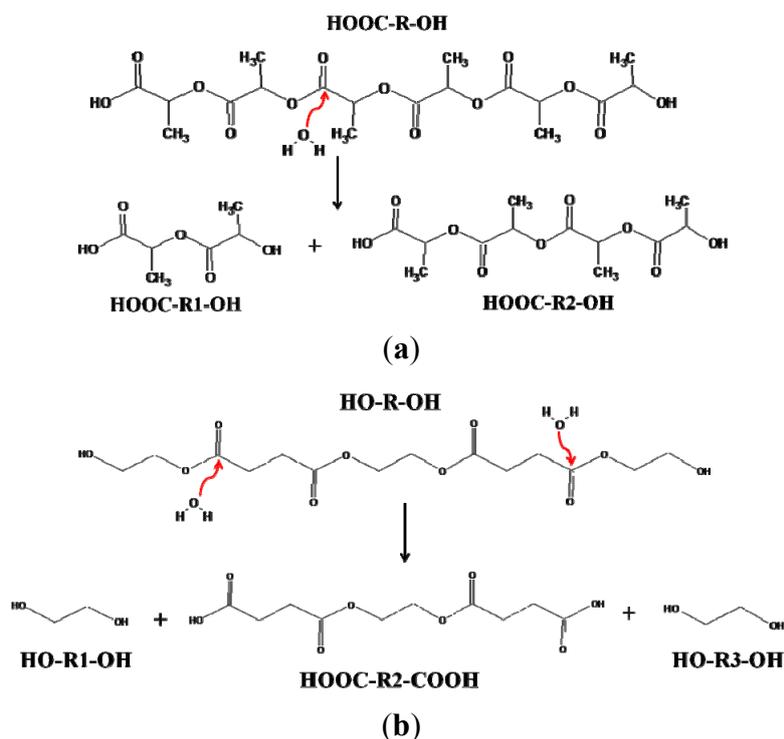
“Chain extenders” are typically introduced to minimize the drop in molecular weight during processing of condensation polymers such as polyesters and polyamides [18]. In addition, chain extenders historically are used to recover the molecular weight associated with polyester recycling efforts. The chain extenders have two or more functional groups that react with the chemical groups formed during the degradation reaction. It is possible to re-link the degraded chains, thus restoring the polymer molecular weight and countering the effects of molecular weight degradation. In theory, di-functional molecules should be sufficient to function as chain extenders. However, in practice, multifunctional chain extenders are often used as they provide a higher efficiency compared to di-functional chain extenders [18]. In fact, multifunctional epoxy based reactive oligomers have been commercialized as efficient chain extenders that can maximize chain extension while delaying the incidence of gelation [19].

Commercially available epoxy based chain extenders, especially Joncryl 4368, have proven to be extremely effective for maintaining molecular weight during polyester processing [14,20–22]. Joncryl 4368 is an oligomeric copolymer based on glycidyl methacrylate, styrene and other acrylates with a

functionality described only as “greater than four” [19]. To our knowledge, an apparent gap in the open literature is that no experimental characterization of the functionality has been reported for any of these additives. Furthermore, other reactive oligomers, with lower or higher average functionalities than Joncryl 4368 have not been explored. Hence, an understanding of the effect of functionality of the reactive oligomers on the chain extension process in PLA is unavailable. Thus a systematic study on the effect of the functionality of the reactive oligomers on the chain extension in PLA has been performed by studying varying functionality reactive oligomers as chain extenders for PLA.

PLA degrades during melt processing (180 °C and above) because of the hydrolysis of the ester linkages or because of main chain scission by a β C–H transfer reaction [20]. As PLA is a hydroxy-acid based polyester, upon hydrolysis of a poly(lactic acid) chain, the two newly created chains each have a carboxylic acid group at one end and a hydroxyl group at the other end (Figure 1a). This is in contrast to other common polyesters such as poly(ethylene terephthalate) (PET), where, because of their diol-diacid nature, the hydrolytic degradation pathways can lead to chains that have both ends with acid groups, or both ends with hydroxyl groups, or one end with acid and the other end with hydroxyl group depending on the site of attack of the water molecules [20] (Figure 1b).

Figure 1. (a) Hydrolytic degradation pathway for poly(L-lactic acid) (PLA) (hydroxyl acid based polyesters); (b) Hydrolytic degradation pathway for diol-diacid based polyesters.



Even in other modes of PLA degradation, such as random main chain scission due to a β C–H transfer reaction, the degraded chains can never possess carboxylic acid groups on both chain ends [20]. It is well known that the electrophilic epoxy group reacts preferentially with the carboxylic acid group as compared to the hydroxyl group [23]. In an epoxy-polyester blend, it has been shown that the glycidyl to carboxyl end group esterification reaction precedes the slower glycidyl to hydroxyl group etherification reaction. The reactions of glycidyl to secondary hydroxyl etherification and the

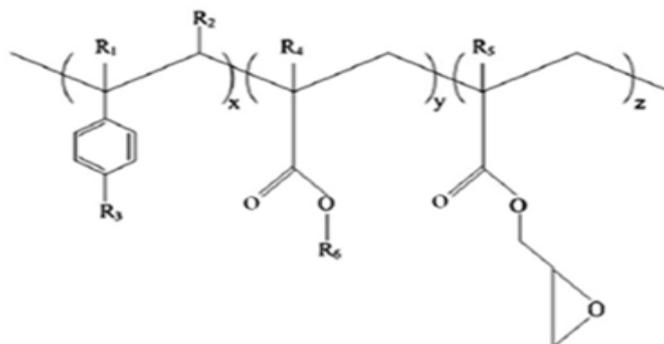
transesterification of primary and secondary hydroxyl chain ends onto polyester chains are slower reactions than the corresponding primary reactions [21,24]. In fact, model compounds studies have shown that no reaction occurs between the hydroxyl group and the epoxy group up to 220 °C. In contrast, rapid reaction always occurs between the carboxylic acid group and the epoxy group at temperatures lower than 200 °C [24]. The epoxy group clearly exhibits different reactivity with the functional groups present at the two ends of a degraded PLA chain.

In this paper, apart from the commercially available Joncryl 4368, three other reactive random copolymers based on glycidyl methacrylate, styrene and other acrylates were studied. They possess, on average, functionality that is either lower or higher than that of Joncryl 4368. The increase in functionality can have two effects. First, because of the preferential reaction of the epoxy group with the carboxylic acid group, more PLA chains will be grafted onto the reactive oligomer chains leading to a larger increase in molecular weight, or second, cross linking may take place with increasing functionality of the chain extender if sufficient hydroxyl groups react with the epoxy groups. Therefore, in this study, we have attempted to quantify the functionality of various reactive oligomers and characterize their effects on the molecular weight increase of PLLA, and the stereocomplex crystallization, mechanical properties and hydrolytic stability of triblock copolymer/PLLA/Plasticizer blends. For the first time, this study demonstrates that the functionality of the reactive oligomers is an important parameter that affects the efficiency of the chain extension reaction of PLLA based materials. The resultant effects on hydrolytic stability, crystallinity and mechanical properties are also reported.

2. Experimental Section

2.1. Materials

PLLA (4.2% D) (PLA2002D) was obtained from Natureworks (Minnetonka, MN, USA). Molecular plasticizer bis-[2-(2-butoxyethoxy)ethyl] hexane dioate was obtained from Dow Chemical (Midland, MI, USA). PDLA2800-PEPG12000-PDLA2800 triblock copolymer was synthesized as described previously [15]. Glycidyl methacrylate (GMA), 2-(2-ethoxyethoxy ethyl) acrylate (E2EA), methyl isobutyl ketone (MIBK), dicumyl peroxide (DCP) and 1-octanethiol were purchased from Sigma Chemical Co. (St. Louis, MI, USA). GMA and E2EA were passed through a basic alumina column to remove the inhibitor before polymerization. Reactive oligomers (chain extenders) Joncryl 4385 (EEW 450 g/eq) and Joncryl 4368 (EEW 285 g/eq) were obtained from BASF (Florham Park, NJ, USA). EEW stands for epoxy equivalent weight. Reactive oligomer PlussOptiPET (EEW 215 g/eq) was obtained from Pluss Polymers Pvt. Ltd., Gurgaon, India. All of these oligomers have the basic structure as shown in Figure 2. The three reactive oligomers will be referred to as chain extenders (CE), CE 450, CE 285 and CE 215, and have low, medium and high epoxy functionality respectively. The numbers represent their epoxy equivalent weights (EEW). The EEW values for Joncryl 4368 are obtained from the technical data sheets from BASF. The EEW values for Joncryl 4385 and PlussOptiPET are obtained from the technical data sheets from BASF and Pluss Polymers Pvt. Ltd.

Figure 2. General structure of reactive oligomers (chain extenders).

2.2. Synthesis of High Functionality Reactive Oligomer

A reactive oligomer with epoxy functionality higher than the procured reactive oligomers, and with a low T_g , was synthesized by copolymerizing glycidyl methacrylate with 2-(2-ethoxyethoxy ethyl) acrylate (E2EA). A low T_g reactive oligomer was synthesized to test if the low T_g of the reactive oligomer can improve the flexibility and rubbery property of the blend. It is known that the epoxy functionality of the reactive oligomers can be controlled by changing the mole content of glycidyl methacrylate in the copolymer and the molecular weight of the copolymer [18]. E2EA was chosen as the co-monomer in order to obtain a low T_g reactive oligomer and for its miscibility with PLLA because of its similar solubility parameter value with PLLA ($10.1 \text{ (cal/cm}^3)^{1/2}$) and PE2EA ($9.36 \text{ (cal/cm}^3)^{1/2}$) calculated using the group contribution method). Molecular weight was controlled using 1-octanethiol as a chain transfer agent.

Synthesis was performed using free radical polymerization of E2EA and GMA at $120 \text{ }^\circ\text{C}$ in methyl isobutyl ketone (MIBK) using dicumyl peroxide (DCP) as the initiator and 1-octanethiol as the chain transfer agent. To obtain a copolymer with 57 mol% GMA [P(E2EA-co-57GMA)], with an epoxy equivalent weight of 285 and molecular weight of $\sim 12,000 \text{ g/mol}$, the following procedure was used: 3.8 mL (28.15 mmol) GMA and 4.4 mL (21.24 mmol) E2EA were taken in a 25 mL round bottom flask along with 0.08 g DCP (1 wt%), 0.07 mL 1-octanethiol ($[\text{Monomer}]/[\text{Chain transfer agent}] = 115$) and 12.5 mL MIBK. The above mixture was degassed for one hour with N_2 and heated in an oil bath at $120 \text{ }^\circ\text{C}$. The reaction was continued for six hours. $^1\text{H NMR}$ spectra confirmed complete conversion of the monomers as evident by the absence of the resonances associated with the alkenyl protons of the monomers. At the end of the reaction, MIBK was removed using a rotary evaporator and the copolymer was obtained as a viscous liquid. It was further dried in vacuum at $120 \text{ }^\circ\text{C}$ to remove trace amounts of solvent. This copolymer will be referred to as S285. In order to determine the degree of polymerization (DP) by MALDI (Matrix-assisted laser desorption/ionization spectroscopy), a low molecular weight homopolymer of E2EA was also synthesized using a $[\text{Monomer}]/[\text{Chain transfer agent}]$ ratio of 10 as MALDI data could not be obtained for the reactive copolymers.

2.3. PLA Based Blends Investigated

Blends were prepared by using a 15 cc DSM twin screw mini-extruder. PLLA and the triblock copolymer were dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for two hours before processing. The triblock

copolymer, PLLA, plasticizer and the reactive oligomer were introduced into the extruder and mixed for 7 min at 190 °C and 80 rpm. The melt force was monitored during mixing to follow the extent of chain extension reaction as used in the literature [19–22]. Dog-bone samples for tensile testing were obtained using a 10 cc DSM mini-injection mold. The pressure used was 3 bars, the melt from the mini-extruder for injection molding was collected at 190 °C and the mold was maintained at 40 °C. The blends containing 3–5 wt% of the reactive oligomers are shown in Table 1. In all blends 1.3–1.6 mmol epoxy groups are present, well in excess of the amount of carboxylic acid groups present (0.6 mmol) as determined from acid value titration measurements on the processed blend. Because of the lower epoxy equivalent weight of CE 450, a higher amount of CE 450 was used (5 wt%, blend D) to keep the epoxy content in this blend similar to the other blends. The amount of reactive oligomer used is higher than that used in the literature (1 wt%), [14,20–22] as our experiments showed that there was no increase in molecular weight in blends containing 1 wt% of the reactive oligomers.

Table 1. Blends prepared.

Sample	PLLA (wt%)	Triblock (wt%)	Plasticizer (wt%)	Epoxy functional oligomer (wt%)	Epoxy supplied (mmol)	
J0	60	30	10	0	None	0
A	59	29	9	3	S 285	1.3
B	59	29	9	3	CE 215	1.6
C	59	29	9	3	CE 285	1.3
D	57	29	9	5	CE 450	1.4

2.4. Characterization Techniques Employed

¹H-Nuclear magnetic resonance (NMR) (300 MHz) spectra were obtained using a Bruker DPX-300 NMR spectrometer (The Woodlands, TX, USA). The spectra were measured in CDCl₃, and the chemical shifts were calibrated to the solvent's residual proton signal (¹H NMR signal: δ 7.26 ppm for CHCl₃). The molecular weight and dispersity were determined by GPC (chloroform) (Agilent, Santa Clara, CA, USA). The molecular weights measured are reported with respect to polystyrene standards. Where possible, MALDI was used for absolute molecular weight measurement. Dithranol was used as the matrix. Acid value was determined by titration of 20 mL of 15mg/mL chloroform solution of the polymer against 0.1 N alcoholic KOH. pH was monitored using an Oakton PHE1100 pH meter (Vernon Hills, IL, USA). Thermal characterization was performed on a TA Q100 differential scanning calorimeter (DSC) (TA Instruments, New Castle, DE, USA) which was calibrated against an indium standard. The samples (5–10 mg) were heated from –60 °C to 220 °C at the rate of 20 °C·min^{–1} in the first heating cycle to study the morphology of the samples formed under the processing conditions. Tensile testing was performed using an Instron universal testing machine (Norwood, MA, USA) according to ASTM D638 standard [25] for tensile testing, using type IV dog bone specimens. Testing was performed at a crosshead speed of 50.8 mm/min with a 5 Kn load cell. For each sample, 3 individual specimens were tested in 3 individual analyses and the reported data are the calculated means. Because of material quantity limitations, sample size was restricted to three specimens.

2.5. Hydrolytic Stability Test

In order to investigate the effect of the reactive oligomer on the hydrolytic stability, the PLLA triblock based blend films were processed in the presence and absence, of 5 wt% of S285 reactive oligomer. The films were made by attaching a film die to the mini extruder. The blend components were mixed at 190 °C and 80 rpm for 7 min before extrusion. These films were placed in environmental chambers (Thermotron Industries, Holland, Mi, USA) maintained at 90% relative humidity, at 20, 40 and 60 °C. The films were removed from the environmental chambers at regular time intervals (day 2, day 4, *etc.*, labeled as d2, d4, *etc.*) and their molecular weights were determined using GPC.

3. Results and Discussion

3.1. Functionality of the Reactive Oligomers

The epoxy functionality (F) of the reactive oligomers is expressed as follows:

$$F = M \times DP \quad (1)$$

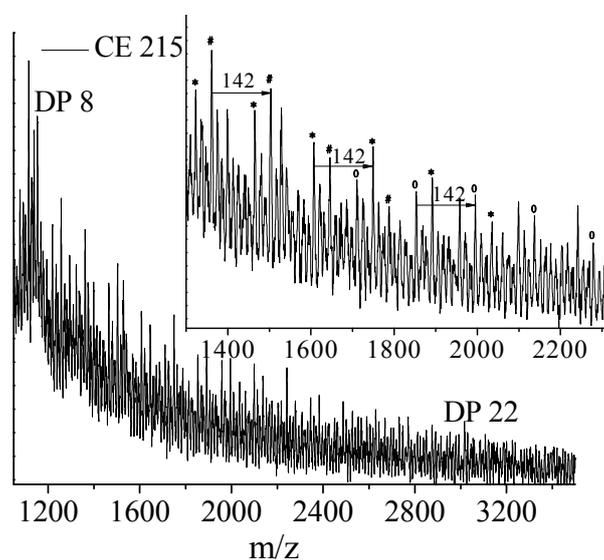
Where, M is the mole percent of glycidyl methacrylate in the copolymer and DP is the degree of polymerization of the copolymer [18]. M in the copolymer can be estimated from the epoxy equivalent weight of the copolymer and the molecular weight of the co-monomer used. As known from literature and our ^1H NMR, IR and DSC data, the procured reactive oligomers are copolymers of glycidyl methacrylate (GMA), styrene (S) and butyl acrylate (BA). The determination of the relative amounts of styrene and butyl acrylate in these copolymers using ^1H NMR is difficult because of overlapping resonances. This, in fact, is not necessary for our analysis, as only a small variation in the GMA mol% occurs if the co-monomer is assumed to be entirely either styrene or butyl acrylate. Hence, to determine M , it is only necessary to consider their aggregate molar mass, treating the copolymers consisting of GMA and comonomer B. As shown in Table 2, the range of M estimated for CE 215, CE 285 and CE 450 are 59%–64%, 42%–47% and 29%, respectively. The M for CE 450 can be accurately measured since infrared and DSC data have shown that the comonomer is only butyl acrylate. These numbers are calculated using an iterative method. M is varied and the EEW values generated are analyzed. This iterative procedure is continued until the targeted EEW value for the reactive oligomer is found. The composition which generates the targeted EEW value is used to determine the mole % of GMA in the copolymer.

Table 2. Estimation of mole percent of Glycidyl methacrylate (GMA) in the copolymers (reactive oligomers).

Copolymer	Comonomer	GMA (mol%)	Comonomer (mol%)	Comonomer M_w (g/mol)	EEW (g/eq)
CE 215	Styrene	59	41	104	214
	Butylacrylate	64	36	128	214
CE 285	Styrene	42	58	104	286
	Butylacrylate	47	53	128	286
CE 450	Butylacrylate	29	71	128	455

In order to estimate the *DP* of the three copolymers, a combination of MALDI and GPC analyses was used. MALDI data was obtained on the CE 215 copolymer and is shown in Figure 3. The range of *DP* estimated is from 8 to 22 units assuming a composition of 60 mol% GMA and 40 mol% Styrene (Table 2). As the dispersity of these copolymers is ~ 3 there is a wide range in the *DP* values. It must be noted that in systems with dispersity >1.5 , MALDI can underestimate the molecular weight of high molar mass components resulting in lower molecular weight values [26–28]. Other experimental parameters including solvent or the cationization agent used can also affect the molecular weight values. The molecular weight data obtained from MALDI is therefore a conservative estimate of the sample actual molecular weight. The MALDI spectrum is fairly complex because of the distribution of compositions, typical of a random copolymer [29]. Even with the low signal to noise ratio observed, it still can be seen a pattern exists in the spectra with peaks separated by 142 atomic mass units (Figure 3 inset), the molecular weight of one GMA unit.

Figure 3. MALDI spectra of CE 215 reactive oligomer (inset: details showing the pattern).



With its inherent deficiencies, MALDI cannot be employed to assess the *DP*s of the three copolymers [26–28]. To calculate the *DP* of CE 450 and CE 285, the following procedure was followed. Figure 4 shows the GPC traces of the three copolymers. The number average molecular weights obtained from GPC allows comparison of the molecular weights of CE 215 with CE 285 and CE 450. These data show that CE 285 and CE 450 have molecular weights ~ 0.6 and 0.5 times that of CE 215 (Table 3) with similar dispersities. Thus the *DP* can be estimated and is shown in Table 3. Although not absolute, this analysis allows a comparison of the three reactive oligomers. As the *DP* and the mole percent of GMA in the copolymers is known, the epoxy functionality can be estimated using equation 1 and is shown in Table 3.

Further characterization of the functionality of the reactive oligomers was performed by reacting epoxy functional oligomers with 1.1 equivalents of stearic acid at 180–190 °C for seven minutes in a 20 mL glass vial using an overhead mechanical stirrer. An excess of stearic acid was used to ensure complete consumption of the epoxy groups. It was not necessary to separate the excess stearic acid from the product mixture as it did not overlap with the GPC traces of the reactive oligomers. The

expectation is that the higher the functionality, the higher will be the number of stearic acid molecules grafted per chain of the oligomer and higher will be the increase in the molecular weight. The results obtained are shown in Figure 5. It can be seen that the increase in peak molecular weight is in excellent correlation with the functionality of the reactive oligomer. The increase in peak molecular weight ΔM_p is 1650, 3200 and 7500 g/mol for CE 450, CE 285 and CE 215 respectively. This experiment provides a direct proof of the difference in the functionalities of the three reactive oligomers in the order, CE 450 < CE 285 < CE 215. This trend is in agreement with the MALDI and GPC analysis. Although an absolute measurement of functionality, F , is not possible, the relative functionality of different epoxy oligomers can be conveniently compared.

Table 3. Estimation of degree of polymerization (DP) and functionality of the copolymers.

Copolymer	GPC (M_n , g/mol)	Factor	DP range	GMA (mol%)	Functionality
CE 215	5000	1	8–20 *	61	5–11
CE 285	3000	0.6	4–16	44	2–7
CE 450	2600	0.5	3–15	29	1–4

Note: * From MALDI.

Figure 4. GPC traces of CE 450, CE 285 and CE 215. (M_n , \bar{D} shown in parentheses).

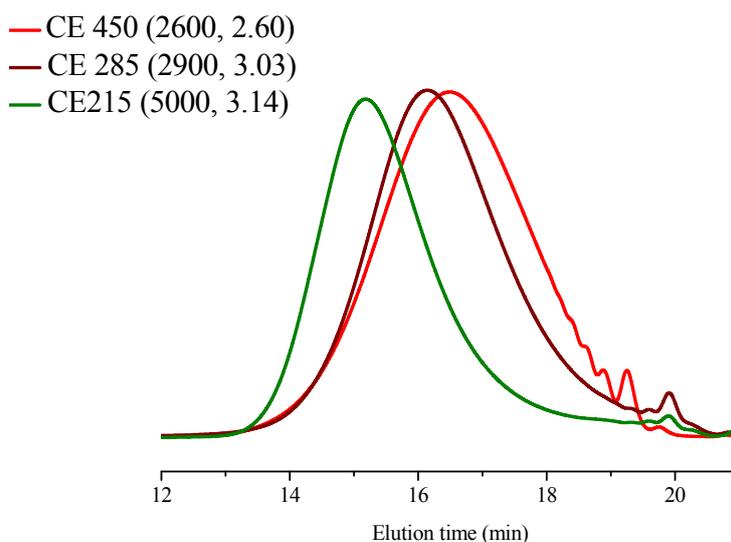
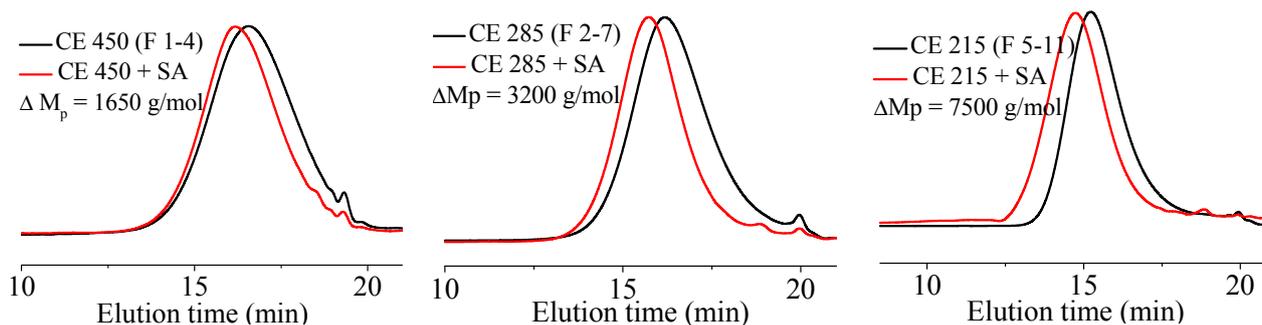


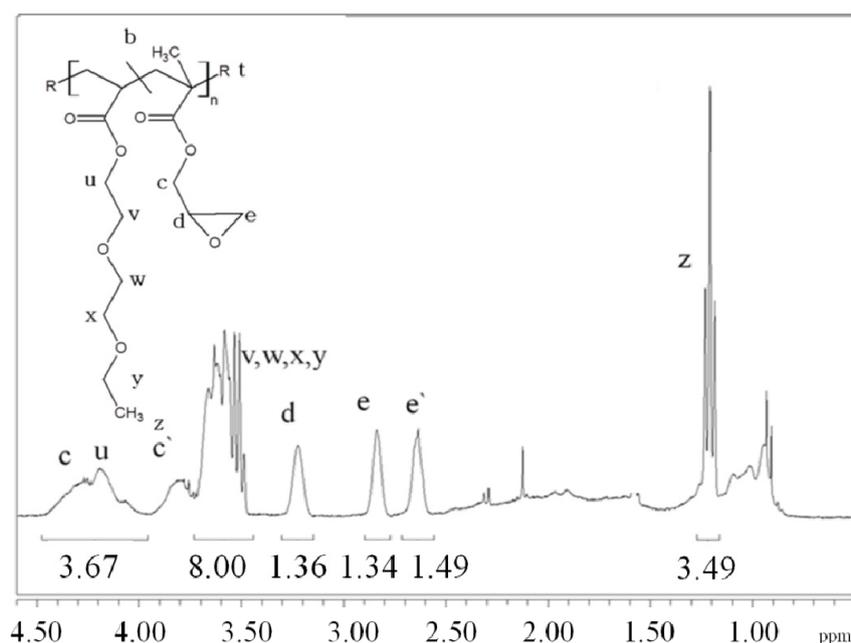
Figure 5. GPC traces of stearic acid grafted epoxy functional reactive oligomers with low, medium and high functionality before and after reaction.



3.2. Synthesis of a Highly Functional Reactive Oligomer

The ^1H NMR spectra of the copolymer synthesized is shown in Figure 6. The measured epoxy content is in excellent agreement with the targeted value of 57 mol%. The epoxy content is determined by comparison of the integration values of the resonance centered at $\sim\delta$ 3.2 ppm corresponding to the methine proton on the epoxy group (proton *d*) with the resonances at δ 3.5–3.8 ppm corresponding to the methylene protons of the ethoxy-ethoxy ethyl repeat unit (protons *v*, *w*, *x*, *y*) in the copolymer. Based on the integrated values, the ratio of glycidyl methacrylate to ethoxy-ethoxy ethyl acrylate in the copolymer is 1.36. Thus, the mole fraction of glycidyl methacrylate in the copolymer is $(1.36/(1 + 1.36)) = 0.57$.

Figure 6. ^1H NMR spectra of P(E2EA-co-57GMA).



The *DP* was determined by a combination of MALDI and GPC. MALDI data was obtained on the low molecular weight homopolymer of 2-(2-ethoxyethoxy ethyl) acrylate (PE2EA 10) and is shown in Figure 7a. The *DP* range for this oligomer is \sim 5–20. The number average molecular weight with respect to PS standards of P(E2EA 10) and S285 was determined from GPC (Figure 7b) are 2100 and 12,400 g/mol respectively. Thus the molecular weight of S285 is \sim 5–6 times that of P(E2EA). Hence, the *DP* of S285 can be calculated to be well above 25 units and its functionality will be greater than $0.57 \times 25 \sim 14$ –15 units, well above the value of CE215. The increase in the M_w after reacting with stearic acid (SA) is similar to that for CE 215. (Figure 7c) However, there is a high molecular weight shoulder which confirms the presence of chains with very high functionality in this reactive oligomer. Analysis of the molecular weight distribution in S285 and CE 215 after reaction with SA shows that in S285 + SA (Figure 7c) \sim 17% chains have molecular weights $>100,000$ g/mol while in CE 215 + SA \sim 1% chains have molecular weights $>100,000$ g/mol. Thus, in this study, four reactive oligomers with low, medium, high and very high epoxy functionality are available and summarized in Table 4.

Figure 7. (a) MALDI spectra of P(E2EA) 10; (b) GPC traces of P(E2EA) 10 and S285 (M_n , \bar{D} shown in parentheses); (c) GPC traces of stearic acid grafted reactive oligomer before and after the reaction.

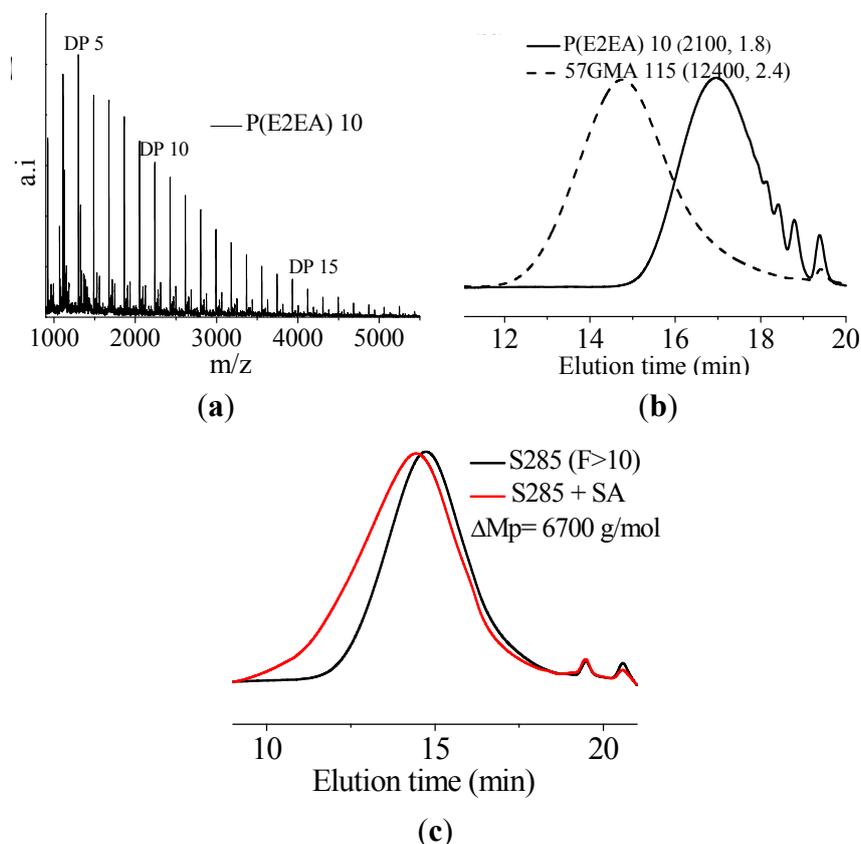


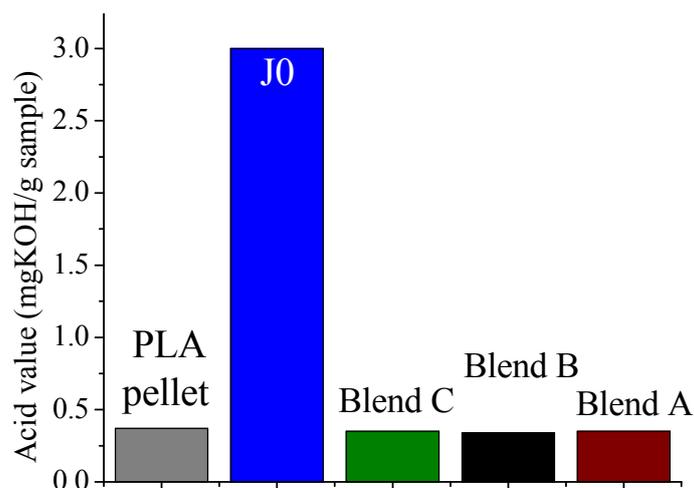
Table 4. List of varying functionality reactive oligomers studied.

Reactive oligomer	Nomenclature	EEW (g/eq)	GMA (mol%)	DP	Functionality	T_g (°C)
Joncryl 4385	CE 450	450	29	3–15	1–4	–38
Joncryl 4368	CE 285	285	44	4–16	2–7	54
PlussOptiPET	CE 215	215	61	8–20	5–11	49
P(E2EA-co-57GMA) 115	S 285	285	57	>25	>15	–22

3.3. Blend Characterization

Acid Value Found

The acid value increases from 0.4 ± 0.1 mg KOH/g for the as received PLA to 2.5 ± 0.5 mg KOH/g for the PLA/triblock/plasticizer blend processed at 190–200 °C for 7 min (J0) corresponding to ~ 0.6 mmol of carboxylic acid groups in 12 g of blend sample prepared (Figure 8). This indicates that because of the hydrophilic nature of the triblock copolymer and the elevated temperatures used in the melt processing, the degradation of PLLA is accelerated in these blends. When the blend is processed in the presence of the reactive oligomers, as excess epoxy groups are supplied in all the blends (1.3–1.6 mmol) the acid values measured after processing are very low, within the limits of the measurement. This indicates that greater than 80 percent of the acid groups generated during degradation are consumed by the epoxy groups.

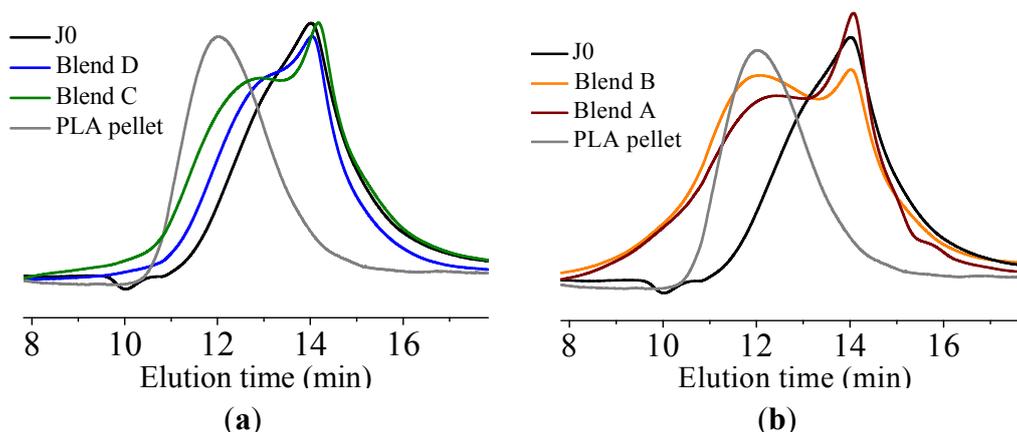
Figure 8. Acid value of the blends (blend compositions shown in Table 1).

3.4. Molecular Weight

The GPC traces of the blends are shown in Figure 9. As expected from the acid value data, the M_w of untreated blends exhibits a significant drop as compared to the as received PLA (120,000 as compared to 30,000 g/mol). When reactive oligomers (>3 wt%) are introduced into the blend during processing, depending on the functionality of the oligomers, a drop in molecular weight or even an increase in molecular weight occurs (Table 5). It should be noted that experiments with 1 wt% of the reactive oligomers were performed and no increase in molecular weight of PLLA was observed. In addition beyond a concentration of 3 wt%, a plateau in molecular weight increase was found. This indicates that a concentration of 3 wt% is needed for the chain extension reaction to be faster than the degradation reaction, higher than the 1 wt% reported previously [14,20–22]. In blends D and C where low and medium functionality oligomers are used, the increase in molecular weight is modest from 30,000 g/mol to 39,000 g/mol and 45,000 g/mol in blend D and C respectively. When high functionality oligomer is used, (Blend B) a large increase in the molecular weight is seen (59,000 g/mol) (Figure 9b) This increase in molecular weight with increase in functionality is similar to the results shown in Figure 5, where a model mono-functional acid is reacted with the reactive oligomers. Our data is thus consistent with the primary reaction taking place between the carboxylic acid and epoxy groups.

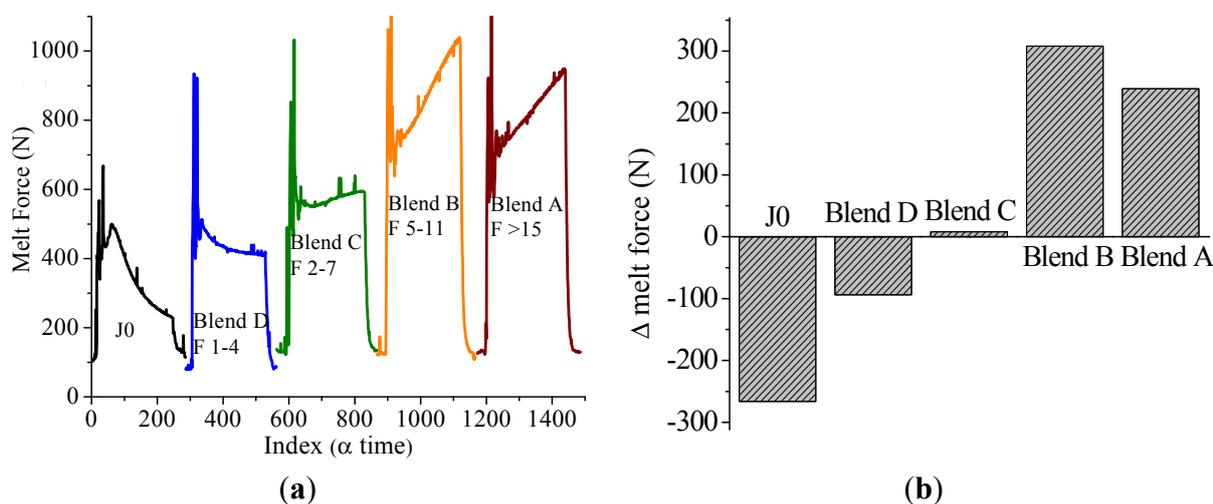
When very high functionality oligomer is used (Blend A) the molecular weight increase is similar to that in Blend B. This indicates that beyond a functionality of 5–11, further functionality increase does not lead to additional grafting of PLA chains to the epoxy groups. This can be attributed to other factors including steric hindrance. Furthermore, there is no observable change in the molecular weight of the triblock copolymer. This is likely because, as the PDLA block in the triblock copolymer is terminated in hydroxyl groups, their reactivity with epoxy groups is negligible at the temperature and time used for melt blending. In addition, as PDLA is only ~10 wt% of the blend, its degradation is less likely and was not detected using GPC.

Figure 9. (a) and (b): GPC traces of the blends.



The melt force data (Figure 10) is also consistent with the molecular weight measurements. It should be noted that the melt force measured depends on the amount of material in the extrusion chamber. Thus, the relative increase or decrease in force with blending time is the data which can be compared and analyzed. The change in the melt force before and after melt blending is plotted in Figure 10b. A large drop in melt force occurs in the absence of the reactive oligomers and indicates a large drop in molecular weight due to degradation. With increasing functionality of the epoxy oligomers the melt force measured is consistent with an increase in molecular weight (Figure 10).

Figure 10. (a) Melt force as a function of blending time (Blending time is ~7 min); **(b)** Change in melt force before and after melt blending for 7 min at 190 °C.



It was found that no gelation (network formation) occurred despite the high functionalities and concentration of the oligomers used. All the samples were completely soluble in chloroform and amenable for GPC analysis. Studies on chain extension of PET using Joncryl 4368 have shown that micro-gel formation occurred when >1.5 wt% of reactive oligomers were used [19]. As mentioned above, the gelation probability is higher in degraded PET as acid groups may exist at both chain ends. In addition, typically PET is processed at higher temperatures (280 °C). Hence the reactivity of the hydroxyl group will be correspondingly higher. No gelation of PLA has been reported in the literature,

under the processing time scales we used in this study [14,21]. The only report of gelation has been when the reaction is performed for a time greater than one hour [30]. This indicates that it is possible to prevent gelation from taking place in PLA because of the extremely low reactivity of the hydroxyl group with the epoxy group at temperatures relevant for PLA processing [24]. However, it should be noted that the reactivity of the hydroxyl group with the epoxy group is negligible, it is not completely absent, particularly if the reaction is performed for a sufficiently long time, or at elevated temperatures.

Table 5. Molecular weight and dispersity measured using GPC.

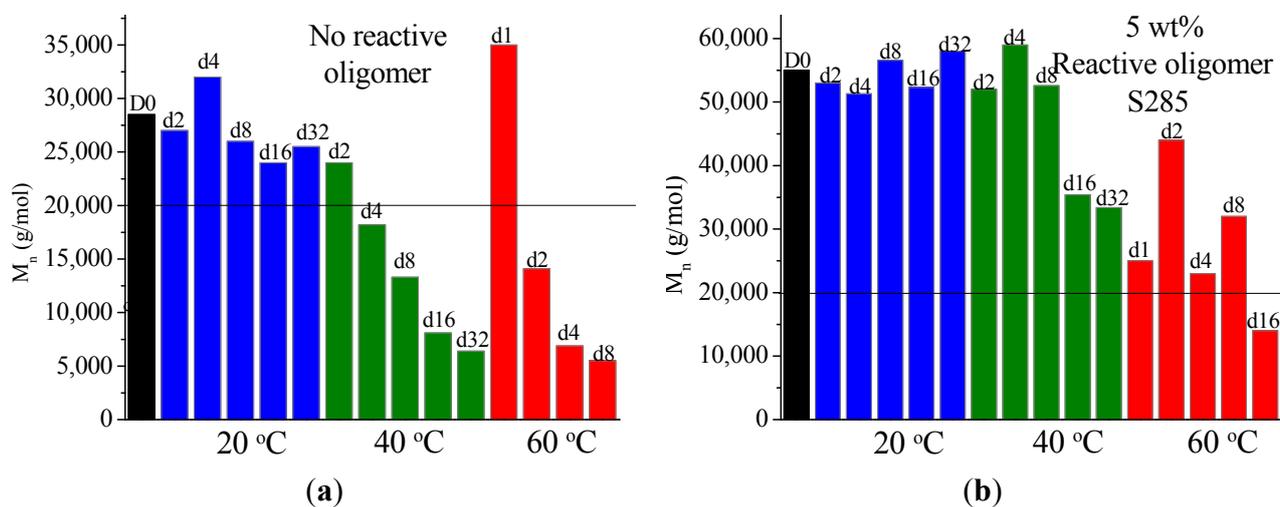
Blend	M_n (g/mol) *	D
J0	30,000	2.55
A	53,000	6.4
B	59,000	5.8
C	45,000	3.3
D	39,000	2.9
PLA pellet	120,000	1.67

Note: * With respect to PS standards.

3.5. Hydrolytic Stability Measured

For hydrolytic stability tests, the control blend sample was processed in the absence of the reactive oligomer with the other samples being processed in the presence of 5 wt% of S285 reactive oligomer. It can be seen (Figure 11) that the reactive oligomer blend has a starting molecular weight twice that of the control blend after processing (D0). When the films are placed in the environmental chambers at 90% relative humidity and temperatures of 40 and 60 °C, a drop in the molecular weight occurs because of hydrolytic degradation. The control blend exhibits a molecular weight of less than 20,000 g/mol after four days at 40 °C and 90% relative humidity, while that of the reactive oligomer blend remains above 20,000 g/mol needed to maintain mechanical properties even after 32 days at 40 °C and 90% relative humidity. Thus the use of the reactive oligomer S285 causes a substantial improvement in the hydrolytic stability of the PLA based blend.

Figure 11. Molecular weight as a function of time and temperature of the (a) control blend and (b) reactive oligomer blend.



3.6. Morphology and Properties

Because of the multifunctional nature of the reactive oligomers used, the molecular weight increase is a result of grafting of the PLLA chains onto the reactive oligomers. The resultant structures may be branched and can thus affect the crystallization kinetics of the stereocomplex crystals [31]. As seen from Figure 12, the stereocomplex melting endotherm is observed in all the blends. Thus, despite the presence of branched structures, stereocomplex formation between the triblock copolymer and PLLA is not prevented. However, as seen from Table 6, the degree of stereocomplex crystallinity and hence the fraction of triblock participating in the stereocomplex formation is lower in the blends where high functionality epoxy oligomers are used, indicating that branching leads to a slight disruption in the co-crystallization between PLLA and the triblock copolymer.

Figure 12. Differential scanning calorimeter (DSC) traces of the blends.

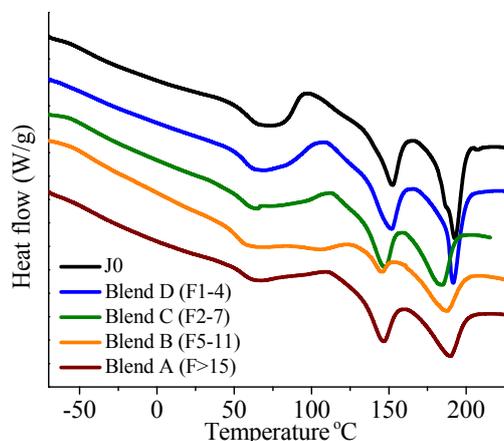
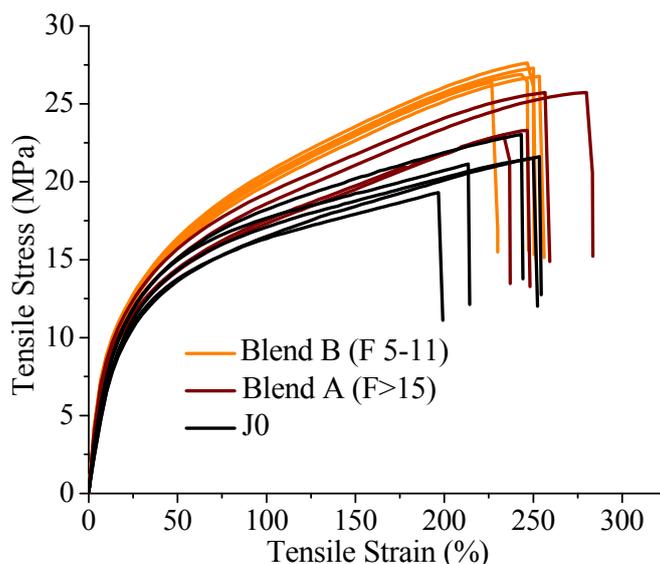


Table 6. DSC data of the blends.

Sample	ΔH stereocomplex (J/g)	Stereocomplex crystallinity (%)	Triblock participating (%)
J0	16	11	59
A	14	10	51
B	11	8	40
C	10	7	37
D	11	8	40

As seen from Figure 13 and Table 7, the use of reactive oligomers retains the low modulus and high elongation at break possessed by the PLA/triblock/Plasticizer blend as desired. In addition, there is an increase in the ultimate tensile strength in the high functionality epoxy oligomer blend because of the higher molecular weight of the blend. Furthermore, it is found that the use of a low T_g reactive oligomer (Blend A) does not reduce the blend modulus. This indicates that because of the low amount of the reactive oligomer used (3 wt%), the reactive oligomer T_g does not cause a significant change in blend T_g .

Figure 13. Mechanical properties of the blends.**Table 7.** Mechanical properties.

Sample	Modulus (MPa)	ϵ_b (%)	T_g (oligomer)
J0	90 ± 15	230 ± 24	NA
C	117 ± 15	240 ± 12	$50 \text{ }^\circ\text{C}$
B	131 ± 2	245 ± 11	$48 \text{ }^\circ\text{C}$
A	121 ± 6	244 ± 30	$-22 \text{ }^\circ\text{C}$

4. Conclusions

For the first time, the effect of functionality of the epoxy functional reactive oligomers on the molecular weight increase of PLLA in PLLA/PDLA-softblock-PDLA/Plasticizer based blends has been investigated. Three reactive oligomers with low, medium and high epoxy functionality were studied. In addition, a reactive oligomer with very high functionality was synthesized and studied. The functionality of these reactive oligomers was estimated using MALDI, GPC and epoxy equivalent weight data, and GPC studies on reactive oligomers grafted with a model monofunctional acid.

It was found that acid groups were consumed in all the blends but the molecular weight increase depended on the functionality of the reactive oligomer. The molecular weight of the degraded PLLA chains increased with an increase in the functionality of the reactive oligomer up-to a functionality of 5–11. Further increase in functionality leads to a plateau in the molecular weight increase possibly because of steric effects. No gel formation occurred in these blends despite the high functionality of the reactive oligomers. These results indicate that because of the negligible reactivity of the hydroxyl groups with the epoxy groups under PLA processing conditions, it is possible to kinetically prevent gelation from occurring. Because of the hydroxy-acid nature of PLA, the degraded chains necessarily have only one chain end with the carboxylic acid group. This makes the “reactive functionality” of the PLA chains with epoxy groups to be 1 under normal PLA processing conditions.

On investigation of the hydrolytic stability, it was found that the high functionality reactive oligomer S285 caused a significant improvement in the hydrolytic stability of the blend, as the

molecular weight did not fall below the critical molecular weight (20,000 g/mol) even after 32 days at 40 °C and 90% relative humidity. The molecular weight increase caused a slight reduction in the co-crystallization between the PLLA and the triblock copolymer. The increased molecular weight caused an increase in the ultimate tensile strength of the blends. The use of low T_g reactive oligomer did not have any significant effect on the modulus of the blend because of its use in small amounts.

This study provides a better understanding of the degradation and chain extension reaction of PLA with epoxy functional reactive oligomers and shows how the functionality of the reactive oligomers controls the molecular weight increase of the degraded PLA chains. We showed that in modified PLA based systems where the rate of degradation is increased, higher functionality epoxy oligomers, at higher concentrations, than those used for unmodified PLA need to be used to bring about a sufficient increase in the molecular weight. Use of the high functionality reactive oligomers causes a significant increase in the blend molecular weight and hence the hydrolytic stability and processability. These findings will be useful for increasing the hydrolytic stability and durability of PLA based blends and composites.

Author Contributions

Over the last 4 years, this collaboration between Saint Gobain and the University of Massachusetts (Amherst) has been directed at modifying the physical properties of poly(lactic acid) (PLA) turning it from a brittle semicrystalline polymers into a rubbery polymer. Shaw Ling Hsu has been studying the structure and properties of biomass based polymers, especially PLA, since the early 90s. Sahas Rathi was a doctoral student at the Polymer Science and Engineering Department of the University of Massachusetts (Amherst) jointly supervised by Bryan Coughlin and Shaw Ling Hsu. Sahas R. Rathi was responsible for the synthesis and characterization of various PLA oligomers and derivatives at the University of Massachusetts. He has now graduated and is employed at Saint Gobain. The Saint Gobain team is led by Michael Tzivanis. That team is responsible for all the degradation experiments of various PLAs, including blends and functionalized derivatives. Charles Golub has been instrumental in developing PLA derivatives to be used in various flexible tubing and film applications. Gerald Ling is responsible for the structural characterization at Saint Gobain.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Shen, L.; Worrell, E.; Patel, M. Present and future development in plastics from biomass. *Biofuels Bioprod. Bioref.* **2010**, *4*, 25–40.
2. Jamshidian, M.; Tehrany, E.A.; Imran, M.; Jacquot, M.; Desobry, S. Poly-Lactic Acid: Production, Applications, Nanocomposites, and Release Studies. *Compr. Rev. Food Sci. Food Saf.* **2010**, *9*, 552–571.
3. Bhardwaj, R.; Mohanty, A.K. Advances in the properties of polylactides based materials: A review. *J. Biobased Mater. Bioenergy.* **2007**, *1*, 191–209.

4. Rasal, R.M.; Janorkar, A.V.; Hirt, D.E. Poly(lactic acid) modifications. *Prog. Polym. Sci.* **2010**, *35*, 338–356.
5. Yang, L.X.; Chen, X.S.; Jing, X.B. Stabilization of poly(lactic acid) by polycarbodiimide. *Polym. Degrad. Stab.* **2008**, *93*, 1923–1929.
6. Liu, H.; Zhang, J. Research Progress in Toughening Modification of Poly(lactic acid). *J. Polym. Sci. Part B Polym. Phys.* **2011**, *49*, 1051–1083.
7. Anderson, K.S.; Schreck, K.M.; Hillmyer, M.A. Toughening polylactide. *Polym. Rev.* **2008**, *48*, 85–108.
8. Fukushima, K.; Abbate, C.; Tabuani, D.; Gennari, M.; Camino, G. Biodegradation of poly(lactic acid) and its nanocomposites. *Polym. Degrad. Stab.* **2009**, *94*, 1646–1655.
9. Dong, W.Y.; Jiang, F.H.; Zhao, L.P.; You, J.C.; Cao, X.J.; Li, Y.J. PLLA Microalloys versus PLLA Nanoalloys: Preparation, Morphologies, and Properties. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3667–3675.
10. Yu, L.; Dean, K.; Li, L. Polymer blends and composites from renewable resources. *Prog. Polym. Sci.* **2006**, *31*, 576–602.
11. Nijenhuis, A.J.; Colstee, E.; Grijpma, D.W.; Pennings, A.J. High molecular weight poly(L-lactide) and poly(ethylene oxide) blends: Thermal characterization and physical properties. *Polymer* **1996**, *37*, 5849–5857.
12. Tsui, A.; Wright, Z.C.; Frank, C.W. Biodegradable Polyesters from Renewable Resources. In *Annual Review of Chemical and Biomolecular Engineering*; Prausnitz, J.M., Ed.; Annual Reviews: Palo Alto, CA, USA, 2013.
13. Meng, Q.K.; Heuzey, M.C.; Carreau, P.J. Control of thermal degradation of polylactide/clay nanocomposites during melt processing by chain extension reaction. *Polym. Degrad. Stab.* **2012**, *97*, 2010–2020.
14. Najafi, N.; Heuzey, M.C.; Carreau, P.J.; Wood-Adams, P.M. Control of thermal degradation of polylactide (PLA)-clay nanocomposites using chain extenders. *Polym Degrad. Stab.* **2012**, *97*, 554–565.
15. Rathi, S.R.; Coughlin, E.B.; Hsu, S.L.; Golub, C.; Ling, G.; Tzivani, M. Effect of mid-block on the morphology and properties of blends of ABA triblock copolymers of PDLA-mid-block-PDLA with PLLA. *Polymer* **2012**, *53*, 3008–3016.
16. Rathi, S.R.; Chen, X.; Coughlin, E.B.; Hsu, S.L.; Golub, C.; Tzivani, M. Toughening semicrystalline poly(lactic acid) by morphology alteration. *Polymer* **2011**, *52*, 4184–4188.
17. Rathi, S.R. Toughening Semicrystalline Poly(lactic acid) by Morphology Alteration. Ph.D. Thesis, University of Massachusetts Amherst, Amherst, MA, USA, 1 January 2013.
18. Blasius, W.G.; Deeter, G.A.; Villalobos, M. Oligomeric Chain Extenders for Processing, Post-Processing and Recycling of Condensation Polymers, Synthesis, Compositions and Applications. US6984694 B2, 10 January 2006.
19. Villalobos, M.; Awojulu, A.; Greeley, T.; Turco, G.; Deeter, G. Oligomeric chain extenders for economic reprocessing and recycling of condensation plastics. *Energy* **2006**, *31*, 3227–3234.
20. Al-Itry, R.; Lamnawar, K.; Maazouz, A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym. Degrad. Stab.* **2012**, *97*, 1898–1914.

21. Corre, Y.M.; Duchet, J.; Reignier, J.; Maazouz, A. Melt strengthening of poly(lactic acid) through reactive extrusion with epoxy-functionalized chains. *Rheol. Acta* **2011**, *50*, 613–629.
22. Zhang, Y.C.; Yuan, X.; Liu, Q.; Hrymak, A. The Effect of Polymeric Chain Extenders on Physical Properties of Thermoplastic Starch and Polylactic Acid Blends. *J. Polym. Environ.* **2012**, *20*, 315–325.
23. Haralabakopoulos, A.A.; Tsiourvas, D.; Paleos, C.M. Chain extension of poly(ethylene terephthalate) by reactive blending using diepoxides. *J. Appl. Polym. Sci.* **1999**, *71*, 2121–2127.
24. Japon, S.; Boogh, L.; Leterrier, Y.; Manson, J.A.E. Reactive processing of poly(ethylene terephthalate) modified with multifunctional epoxy-based additives. *Polymer* **2000**, *41*, 5809–5818.
25. American Society for Testing and Materials (ASTM). *Standard Test Method for Tensile Properties of Plastics*; ASTM D638; ASTM International: West Conshohocken, PA, USA.
26. Schriemer, D.C.; Li, L. Mass discrimination in the analysis of polydisperse polymers by MALDI time-of-flight mass spectrometry. 1. Sample preparation and desorption/ionization issues. *Anal. Chem.* **1997**, *69*, 4169–4175.
27. Schriemer, D.C.; Li, L. Mass discrimination in the analysis of polydisperse polymers by MALDI time-of-flight mass spectrometry. 2. Instrumental issues. *Anal. Chem.* **1997**, *69*, 4176–4183.
28. Hassan, R.; Baochuan, G. Use of MALDI-TOF to Measure Molecular Weight Distributions of Polydisperse Poly(methyl methacrylate). *Anal. Chem.* **1998**, *70*, 131–135.
29. Kalish, J. Effects of Molecular Architecture on Crystallization Behaviour of Poly(lactic acid) and Random Ethylene-Vinyl Acetate Copolymers. Ph.D. Thesis, University of Massachusetts Amherst, Amherst, MA, USA, September 2011.
30. Wang, Y.L.; Fu, C.H.; Luo, Y.X.; Ruan, C.S.; Zhang, Y.Y.; Fu, Y. Melt Synthesis and Characterization of Poly(L-lactic Acid) Chain Linked by Multifunctional Epoxy Compound. *J. Wuhan Univ. Technol. Mater. Sci. Ed.* **2010**, *25*, 774–779.
31. Geschwind, J.; Rathi, S.; Tonhauser, C.; Schömer, M.; Hsu, S.L.; Coughlin, E.B.; Frey, H. Stereocomplex Formation in Polylactide Multiarm Stars and Comb Copolymers with Linear and Hyperbranched Multifunctional PEG. *Macromol. Chem. Phys.* **2013**, *214*, 1434–1444.