Reactive Extrusion of Poly(L-Lactic Acid) with Glycidol

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ABSTRACT: Glycidol modified polylactic acid (PLLA) polymers have been prepared by reactive extrusion. Influences of residence time and the concentration of glycidol on the extent of reaction with different weight average molecular weight (45,000, 65,000, and 100,000) PLLA's were studied. Structure–property relationship has been established by measuring molecular, mesoscopic, and macroscopic properties. Under reactive extrusion conditions glycidol reacted with the end groups of PLLA to initiate chain extension. Low-molecular weight PLLA reacted with glycidol faster than the medium molecular weight PLLA, whereas high-molecular weight PLLA did not show significant reactions. The glass transition temperature, melting temperature, crystallization temperature, and heat of fusion were measured for unmodified and modified PLLA's. Chain extended PLLA had higher T_g and T_m than the unmodified samples. Time sweep rheological experiments were performed to test the melt stability of PLLA. Chain extended PLLA's were found to retain viscoelastic properties for much longer time than the unreacted samples. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1391–1398, 2009

Key words: biodegradable; reactive extrusion; rheology; structure–property relations; thermal properties

INTRODUCTION

Poly(L-lactic acid) (PLLA) is a linear aliphatic thermoplastic polyester derived from 100% renewable resources. PLLA offers a wide range of properties depending on its stereochemical make up. It is a biodegradable, bioabsorbable and biocompatible polymer with several applications in the biomedical industry. Being biodegradable, PLLA is increasingly considered for replacing petroleum derived plastics in application such as loose-fill packaging, compost bags, food packaging and in agricultural applications. The physical properties of linear PLLA[1–3] are not optimal to facilitate widespread substitution of fossil fuel based plastics at present time. In particular the processing characteristics, heat resistance, and physicomechanical properties of PLLA need further improvements. To this end reactive extrusion technology has been used to modify PLLA by either copolymerization with comonomers or compounding with fillers/reinforcements or with various additives like impact modifiers, processing stabilizers, chain extenders, end capping agents, branching agents, and crosslinking agents. One of the major limitations of PLLA is its poor thermal stability upon melting. Degradation of PLLA can occur even at 160°C during injection molding.[4] Several stabilizers and metal deactivators are used to reduce degradation of PLLA during melt processing.[5,6]

Another shortcoming of PLLA is its low melt viscosity, which may limit its extrusion processability. Chain extension is a useful technique to increase the molecular weight of polycondensates and hence their melt viscosity. Commercially, aromatic polyesters such as polyethylene terepthalate are chain extended to produce special grades that have rheological properties suitable for blow molding and film blowing applications. Chain extended high-molecular weight polymers also have good mechanical properties such as high strength, stiffness, fatigue and low shrinkage. Chain extension is a process that couples polycondensate end groups of lower molecular weight chains in a statistical way to produce high-molecular weight chains. Typically, a chain extender couples two equal end groups, e.g., two amines, two hydroxyls or two carboxyls groups. Solid state postcondensation technology is employed to increase the molecular weight of polycondensates.[7–11] Chain extension of PLLA in reactors has been reported using various chain extenders such as diisocyanates, oxazolines and hydroxyl-functionalized epoxides.[12–16] Block copolymers of poly(glycidol) and PLLA have also been reported.[17,18]

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TABLE I
Formulations Used For This Work

S. no	Residence time (mins)	PLLA-A (%)	Glycidol (%)	PLLA-B (%)	Glycidol (%)	PLLA-C (%)	Glycidol (%)
1		As synthesized		As synthesized		As synthesized	
2	5	100	0.0	100	0.0	100	0.0
3		99.5	0.5	99.5	0.5	99.5	0.5
4		99	1.0	99	1.0	99	1.0
5	10	100	0.0	100	0.0	100	0.0
6		99.5	0.5	99.5	0.5	99.5	0.5
7		99	1.0	99	1.0	99	1.0

Reactive extrusion technology can also be used for chain extension. It offers the advantages of being faster, cheaper and thus can be used to process large volumes of polymers. Reactive extrusion has been used for melt stabilization and peroxide induced branching of PLLA.[19–21] In this work we report on reactive extrusion of glycidol with PLLAs of different molecular weights using a micro-scale twin screw compounder. Influences of residence time, concentration of glycidol, and molecular weight of PLLA on the chain extension reaction were studied. Structure–property relationships of modified PLLA have been established by measuring their molecular, mesoscopic and macroscopic properties.

EXPERIMENTAL

Materials

L-Lactide (97%), purchased from Purac, was dried under vacuum for 12 h before use. The L-Lactide was polymerized by ring opening polymerization at 180°C for varying times from 45 to 60 min to give PLLA of different molecular weights. Tin octoate [$Sn(Oct)_2$-(95%)] catalyst purchased from Aldrich was used as received, and a concentration of 0.05–0.1 wt % was used for polymerization. HPLC grade chloroform (>99.8%) was used without further purification. All glassware, ground-glass syringes, and needles were oven-dried at 160°C for at least 24 h and cooled under argon directly before use. Glycidol (96%) purchased from Aldrich was used as received for reactive modification of synthesized PLLA. PLLA of three different molecular weights viz., 45,000 g/mol (PLLA-A), 65,000 g/mol (PLLA-B) and 100,000 g/mol (PLLA-C) were chosen for all studies.

Reactive extrusion

Reactive extrusion was performed using a 5 cc microcompounder (DSM, The Netherlands). The extrusion temperature was set at 180 or 190°C depending on the molecular weight of the polymer. PLLA-A and PLLA-B were processed at 180°C, whereas PLLA-C was processed at 190°C. Screw speed was maintained at 100 rpm for all formulations. PLLA was dried in vacuum oven at 55°C for 12 h before processing. Inert atmosphere was maintained for all reactions by purging nitrogen gas into the microcompounder. Five gram of premixed formulation was charged into the microcompounder for all reactive extrusion studies. Various formulations were prepared by changing the residence time, concentration of glycidol and molecular weights of PLLA's. Specifically, the three different molecular weight PLLA's were compounded with 0.5 and 1 wt % glycidol at two different residence times of 5 and 10 min. Details of the different formulations used in this work are listed in Table I. For comparative purposes additional samples were generated by processing 5 g PLLA in the microcompounder for 5 and 10 min residence times at the same processing temperatures and at the same screw speed but in the absence of glycidol. The torque on the screws was recorded as a function of time and is shown in Figure 1(a–c).

Characterization

Molecular weights (M_n and M_w) were determined with respect to polystyrene standards by size exclusion chromatography on a Thermo Finnigan Spectra Series AS300 machine at 25°C by eluting PLLA solutions of 10 mg/mL concentration in $CHCl_3$. Toluene was used as internal standard. A series of five μ-Styragel columns of pore sizes 10^5, 10^4, 10^3, 500, and 100 A°, respectively, and length 30 cm each was used. $CHCl_3$ was used as the mobile phase (flow rate 1 mL/min), and a refractive index detector (Spectra Series RI-150) was used for detection of different molecular weight fractions. The absorption peaks in infra red for linear PLLA, glycidol, and PLLA containing 1% glycidol before and after reactive extrusion were recorded in transmission mode by using a Perkin-Elmer FT-IR spectrometer. The glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and heat of fusion (H_m) were measured by a differential scanning calorimeter (TA Instruments DSC Q100) under a nitrogen purge stream of 10 mL/min. The

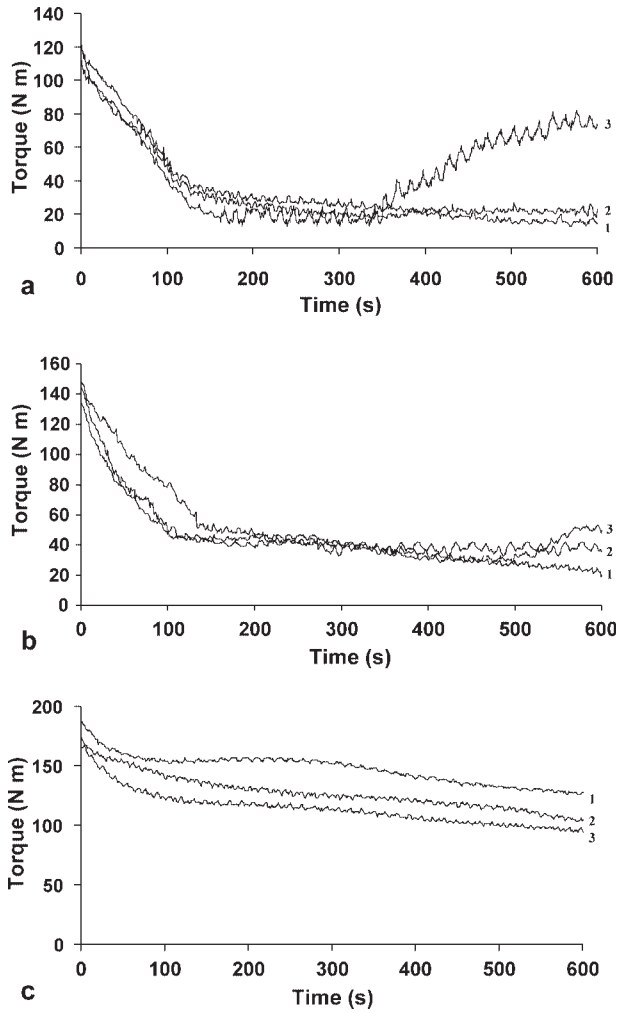


Figure 1 a: Torque data for PLLA-A with glycidol (1: PLLA-A as synthesized, 2: PLLA-A + 0.5% glycidol, and 3: PLLA-A + 1% glycidol). b: Torque data for PLLA-B with glycidol (1: PLLA-B as synthesized, 2: PLLA-B + 0.5% glycidol, and 3: PLLA-B + 1% glycidol). c: Torque data for PLLA-C with glycidol (1: PLLA-C as synthesized, 2: PLLA-C + 0.5% glycidol, and 3: PLLA-C + 1% glycidol).

instrument was calibrated with an indium standard. Approximately 5–10 mg of PLLA was used for each analysis. Samples were heated from 23°C up to 220°C at the rate of 10°C/min in aluminum pans in the first heating scan. Cooling was performed at 50°C/min from 220°C to 23°C, and subsequently the samples were reheated to 220°C in the second heating scan. Rheological measurements were performed on a strain controlled ARES rheometer. A 25-mm diameter cone and plate fixture having 2° cone angle was used for all rheological tests. Disks of 25 mm diameter were cut from solution cast films. Time sweep experiments comprising of isothermal oscillatory tests at a frequency of 10 rad/s and strain amplitude of 10% were performed to test the melt stability of PLA at 180°C. Temperature was set using heated N_2 gas fed into the forced convection oven (sample chamber) of the rheometer. The viscoelastic parameters namely, storage modulus, loss modulus, phase angle and complex viscosity were recorded.

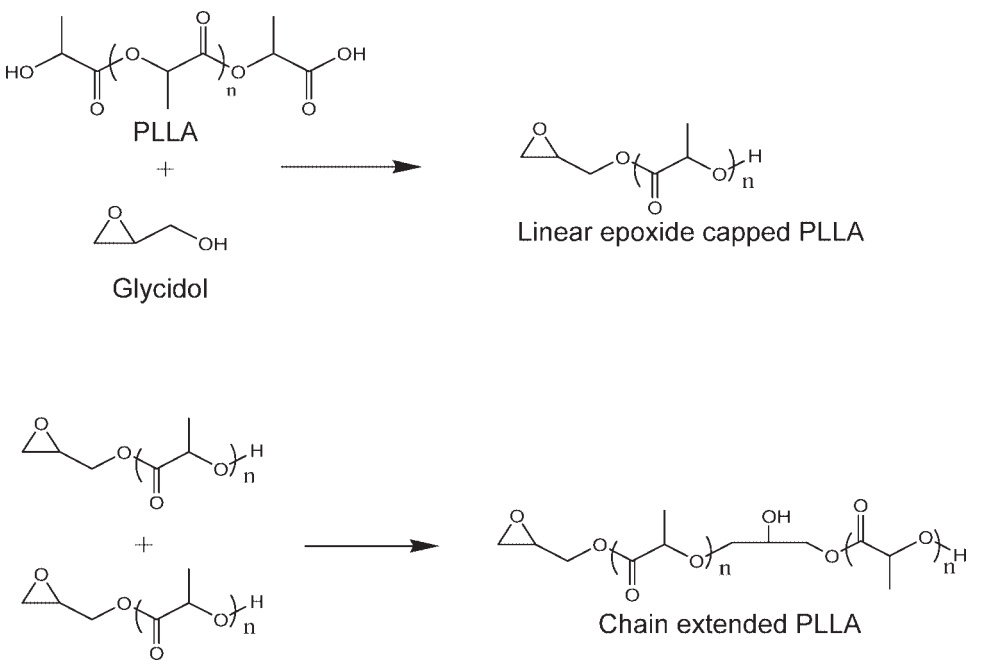
RESULTS AND DISCUSSION

Reaction mechanism

The possible reactions between PLLA and hydroxyl functionalized epoxides have been outlined in Scheme 1. The carboxylic acid end group of a PLLA chain reacts with the primary hydroxyl group of glycidol to form end-capped linear PLLA. A hydroxyl end group of another PLLA chain opens the oxirane ring of the glycidol to initiate chain extension and formation of a pendant hydroxyl group. Thus, glycidol can be considered as an equivalent 3-hydroxyl compound. The pendant hydroxyl group can potentially react with the oxirane ring of another end-capped PLLA chain to form a branch. The possibility of formation of branched polyester depends on the difference in reactivity of the primary and the secondary (i.e., pendant) hydroxyl groups with the epoxy functional group. Because the pendant hydroxyl groups are less reactive than the primary hydroxyl groups, higher temperature and longer time of reaction are required to produce branches.[15] In a reactive extrusion process of limited residence time, we can expect predominant formation of linear chain extended PLLA containing pendant hydroxyl groups.

Effect of concentration and residence time on reaction

The torque on microcompounder screws during extrusion was recorded for all samples as a function of time and is shown in Figure 1(a–c). We found that when compounding in the presence of gycidol the torque first decreased till a certain time and then increased; the relative magnitudes of these changes and the time at which they occurred were found vary with the molecular weight of PLLA. In the absence of gycidol the torque always decreased continuously with time. The decrease in torque was the highest for PLLA-A (88%) followed by PLLA-B (85%) and PLLA-C (32%). We attribute this decrease to a combination of melting and degradation, as will be substantiated later by gel permeation chromatography data. For PLLA-A compounded with 0.5% glycidol, the torque decreased from 122 to 21*N* m during 5 min mixing time and then remained stable at 23*N* m for the next 5 min. Similarly, for PLLA-A compounded with 1% glycidol the torque decreased from 113 to 25*N* m during 5 min of mixing time and then increased to 73*N* m over the next 5 min. We



Scheme 1 Reaction between PLLA and glycidol.

argue that these trends reflect chain scission followed by chain extension of PLLA with glycidol. Qualitatively similar trends were observed for the case of PLLA-B samples. The only notable difference was that while the increase in torque in case of PLLA-A was observed from 5 min after feeding the materials into the compounder, a similar increase for PLLA-B was observed 8 min after feeding. The relatively longer time taken in case of PLLA-B may be due to the lower concentration of end groups present in this higher molecular weight polymer compared with the end group concentration of PLLA-A. In the case of PLLA-C a continuous decrease in torque for both 0.5% glycidol and 1% glycidol was observed during the entire 10 min residence time of the experiment. This indicates no significant reaction between PLLA-C and glycidol, which may be attributed to the even lower concentration of end groups in this highest molecular weight polymer.

Evidence of reaction

Figure 2 shows the infrared transmission spectra of as-synthesized PLLA, as-received glycidol, unmodified PLLA containing 1% glycidol physically mixed with it before the extrusion experiment, and modified PLLA after the extrusion experiment. The absorbance at 3500/cm in Figure 2 for as-synthesized PLLA indicates the presence of terminal hydroxyl groups. The absorbances at 905/cm and 3384/cm for pure glycidol indicate respectively, the epoxy group and the hydroxyl group of glycidol. We observed that in the case of the PLLA + 1% glycidol mixture before extrusion the peak at 905/cm is clearly visible suggesting the presence of unreacted glycidol as might be expected. Similarly, the peak corresponding to the hydroxyl groups is broad and can be deconvoluted into a peak at 3500/cm and a peak at 3384/cm, which correspond respectively, to the hydroxyl groups of the PLLA and unreacted glycidol. In contrast for the case of PLLA melt compounded with 1% glycidol, the peaks at 905/cm and 3384/cm are not visible. This indicates clearly that both the epoxy group and the hydroxyl group of glycidol have participated in the reaction with PLLA.

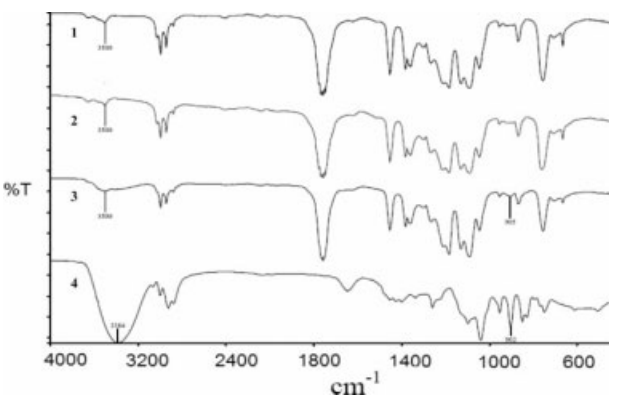


Figure 2 IR spectrum PLLA, glycidol, premixture, and extruded of PLLA and glycidol (1: PLLA-A as synthesized, 2: PLLA-A + 1% glycidol 10 min, 3: PLLA-A + 1% glycidol + Premixture, and 4: Neat glycidol).

TABLE II
GPC Data of PLLA

S. no	Sample	PLLA-A ($\times 10^4$ g/mole)		PLLA-B ($\times 10^4$ g/mole)		PLLA-C ($\times 10^4$ g/mole)	
		(M_w)	(M_n)	(M_w)	(M_n)	(M_w)	(M_n)
1	PLLA as-synthesized	45	18	65	30	100	36
2	PLLA + 0% G 5 min	35	15	50	21	92	43
3	PLLA + 0.5% G 5 min	32	20	52	32	93	53
4	PLLA + 1% G 5 min	38	23	53	37	96	54
5	PLLA + 0% G 10 min	32	15	47	23	80	33
6	PLLA + 0.5% G 10 min	38	23	50	28	83	44
7	PLLA + 1% G 10 min	73	46	53	34	78	49

Molecular properties of modified PLA

Table II shows GPC data for all formulations studied in this work. It can be seen that the molecular weights of all three PLLA polymers decreased on melt compounding in the absence of glycidol. This confirms degradation during processing in the absence of stabilizers. The molecular weights of all three PLLA polymers decreased when compounded with 0.5 and 1% glycidol for 5min. After 10 min of compounding with 0.5% glycidol the molecular weights of all three PLLAs were found to be slightly higher than the molecular weights of the same polymers when compounded in absence of glycidol for the same time. This indicates that chain extension reactions had occurred after about 10 min of compounding with 0.5% glycidol. This agrees qualitatively with the torque data shown in Figure 1. The torque values at 10 min for samples containing 0.5% glycidol were higher than the torque values of neat polymers compounded in the absence of glycidol for the same time. In case of formulations in which 1% glycidol was compounded with PLLAs for 5 min, a mild increase in molecular weight was observed for all three polymers compared with the neat polymers compounded without glycidol for the same time. After 10 min of compounding with 1% glycidol a dramatic increase in molecular weight was observed for PLLA-A. The increase in molecular weight for PLLA-B was relatively lower, whereas PLLA-C did not show any increase compared with the corresponding polymer that was melt processed in the absence of glycidol. Thus the molecular weight data obtained from GPC confirms significant chain extension of PLLA-A, and a lower extent of chain extension for PLLA-B. It is also noteworthy to observe the GPC elution data for PLLA-A based formulations as shown in Figure 3. The as-synthesized PLLA-A and the same polymer after melt processing for 10 min in the absence of glycidol showed two peaks corresponding to the presence of low-molecular weight species. After compounding for 10 min with 0.5 and 1% glycidol the peaks for the low-molecular weight species disappeared indicating that they have taken part in the chain extension reactions. Similar effects were observed after compounding PLLA-A for 5 min with glycidol, and also for PLLA-B and PLLA-C polymers for both 5 and 10 min of compounding with glycidol. The M_w and M_n values shown in Table III for all formulations also show that the polydispersity of the polymers decreased on reaction with glycidol. The decrease was largely due to an increase in M_n values caused by the consumption of the low-molecular weight species.

Influence of chain extension on thermal properties of PLLA

The T_g, T_m, T_c, and H_m obtained from the second heat DSC scans of all formulations prepared in this work are summarized in Table III. The PLLA-A samples which were melt processed in the absence of glycidol for 5 min and 10 min showed lower T_g and T_m compared with the as-synthesized polymer. Reactive extrusion for 5 min with 0.5 and 1% glycidol also decreased the T_g and T_m. Reactive extrusion for 10 min with 0.5% glycidol increased the T_g and T_m; the increase was substantial in case of the formulation containing 1% glycidol. The heat of melting and

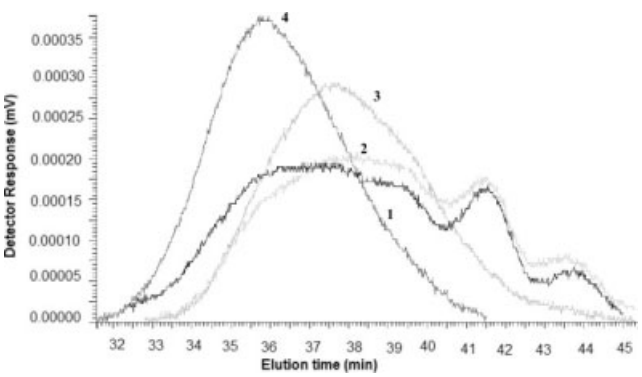


Figure 3 Elution diagram of linear, baseline, and modified PLLA-A (1: PLLA-A as synthesized, 2: PLLA-A + 0% glycidol 10 min, 3: PLLA-A + 0.5% glycidol 10 min, and 4: PLLA-A + 1% glycidol 10 min).

TABLE III
Glass transition, crystallization, melting temperature, and heat of fusion of PLLA

S. no	Cycle / Sample ID	First heat		Second heat			
		H_m (J/g)	T_m (°C)	T_g (°C)	T_c (°C)	H_m (J/g)	T_m (°C)
1	PLLA-A as synthesized	56	171	56	97	46	169
2	PLLA-A + 0% G 5 min	67	169	54	92	46	167
3	PLLA-A + 0.5% G 5 min	37	170	44	80	48	167
4	PLLA-A + 1% G 5 min	23	155	40	86	39	157
5	PLLA-A + 0% G 10 min	58	168	51	89	55	165
6	PLLA-A + 0.5% G 10 min	57	169	54	89	57	167
7	PLLA-A + 1% G 10 min	87	176	61	95	55	174
8	PLLA-B as synthesized	70	168	54	106	45	172
9	PLLA-B + 0% G 5 min	59	171	51	88	51	168
10	PLLA-B + 0.5% G 5 min	54	169	48	86	52	165
11	PLLA-B + 1% G 5 min	55	170	51	88	54	167
12	PLLA-B + 0% G10 min	57	170	51	91	42	168
13	PLLA-B + 0.5%G 10 min	72	174	58	94	64	172
14	PLLA-B + 1% G 10 min	69	174	58	94	77	172
15	PLLA-C as synthesized	42	173	57	102	47	172
16	PLLA-C + 0% G 5 min	47	175	62	96	45	175
17	PLLA-C + 0.5% G 5 min	57	175	61	97	49	174
18	PLLA-C + 1% G 5 min	41	175	61	98	39	174
19	PLLA-C + 0% G 10 min	50	175	61	96	46	175
20	PLLA-C + 0.5% G 10 min	46	174	61	97	47	174
21	PLLA-C + 1% G 10 min	94	173	59	97	92	173

the peak temperature for crystallization (T_c) after T_g also showed similar trends. Comparing these changes in thermal properties with the molecular weight data obtained from GPC (Table II) we can see that the increase in T_g and T_m for PLLA-A formulations correlated well with the extent of chain extension. It may be noted that merely a conversion of the low-molecular weight species in the as-synthesized polymer by reaction with glycidol is not sufficient to cause an increase in the T_g and T_m. For example, PLLA-A processed for 10 min with 0.5% glycidol showed absence of the low-molecular weight species from the GPC elution curves (Fig. 3) but showed nearly the same T_g and T_m as for the as-synthesized polymer. Only those formulations that showed a significant increase in molecular weight also showed corresponding increase in T_g and T_m. The increase in T_g and T_m with molecular weight is a well known phenomenon and is caused by the reduction in chain end concentration, which decreases the free volume and the concentration of defects that could otherwise hinder chain folded crystallization. In the present case, the reaction between PLLA and glycidol results in the formation of a chain extended higher molecular weight polymer having two chain ends and a pendant hydroxyl group in the chain. The latter is not expected to have the same mobility as a chain end, and hence the overall reduction of the mobile chain end concentration causes the improvement in T_g and T_m. Because extensive branching typically leads to lowering of T_g and T_m compared with linear PLLA,[15] the increase in T_g and T_m seen for PLLA-A suggests that the reactive extrusion process resulted in the formation primarily chain extended linear polymers. Similar trends in T_g and T_m, albeit of lower magnitude, were observed for PLLA-B with respect to concentration of glycidol and residence time. For PLLA-C, no significant changes were noticed. This corroborates the GPC evidence that no substantial reaction occurred for this high-molecular weight polymer due to its lower end group concentration.

Melt stability of modified PLA

Isothermal time sweep experiments in dynamic oscillatory mode under nitrogen environment were performed to test the melt stability of PLLA formulations. The complex viscosity of PLLA-A based formulations compounded for 10 min with and without glycidol are compared in Figure 4(a). Similar comparisons are shown in Figure 4(b,c) respectively, for PLLA-B and PLLA-C formulations. The as-synthesized PLLA-A showed a melt viscosity of about 12 Pa s at 180°C. The viscosity remained constant for about 200 s after which a decrease in the viscosity was observed indicating degradation of the melt under isothermal conditions. Melt processing of the as-synthesized PLLA-A for 10 min in the micro-compounder resulted in a further decrease in the viscosity because of degradation, as suggested by the GPC data. The corresponding melt viscosity of the as-processed PLLA-A was about 6 Pa s. It further decreased with time on holding the melt at

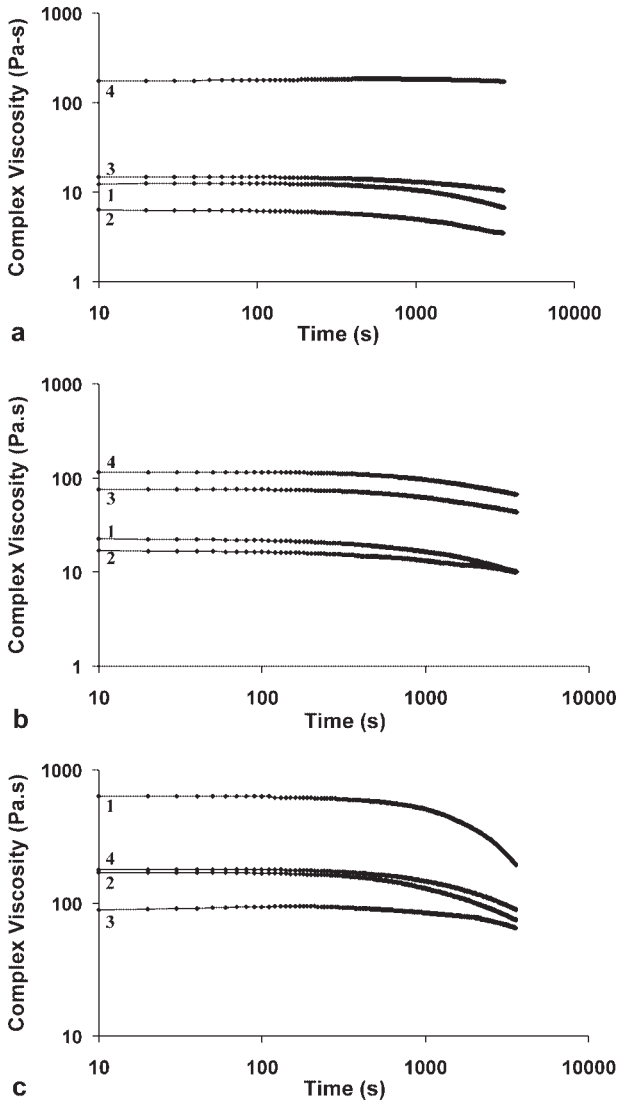


Figure 4 a: Complex viscosity of linear and modified PLLA-A (1: PLLA-A as synthesized, 2: PLLA-A + 0% glycidol 10 min, 3: PLLA-A + 0.5% glycidol 10 min, and 4: PLLA-A + 1% glycidol 10 min). b: Complex viscosity of linear and modified PLLA-B (1: PLLA-B as synthesized, 2: PLLA-B + 0% glycidol 10 min, 3: PLLA-B + 0.5% glycidol 10 min, and 4: PLLA-B + 1% glycidol 10 min). c: Complex viscosity of linear and modified PLLA-C (1: PLLA-C as synthesized, 2: PLLA-C + 0% glycidol 10 min, 3: PLLA-C + 0.5% glycidol 10 min, and 4: PLLA-C + 1% glycidol 10 min).

180°C after about 200 s. PLLA-A when compounded with 0.5% glycidol for 10 min showed a higher viscosity than the PLLA-A which was melt processed in the absence of glycidol. Finally, PLLA-A compounded with 1% glycidol for 10 min showed a remarkable rise in viscosity, which agrees with the significant increase in molecular weight seen in the GPC data. Further, it is interesting to note that this chain extended polymer was more stable than all the other formulations shown in Figure 4(a) in that the viscosity remained almost constant over the 1 h test duration whereas the viscosity of other samples clearly decreased with time. Thus, the glycidol acts as an effective chain extender and a melt stabilizer. Melt stabilization may be due to a combination of at least two effects namely, removal of residual monomer from the polymer during compounding and reduction of end group concentration due to increase in molecular weight. These features are qualitatively seen also for the PLLA-B based formulations as shown in Figure 4(b). In the case of PLLA-C based formulations the reactively extruded samples had lower viscosity than the as-synthesized polymer because the extent of chain extension reaction was poor as discussed earlier.

CONCLUSIONS

In this work we have demonstrated the use of glycidol as an effective chain extender for poly(L-lactic acid) in a reactive extrusion process. No additional catalyst is required for this reaction to progress. The mechanism of reaction between glycidol and PLLA suggests that both chain extension and branching are possible. However, the latter is expected to require higher activation energy and longer reaction times. Hence, the reactive extrusion process produces primarily chain extended linear polymers. It is also noteworthy that glycidol can react with both end groups of PLLA namely, the carboxyl and the hydroxyl groups. The effects of chain extension were directly observed in terms of increase in torque on screws during the reactive extrusion process. The occurrence of the reaction was supported by FT-IR studies. Further corroboration for chain extension was obtained from measurements of molecular weights using GPC and from rheological data. Chain extension was found to be more effective in case of the low-molecular weight PLLA polymer. The extent of increase in molecular weight was higher while the time required for chain extension was lower for the low-molecular weight PLLA compared with those for the high-molecular weight PLLA polymers. This is attributed to the higher concentration of chain ends in the low-molecular weight polymer. The chain extended polymers showed increased glass transition temperature and melting temperature. Finally, we found that reactive extrusion of glycidol with PLLA increased the melt stability of the polymer. This may be due to a combination of removal of residual monomer from the polymer during compounding and reduction of end group concentration due to increase in molecular weight. As a final comment, it may be noted that the reaction time required for chain extension of PLLA using glycidol is much higher than that desired in a commercial reactive extrusion process. The reactivity of glycidol with PLLA could be improved by

optimizing the screw design and/or by compounding PLLA with high surface area fillers containing surface grafted glycidol.

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