



Extrusion Blown Films of Poly(Lactic Acid) Chain-Extended with Food Grade Multifunctional Epoxies

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The effectiveness and efficiency of two food grade multifunctional epoxies with low and high epoxy equivalent weights in chain extending/branching poly(lactic acid) (PLA) were studied in a torque rheometer. Processing PLA and chain extender (CE) at 200°C for 300 s not only chain-extended PLA effectively as indicated by a significant increase in the mixing torque as well as PLA's melt viscosity and molecular weight, but also branched it leading to its reduced crystallinity. Chain extension occurred through the ring opening reaction of epoxy groups in the CE with PLA's hydroxyl and/or carboxyl groups. CE with lower epoxy equivalent weight was more efficient due to its higher reactivity. Secondly, the processabilities of PLA films chain-extended and branched with various amounts of the most efficient CE were assessed. Like in torque rheometer, chain extension and branching also occurred during film production as indicated by PLA's increased molecular weight and decreased crystallinity when blended with CE. However, film manufacture was feasible only for blends with up to 0.5% CE, becoming unprocessable above this content due to chain entanglement leading to increased viscosity. Chain extension/branching of PLA was beneficial in overcoming film's brittleness since its impact strength increased almost linearly with the CE content. POLYM. ENG. SCI., 00:000-000, 2019. © 2019 Society of Plastics Engineers

INTRODUCTION

Over the past few years, environmental issues such as pollution, depletion of natural resources, and solid waste disposal have become major global concerns [1]. A specific concern is the field of packaging, which produces great amounts of non-degradable plastic waste that is accumulated in landfills and oceans, causing climate change and harm to terrestrial as well as aquatic life [2]. In fact, 63% of the current plastic waste comes from packaging applications of which less than 14% is recyclable [2]. To circumvent this growing environmental problem caused by non-degradable petroleum-based plastics, research efforts have focused on the development of alternative packaging materials that are compostable and biodegradable [1].

PLA is one of the most extensively researched compostable and biodegradable aliphatic polyester because of its potential to replace conventional petroleum-based polymers for medical and other industrial applications [1]. It has several desirable properties such as high stiffness, reasonable strength, excellent flavor, and aroma barrier, as

well as good grease and oil resistance compared to conventional petroleum-based polymers [3–8]. However, its applicability in flexible packaging is limited due to several drawbacks such as brittleness, poor water barrier properties, and processing difficulties due to its insufficient melt strength and low thermal stability, leading to a narrow processing window [3, 9–12]. The low melt strength of PLA is attributed to the chain scission reactions that occur when it is subjected to shear and high temperature in an extruder [13]. These reactions lower its molecular weight and negatively impact molecular weight-dependent properties such as shear and elongational viscosities, resulting in insufficient melt strength [13]. PLA's inadequate melt strength poses challenges for its manufacture into flexible film through processes that require stretching or orientation, such as blown and cast film extrusion, as well as foaming [14].

Chain extenders (CE) or melt strength enhancers such as multifunctional epoxies, 1,4-butane di-isocyanate, and hexamethylene di-isocyanate among others are often blended with PLA matrix to increase its melt strength [9–11, 15–19]. These additives increase PLA's molecular weight by introducing chain branching, thereby increasing its shear and elongational viscosities. This leads to improved melt strength, which facilitates the blown film extrusion process and other processes such as casting and foaming [9–11, 15–19].

In our previous work, PLA films were successfully manufactured without any CE by controlling the melt rheology through processing temperature and other extrusion-blown processing conditions such as the processing speed ratios and internal air pressures [3]. However, these blown films teared easily due to their brittleness and did not survive several packaging performance tests such as oxygen permeation. Consequently, chain extenders are needed in the formulations to increase PLA's ductility [18].

Although blending PLA with the aforementioned additives increases the ductility of films used in several packaging applications, they also have various drawbacks. For example, multifunctional epoxies have not been approved for food-grade applications by the United States Food and Drug Administration (FDA) [3, 20]. On the other hand, di-isocyanates are under scrutiny due to their toxicity, risk of occupational hazards, and their impact on the inherent biodegradability of PLA [3, 21].

Recently, new FDA approved food-grade multifunctional epoxies with varying reactivities have been developed. Unfortunately, limited studies have been reported on their use to melt strengthen PLA and reduce its brittleness. Accordingly, this study investigated the effectiveness and efficiency of these multifunctional additives in chain extending and branching PLA, improving its processability through the blown film extrusion process and improving the ductility of PLA films.

EXPERIMENTAL

Materials

Poly(lactic) acid (PLA 4044D) with a melt flow rate of 3.95 g/10 min (190°C, 2.16 kg) and density of 1.24 g/cm³,

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obtained from NatureWorks® LLC (Minnetonka, MN) was used as the resin in this study [4, 5]. Two grades of epoxy-functionalized, FDA-approved polymeric chain extenders (CE), Joncryl ADR® 4468 and 4400 in the solid flake form were used, with characteristics listed in Table 1 and general chemical structure shown in Fig. 1.

Compounding of PLA with Multifunctional Epoxies

Firstly, experiments were performed in a torque rheometer to evaluate the effectiveness and efficiency of two multifunctional epoxy CE grades in chain extending PLA. PLA pellets and the two grades of CE listed in Table 1 were oven-dried at 50°C for at least 24 h to remove moisture before compounding. Compounding of PLA pellets with both grades of multifunctional epoxies took place in an electrically heated 60 mL three-piece internal mixer/measuring head (3:2 gear ratio) with counter-rotating roller style mixing blades (C.W. Brabender Instruments, South Hackensack, NJ) at 200°C for 5 min with the rotor speed set at 35 rpm. A 5.6 kW (7.5 hp) Intelli-Torque Plasti-Corder torque rheometer (C.W. Brabender Instruments) powered the mixer [4, 22, 23]. The multifunctional epoxy loading varied from 0.25 to 1 wt%, with an increment of 0.25 wt%. From this experiment, the torque and stock temperature data were recorded as a function of mixing time and analyzed to assess the effectiveness of these chain extenders and identify the most efficient one.

Secondly, the feasibility of utilizing the most efficient CE in extrusion-blown PLA film processing was assessed by dry-blending it at various concentrations (0 to 1 wt%) with PLA in a high-intensity mixer (Blender MX1050XTS from Waring Commercial, Calhoun, GA) at 22,000 rpm for 10 s [4, 5, 8]. The compounded formulations in pellet form were gravity-fed into the hopper of a 19 mm single-screw extruder (C.W. Brabender Instruments) with a length-to-diameter ratio of 30:1 and blown into films as previously described [3–6, 8]. Starting from the hopper to the die, the temperature profile of the extruder was set at 200-200-200-200°C. The speeds of the extruder's rotational screw and the pull-up rollers for film take off were set at 35 and 40 rpm, respectively, while an air pressure of 0.517 kPa (0.075 psi) was used to inflate the film to a blow-up ratio of 5, leading to ~0.027 mm thick films, measured by digital micrometer [3–6, 8].

Property Evaluation

Fourier Transform Infrared Spectroscopy (FTIR). Chain extension reactions between PLA and CE in blends containing various amounts of chain extenders compounded in an internal mixer were studied through Fourier transform infrared spectroscopy using a Shimadzu IR Affinity 1S infrared spectrophotometer (Shimadzu Corporation, Kyoto, Japan) in attenuated total reflectance (ATR) mode.

TABLE 1. Properties of chain extenders.

Properties	Chain extender grades	
	CE 4468	CE 4400
Epoxy equivalent weight (Da)	310	485
Molecular weight (Da)	7,250	7,100
Specific gravity, 25°C	1.08	1.08
Decomposition temperature (°C)	320	320

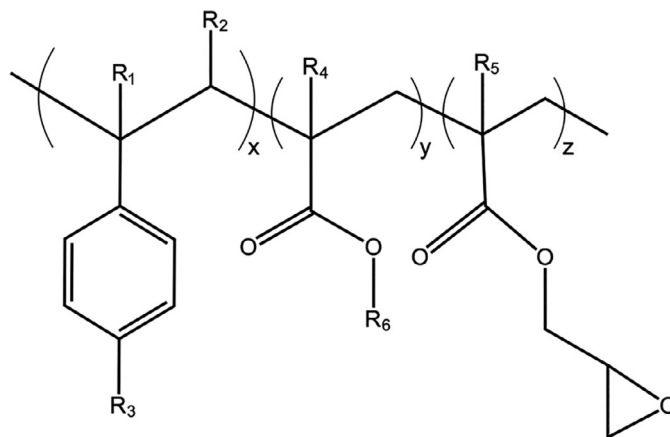


FIG. 1. Chemical structure of multifunctional epoxy chain extenders (Joncryl ADR® 4468 and 4400) where x , y , and z are between 1 and 20; R_1 , R_2 , R_3 , R_4 , and R_5 are H, CH_3 , a higher alkyl group, or a combination of them; R_6 is an alkyl group.

Each spectrum was obtained with triangle apodization using 64 scans in the range of 4,000–400 cm^{-1} , at a wavelength resolution of 4 cm^{-1} [4]. The spectra were smoothed with the boxcar smooth method using 7 smooth points and truncated from 500 to 2,000 cm^{-1} to study the region of interest using WinFIRST software from Thermo Nicolet (Madison, WI). The compounded materials were compression molded into disks before analysis.

Gel Permeation Chromatography (GPC). The number average molecular weight (M_n), weight average molecular weight (M_w), and viscosity average molecular weight (M_v) of materials compounded in both an internal mixer and extruded films were measured by GPC using a Waters instrument (Waters 1515, Waters, Milford, MA) equipped with a series of HR Styragel® columns (HR4, HR3, HR2 (300 × 7.8 mm (I.D))) and a Refractive Index (RI) detector (Waters 2414, Waters, Milford, MA). The test was conducted at a flow rate of 1 mL/min at 35°C using the Mark-Houwink corrected constant $K = 0.000174 \text{ mL/g}$ and $\alpha = 0.736$ for PLA solution in ACS Reagent Grade (99.99% pure) tetrahydrofuran (THF). Polystyrene (PS) standards ranging between 2.9×10^3 and 3.64×10^6 Da were used for calibration. Approximately 20 mg of sample was dissolved in 10 mL of THF. The samples were then filtered and transferred into 2 mL glass vials. A syringe was used to inject 100 μL of samples from the vial into the GPC. The detector and column were maintained at 35°C. The obtained data were analyzed using the Breeze software (version 3.30 SPA, 2002) (Waters, Milford, MA). Samples were tested in triplicates [4].

Melt Flow Index (MFI). The melt flow index (MFI) and melt density (δ_m) of PLA as well as PLA/CE blends compounded in an internal mixer were measured using a Melt Indexer (model LMI 4000) supplied by Dynisco Polymer Testing (Franklin, MA). Methods A and B outlined in ASTM 1238 were employed simultaneously to measure the MFI and melt volume rate (MVR). Three replicates for each sample were tested at 190°C with a dead load of 2.16 kg. This information was then used to calculate the δ_m of the samples using the following equation [3, 7]:

$$\delta_m = \frac{\text{MFI}}{\text{MVR}} \quad (1)$$

The MFI and δ_m were then used to obtain the zero-shear viscosity (η_0) using the following equation [3, 7]:

$$\eta_0 = \frac{\delta_m \times W \times R^4}{8 \times \text{MFI} \times L \times R_A^2} = 4.8547 \times \frac{\delta_m \times W}{\text{MFI}} \quad (2)$$

where R (1.0475 mm) is the bore radius of the die, R_A (4.775 mm) is the bore radius of the cylinder where the polymer melts, L (8 mm) is the length of the die, and W (2,160 g) is the applied dead load.

Differential Scanning Calorimetry (DSC). DSC was performed on at least three samples for PLA and PLA/CE materials compounded in an internal mixer as well as extruded films (6–10 mg) using a Q100 instrument (TA Instruments, New Castle, DE) from 25°C to 200°C at a ramp rate of 10°C/min under nitrogen atmosphere (flow rate: 70 mL/min) as previously described [5, 7]. Generally, the first heating scan is used to assess the film's thermal properties in the as-molded conditions whereas the second heating scan is used to evaluate the material's intrinsic properties after erasing its thermal history. In this study, both heating scans were used to determine the percentage crystallinity (% χ_c) using the software Universal Analysis 2000, V4.5 (TA Instruments, DE).

Residence Time of Blends in the Extruder. The residence times of chain-extended PLA compounds in the single-screw extruder were estimated from their residence time distribution (RTD) curves. These RTD curves for PLA/CE blends were obtained by introducing carbon black as a tracer into the feed stream of the extruder during blown film manufacture using processing conditions previously described. A constant amount of carbon black (50 mg) was directly fed into the single screw extruder instantaneously once the films were inflated to a stable blow-up ratio of 5. Films were collected every 15 s and tracer concentrations in the films determined using a UV-Vis spectrophotometer (Perkin-Elmer Lambda 25, Perkin-Elmer Instruments, Beaconsfield, UK), until the black color imparted by the tracer visually disappeared (approximately 30 min). Since carbon black absorbs light throughout the visible light range (380–720 nm), UV-Vis spectra were obtained over a randomly selected wavelength range of 480–520 nm at a scan rate of 120 nm/min but the tracer contents were determined at a fixed wavelength of 500 nm [4, 5, 24–26]. The obtained tracer concentrations were plotted as a function of sampling times for each film to develop its RTD curve.

Falling Dart Impact Strength. Impact strength of the films was determined using Labthink FDI-01 Falling Dart Impact Tester (Labthink International, Inc., Medford, MA) in agreement with method A described in ASTM D1709 with slight modifications. A customized 10 g dart with diameter of 38.2 mm was dropped from a height of 0.33 m (13 in) into four layers of the film specimens secured by clamp rings with an inside diameter of 76.2 mm. The films were then assessed as fail or non-fail. "Failure" refers to the film rupture allowing the full penetration of the dart through the films, and "non-failure" indicates the films sustain the integrity to hold the dart. Testing followed a stair-step approach with the increment of dart weight of 5 g, meaning that the weight of the

dart increased by 5 g if "non-fail" occurred or decreased by 5 g in case of film failure. Each test required the occurrence of at least ten fails and ten non-fails to complete and generated the failure weight as a measurement of impact strength. This study employed at least three test replicates for each film composition [27].

Statistics

Means were compared by the analysis of variance (ANOVA) and least significant differences (LSD) tests at 5% level of significance using IBM SPSS Statistics 24 (Armonk, NY).

RESULTS AND DISCUSSION

Effectiveness and Efficiency of Multifunctional Epoxy Grades in Chain-Extending PLA

Torque rheometry can be used to follow the chain extension reaction of PLA with CE since an increase in torque is associated with chain extension [28–30].

Typical curves obtained from the Brabender torque rheometer for the torque and stock temperature of PLA as a function of mixing time are shown in Fig. 2. It can be seen that stock temperature reduces when the material is loaded and then increases above the set temperature of 200°C to reach 211°C due to shear generated by the mixer when the material is kneaded by the rotor blades [31]. Similar results were obtained for PLA blended with various CE contents for both grades of CE (Fig. 3a and b). As expected, the stock temperature versus time curves of all PLA/CE blends overlapped during processing and did not change with CE content or grade (Fig. 3a and b). It can also be seen in Fig. 2 that the torque curves reach a maximum torque during the initial loading of neat PLA resin into the mixing chamber; indicating that the chamber is filled with resin. Then the torque gradually decreases and reaches a constant value or an equilibrium when the plastic is melted into a homogenous mass [31]. Similar curves were obtained for PLA/CE blends (Fig. 3c and d).

From these curves, the times required to reach 200°C were recorded (Table 2). A residence time of at least 120 s is recommended by the manufacturer for the reaction of these CE to be over 99% complete at 200°C. Since the total processing time was held constant at 300 s, the residence times provided to PLA/multifunctional epoxy samples at a minimum of 200°C were calculated by the difference between the total mixing times and the times taken to reach 200°C (Figs. 2 and 3), and the results are

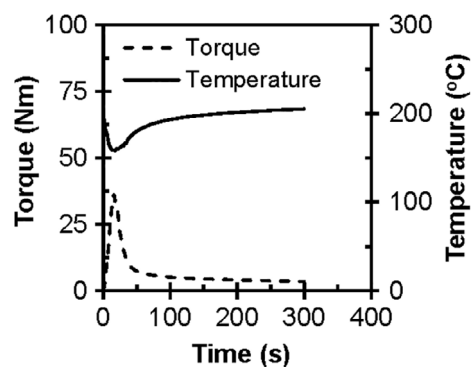


FIG. 2. Typical curves of torque and stock temperature of neat PLA as a function of time generated by a torque rheometer.

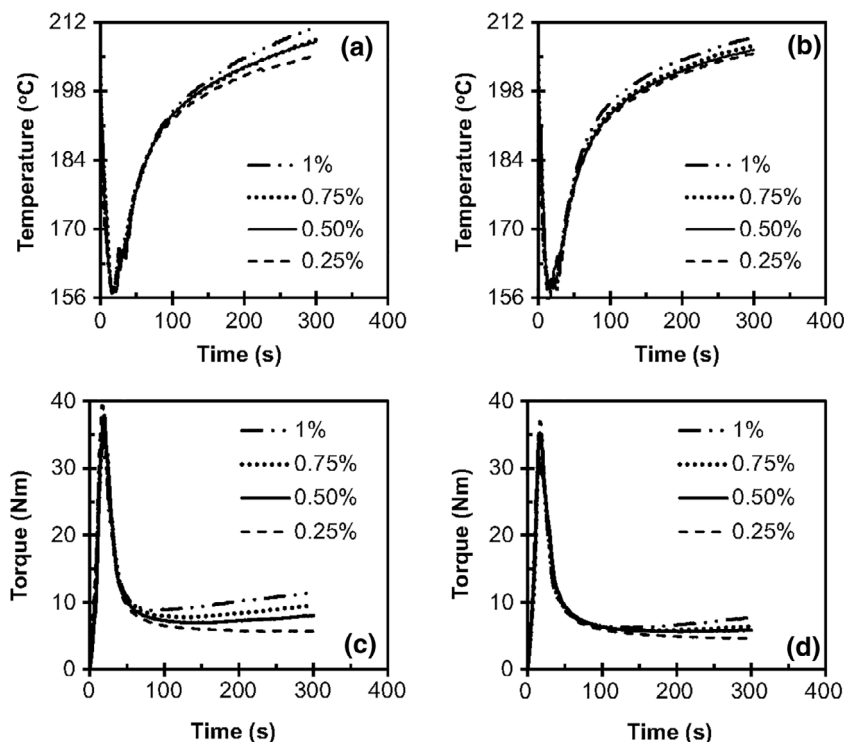


FIG. 3. Typical curves of stock temperature and mixing torque of PLA blends with CE 4468 [(a) and (c)] as well as CE 4400 [(b) and (d)] as a function of time generated by a torque rheometer.

tabulated in Table 2. The experimental residence times for complete chain extension reaction between PLA and both multifunctional epoxy grades exceeded the time recommended by the manufacturer, irrespective of the CE content, clearly indicating that the reaction was over 99% complete. Since the stock temperature continued to increase above the recommended 200°C due to shear generated during processing, it is believed that this increased heat could have accelerated the chain extension reaction between the PLA and CE.

The average values of the time to reach 200°C decreased with CE content whereas an opposite trend was observed for the average values of the total time at 200–211°C, which increased with CE content, irrespective of CE type (Table 2). Comparison between the two chain extender grades with different epoxy equivalent weights indicated that the CE with lower epoxy equivalent weight (CE 4468) experienced slightly shorter times to reach

200°C, that is, longer total times at 200–211°C than the counterpart with high epoxy equivalent weight (CE 4400) (Table 2). Generally, more viscous materials generate higher shear in a mixer when they are kneaded by the rotor blades of the mixer. This additional shear contributes to increased heat, resulting in shorter times to reach the set-point temperature. As the CE content increased, the viscosity of the materials increased, leading to increased shear which contributed to raised temperatures, resulting in reduced times to reach 200°C, irrespective of the CE grade. Moreover, the CE grade with lower epoxy equivalent weight resulted in higher shear due to its higher reactivity and thus reached 200°C in shorter time compared to its counterpart with higher epoxy equivalent weight, regardless of CE content. The increased viscosity of the materials due to the addition of CE and the difference between the reactivities of the two CE grades will be further discussed in the following sections.

The reaction between multifunctional epoxies and polyesters such as PLA has been extensively studied in the literature [28, 32–35]. PLA has two distinct functional end-groups, i.e., carboxyl and hydroxyl, that can react with the epoxy groups in multifunctional epoxies. The reaction proceeds *via* ring-opening of the epoxide group leading to the formation of new secondary hydroxyl groups and ester linkages when reaction occurs with PLA's carboxyl groups and/or ether linkages with PLA's hydroxyl groups (Fig. 4) [28, 32–35]. Fourier transform infrared spectroscopy (FTIR) was used to gain an in-depth understanding of these reaction mechanisms.

The FTIR spectra of neat PLA, CE 4468, and PLA/CE blends compounded in an internal mixer are illustrated in Fig. 5. Table 3 summarizes the band assignments for the wavenumbers of peaks found in these spectra to their corresponding functional

TABLE 2. Mixing time of PLA with both grades of multifunctional epoxies in torque rheometer.

CE (%)	Time to reach 200°C (s)		Total time at 200–211°C (s)	
	CE 4468 ^a	CE 4400 ^a	CE 4468 ^a	CE 4400 ^a
0	180.3 ± 5.1 ^A	180.3 ± 5.1 ^A	119.8 ± 5.1 ^A	119.8 ± 5.1 ^A
0.25	166.1 ± 15.8 ^B	175.0 ± 8.9 ^{A,B}	133.9 ± 15.8 ^B	125.0 ± 8.9 ^{A,B}
0.5	163.5 ± 7.2 ^{B,C}	174.6 ± 1.7 ^{A,B}	136.5 ± 7.2 ^{B,C}	125.4 ± 1.7 ^{A,B}
0.75	156.5 ± 2.4 ^{B,C}	171.5 ± 0.6 ^B	143.5 ± 2.4 ^{B,C}	128.5 ± 0.6 ^B
1	150.0 ± 5.4 ^C	155.5 ± 4.7 ^C	150.0 ± 5.4 ^C	144.5 ± 4.7 ^C

^aSame superscript letters within the same column are not significantly different based on the ANOVA results at 5% significance level.



FIG. 4. Generalized reaction mechanism of a multifunctional epoxy chain extender with the hydroxyl and carboxyl end groups in PLA.

groups [4, 32, 33]. Two distinct trends were observed. Firstly, the peaks at 844, 905, and 1,250 cm^{-1} in CE 4468 spectrum, assigned to the C—O stretching of epoxy group, disappeared in the spectra of PLA compounded with CE, regardless of CE content (Fig. 5). This result indicates that the CE reacted with PLA through ring-opening reaction of epoxy groups as illustrated in Fig. 4 [32, 33]. Secondly, the peaks present at 1,489 and 1,597 cm^{-1} in CE 4468 (Fig. 5), corresponding to C—C stretching in phenyl group (Fig. 1), merged into a broad shoulder in PLA/CE compounds at 1,513–1,547 cm^{-1} (Fig. 5). It should be noted that the phenyl groups in CE 4468 do not participate in the reaction with PLA and could hence be used to detect the presence of CE in the blends since these groups are absent in neat PLA. Thus, the formation of a broad shoulder from 1,513 to 1,547 cm^{-1} in the blends confirmed the presence of CE. As expected, this broad shoulder seemed to intensify as the CE content increased into

PLA matrix probably due to more phenyl groups in the blends with higher CE contents.

The equilibrium torque taken at 300 s in Figs. 2 and 3 (end torque value) is proportional to the apparent viscosity and molecular weight of the materials and depends on polymer chain structure such as branching [28–30]. An increase in the end torque values indicates an increase in the viscosity and molecular weight due to the formation of longer and/or branched chains [18, 19, 28–30]. Consequently, the end torque values could be used to monitor the chain extension reaction of a polymer.

Figure 6 illustrates the end torque values of PLA chain-extended with low and high epoxy equivalent weight multifunctional epoxies obtained from their torque versus mixing time curves (Fig. 3) to determine their effectiveness and efficiency in chain extending PLA. Both multifunctional epoxies chain-extended PLA effectively since they significantly increased the end torque during mixing. However, the efficiency of the multifunctional epoxy grades as chain extenders varied and was dependent on the epoxy equivalent weights. Chain extender's efficiency is defined as the contribution to increase the end torque of the blend per unit of chain extender [36] as expressed in the following equation:

$$\text{CE efficiency} = \frac{\text{End torque}}{\text{CE content}} \quad (3)$$

It is evident from Fig. 6 that the additive with lower epoxy equivalent weight (CE 4468) was more efficient in increasing the end torque of PLA compared to its counterpart with high epoxy equivalent weight (CE 4400) due to the smaller amount of CE needed to increase the end torque at a similar value. For example, by drawing a horizontal line parallel to the x -axis (chain extender

TABLE 3. Band assignments for the wavenumbers of peaks used in FTIR analysis and corresponding functional groups.

Wavenumber (cm^{-1})		Peak assignments [4, 32, 33]	
PLA	PLA blends with 0.25, 0.5, 0.75, and 1% CE		
1,744	1,721	~1,745	Stretching of C=O
-	1,489, 1,597	1,513–1,547	
1,451	1,447	~1,451	Stretching of C—C in phenyl
1,263	-	1,263	Scissoring of CH_3
-	1,250	-	Stretching of C—O in carboxyl and C—O—C stretch
951	-	~952	Stretching of C—O in epoxy
-	844, 905	-	Rocking of CH_3 and stretching of C—C
865	-	~865	Stretching of C—O—C

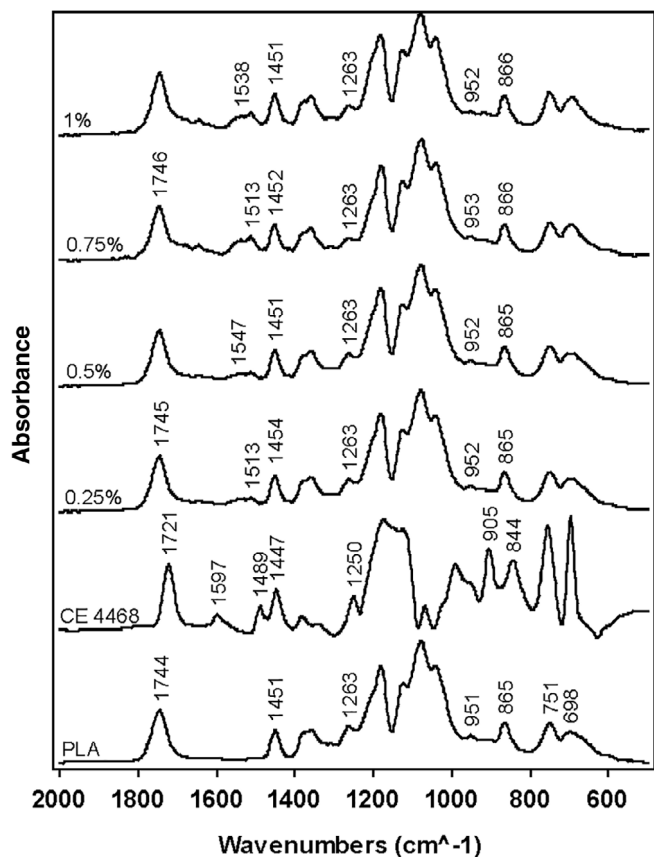


FIG. 5. Infrared spectra of PLA, CE 4468, and PLA blended with different CE contents in an internal mixer. Absorbance in the y -axis is in arbitrary units.

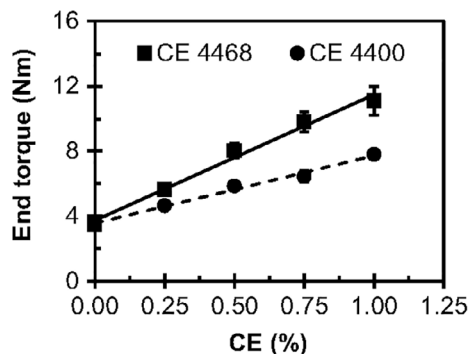


FIG. 6. End torque of PLA chain-extended with low (CE 4468) and high (CE 4400) epoxy equivalent weight multifunctional epoxies as a function of their contents.

content) at an arbitrary end torque value (e.g., 8 Nm in Fig. 6), the data can produce two intersection points [36]. The first intersection point detected at lower chain extender content for CE 4468 (0.5%) and the next seen at higher chain extender content for CE 4400 (1%), which clearly indicates the higher efficiency of CE 4468 in chain extending PLA, as expected from Eq. 3 [36]. This result can be explained by the lower equivalent weight of CE 4468, resulting in more epoxy groups per chain and thus higher reactivity. Since the efficiency of CE with a lower epoxy equivalent weight (CE 4468) was higher than its counterpart with high epoxy equivalent weight (CE 4400), it was then selected for further studies.

Chain extension of PLA with the most efficient grade of CE (CE 4468) was further confirmed by the values of molecular weights and dispersity indices of PLA and PLA/CE blends (Table 4). The addition of CE increased the number (M_n), weight (M_w), and viscosity (M_v) average molecular weights, as well as polydispersity index (DI) of PLA, due to the formation of longer and/or branched chains. Similar results have been reported for PLA chain-extended with other non-food grades of multifunctional epoxies [9, 19, 32] and polyethylene terephthalate chain-extended with 1,6-Diisocyanatohexane [37], among others.

As previously mentioned, chain extension and/or branching can also be monitored by the zero-shear viscosity (η_0) of a polymer melt, which is directly related to its molecular weight (M_w) by the Mark-Houwink equation:

$$\eta_0 = k \times M_w^a \quad (4)$$

with k and a as Mark-Houwink constants.

TABLE 4. Molecular weights, dispersity indices, and melt flow index values of PLA chain-extended with CE 4468.

CE (%)	Molecular weight (kDa)			DI	MFI (g/10 min)
	M_n	M_w	M_v		
0	123 ± 5	212 ± 6	198 ± 6	1.7 ± 0.0	11.51 ± 0.30
0.25	139 ± 3	340 ± 34	296 ± 25	2.4 ± 0.2	5.94 ± 0.03
0.5	157 ± 4	475 ± 44	407 ± 59	3.0 ± 0.4	1.62 ± 0.00
0.75	181 ± 12	503 ± 14	433 ± 9	2.8 ± 0.3	0.22 ± 0.00
1	221 ± 10	583 ± 28	469 ± 15	2.6 ± 0.1	0.05 ± 0.00

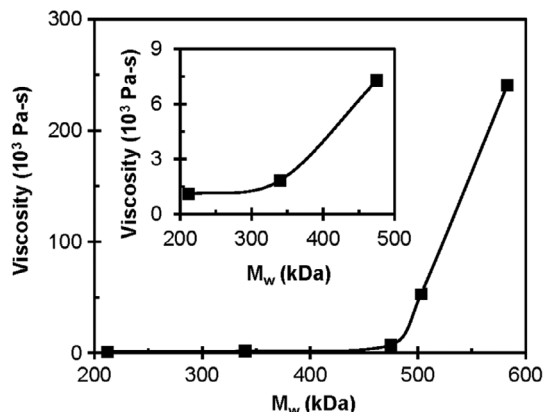


FIG. 7. Zero-shear viscosities as a function of weight-average molecular weights of PLA/CE 4468 blends processed in an internal mixer. Insert shows the viscosity of these blends at low-molecular-weight values.

Figure 7 shows a plot of zero-shear viscosities determined from the MFI data (Table 4) as a function of weight-average molecular weights (M_w) of PLA compounded with different contents of CE (Table 4) in an internal mixer. The viscosity increased with molecular weight at different extents below and above a molecular weight value of 475 kDa, which corresponds to CE content of 0.5% (Table 4). Below 475 kDa, increasing the molecular weight of PLA/CE blends from 212 to 475 kDa gradually increased their viscosities from 1,086 to 7,270 Pa-s, respectively. This trend is not clearly seen in Fig. 7 due to a wide range of viscosity values on the y-axis, which was overcome by truncating and displaying this range of the graph as an insert. In contrast, a sharp increase in viscosity was observed above 475 kDa, where the viscosity of the blends increased from 7,270 to 240,727 Pa-s when the molecular weight varied from 475 to 583 kDa, respectively. This point of inflection indicates the critical molecular weight, that is, the onset of chain entanglements attributable to the high degree of branching. Dalsin and coworkers reported a similar trend for atactic polypropylene wherein a weak dependence of zero-shear viscosity on its molecular weight was reported until a critical molecular weight of 8.5 kDa, after which the zero-shear viscosity increased exponentially with increasing molecular weight [38].

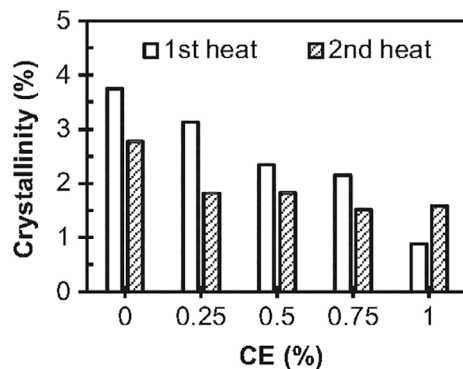


FIG. 8. Effect of CE 4468 content on the crystallinity of PLA processed in an internal mixer.

TABLE 5. Processing parameters recorded during extrusion-blown film and residence times as a function of CE 4468 content in PLA.

CE (%)	Melt temperature ^a (°C)	Pressure ^a (10 ⁴ Pa)	Residence time ^b (s)	Peak time ^b (s)	End time ^b (s)
0	211 ± 0	465 ± 3	-	-	-
0.25	211 ± 0	496 ± 33	132 ± 6	156 ± 10	246 ± 6
0.5	211 ± 0	571 ± 10	176 ± 24	228 ± 30	290 ± 28
0.75	NOT PROCESSABLE				
1	NOT PROCESSABLE				

^aAverage values of at least 45 data points.

^bAverage values of three replicates.

TABLE 6. Molecular weights and dispersity indices of PLA films chain-extended with CE 4468.

CE (%)	Molecular weight (kDa)			DI
	M _n	M _w	M _v	
0	105 ± 7	183 ± 2	170 ± 1	1.7 ± 0.1
0.25	112 ± 5	232 ± 2	208 ± 2	2.1 ± 0.1
0.5	127 ± 9	243 ± 16	219 ± 12	1.9 ± 0.3
0.75	NOT PROCESSABLE			
1	NOT PROCESSABLE			

PLA matrix reduced its degree of crystallinity indicating branching and confirming chain extension, consistent with the trend reported in the literature [39].

Extrusion-Blown Chain-Extended PLA Films

The feasibility of utilizing the identified most efficient CE grade (CE 4468) in extrusion-blown PLA film processing was assessed by dry-blending it with PLA first and then attempting film manufacturing. The melt stock temperature and pressure at the die generated during processing of the blends with various CE concentrations (up to 1 wt%) were recorded and listed in Table 5.

The melt experienced a stock temperature higher than the recommended 200°C (Table 5) due to shear generated during processing. Notice that film manufacture was feasible only with blends containing up to 0.5% CE, becoming unprocessable above this content due to the increased viscosity at this critical molecular weight for chain entanglement (Fig. 7), indicated by the increased melt pressure during processing (Table 5). The melt pressure in the extruder (Table 5), suggestive of the blend’s shear stress, increased with increasing chain extender content attributable to the chain extension reaction between the PLA and CE [18, 19, 30]. The increased molecular weight (Table 6) and decreased crystallinity (Fig. 9) of PLA films with chain extender content corroborated the chain extension and branching of PLA. As expected, these results were similar to those obtained for PLA/CE blends processed in the internal mixer (Table 4 and Fig. 8).

To ensure that the melts experienced the recommended 200°C within 120 s for 99% reaction to occur between PLA and CE, the residence times of processable blends inside the extruder were recorded. Figure 10 shows typical RTD curves of PLA films blended with 0.25 and 0.5% CE. The residence time, peak time, and end time were the three parameters extracted from each RTD curve generated (Table 5). The residence time is defined as the

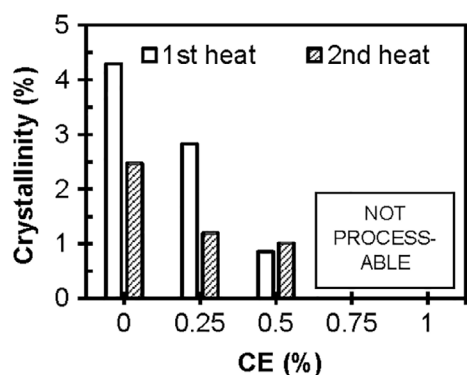


FIG. 9. Effect of CE 4468 content on the crystallinity of PLA films.

The degree of crystallinities of PLA and its blends were also evaluated to corroborate chain branching (Fig. 8) observed through the molecular weight and viscosity data. Generally, dense packing of branched polymer chains is difficult, leading to reduced crystallinity. As expected, the addition of CE into the

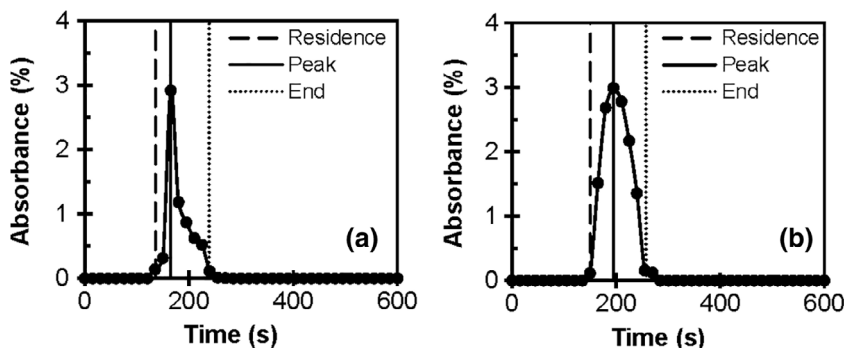


FIG. 10. Typical residence time distribution curves of PLA with (a) 0.25% CE 4468 and (b) 0.5% CE 4468.

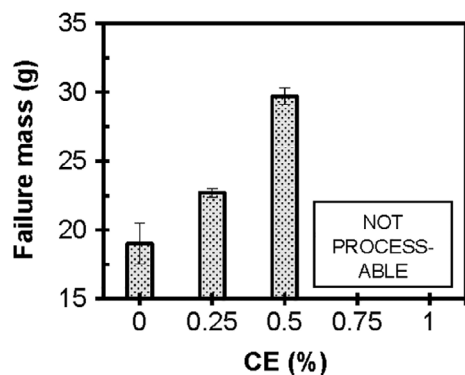


FIG. 11. Failure mass of PLA films with various CE 4468 contents.

first time at which a tracer signal of 5% of the maximum peak height was detected. It relates to the minimum exposure time and duration for PLA to react with CE in the extruder. The peak time, where the maximum signal occurred, represents the average transit or mean processing time. The end time, the time for detection of the last signal of 5% of the maximum peak height, is linked to the maximum time the blends resided in the extruder [24, 25].

PLA/CE blends experienced residence times longer than the recommended 120 s at 200°C, suggesting 99% completion of reaction. The residence time of PLA blended with 0.5% CE was longer than its counterpart with 0.25% (Table 5), due to its higher viscosity (Fig. 7), which provided more resistance to flow resulting in slower movement of the blend through the extruder; thus higher peak and end times (Table 5 and Fig. 10). It is also worth mentioning that the maximum time that the materials stayed in the extruder (end time) was more than twice the 120 s and the melt experienced a temperature of 11°C above the 200°C recommended by the manufacturer (Table 5 and Fig. 10). This clearly indicates that the blends were exposed to extrusion processing conditions (heat and time) that favored chain extension reactions in the films.

Effect of Chain Extender Content on the Dart Impact Strength of PLA Films

Figure 11 shows the failure mass, indicative of the falling dart impact strength of PLA films chain-extended with various amounts of CE 4468 (low epoxy equivalent weight). Chain extension of PLA film was found beneficial in overcoming its brittleness. As seen in Fig. 11, the impact strength of PLA film increased almost linearly with the chain extender content, implying that the film became more ductile by branching the polymer chain and reducing its crystallinity (Fig. 9). Interestingly, the addition of only 0.5% chain extender into the PLA films increased its failure mass by ~56%, due to the chain extension reaction. These results validate the need for chain extenders to reduce the brittleness of PLA films even though neat PLA films without any chain extenders have been successfully manufactured in this and our previous studies [3–6].

CONCLUSIONS

The effectiveness and efficiency of FDA-approved food grade polymeric chain extenders (CE) with low (CE 4468) and high (CE 4400) epoxy equivalent weights in chain extending PLA

were studied using a torque rheometer in the first part of this work. Based on the experimental results, the following conclusions were drawn:

1. The residence time and melt stock temperature exceeded at least 120 s recommended by the manufacturer for the reaction between PLA and CE to be over 99% complete at 200°C, clearly indicating that the blends were processed at conditions favoring chain extension reaction. This chain extension proceeded via the ring opening reaction of epoxide groups in the CE with PLA's hydroxyl and/or carboxyl groups, as confirmed by Fourier transform infrared spectroscopy.
2. Both CE grades were effective at chain extending PLA because they significantly increased PLA's torque during mixing. The torque increase was related to increased melt viscosity caused by molecular weight increase. Additionally, the reduced crystallinity of the blends compared to neat PLA indicated chain branching of PLA. Nevertheless, the CE with lower epoxy equivalent weight (CE 4468) was more efficient in increasing the torque of PLA compared to its counterpart with high epoxy equivalent weight (CE 4400) due to its higher reactivity.

Secondly, the processabilities of PLA films chain-extended and branched with various amounts of the most efficient CE were assessed, and the following conclusions were drawn:

1. Film manufacture was only feasible with blends containing up to 0.5% CE but difficult above this content due to chain entanglement leading to significant increase in melt viscosity. Blends with 0.25 and 0.5% CE experienced residence times and melt temperatures of at least 132 s and 211°C in the extruder, respectively. Exposure to these processing conditions favored 99% completion of the chain extension reaction, confirmed by the increased melt pressure in the extruder as well as the increased molecular weight and decreased crystallinity of PLA/CE blends compared to neat PLA.
2. Chain branching reduced crystallinity and improved the ductility of PLA films. The addition of only 0.5% CE into the PLA films increased its failure mass by ~56%.

The developed ductile PLA/CE films have tremendous potential for food packaging applications.

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