

Thermal Properties of Extruded and Injection-Molded Poly(lactic Acid)-Based Cuphea and Lesquerella Bio-Composites

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ABSTRACT: The degree of compatibility between poly(lactic acid) (PLA) and different bio-fillers was examined using thermal methods. The biofillers were fibers extracted from cuphea and lesquerella seeds. Bio-composites of PLA:Fiber were prepared at 85 : 15, 70 : 30, and 100 : 00 and blended by extrusion and then injection molding. Thermal properties of the extruded (EX) and the extruded-injection molded (EXIM) composites were examined using differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). Composites analysis using DSC provided information essential for determining: (1) glass transition (T_g); (2) crystallization and melting temperatures and ΔH ; (3) percent crystallinity; and (4) Enthalpic Relaxation (ER). TGA was used to measure the mechanism of the thermal decomposition of the composites. The effect of fiber composition, processing conditions, and aging time on the thermal properties of the bio-composites was used to examine the relative compatibility of the fibers with PLA. The data showed that ER increased steadily as a function of aging. Because of the difference in protein content between cuphea and lesquerella, the two fibers influ-

enced the T_g (temperature and ΔC_p) differently. The percent crystallinity of neat PLA was significantly reduced by EX or EXIM, while the enzymatic degradation showed that EX composites are more biodegradable than EXIM. The TGA profiles indicated a multi-step degradation especially in air. The largest value of q , which indicated that, intermolecular interaction was strongest between lesquerella and PLA extruded materials, compared to the other three blends, possibly due to the higher protein content. Results also indicated that intermolecular interaction was least strong ($q = -33.9156$) in the EXIM PLA-cuphea. Although the q values of both cuphea composites were significantly lower than those of the lesquerella samples, this greater effect of extrusion over injection molding on intermolecular interaction was also seen in the q value of the EX and EXIM samples. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 114–124, 2009

Key words: extruded; injection-molded; DSC; TGA; crystallinity; cuphea; lasquerella; degradation mechanism; enthalpic relaxation

INTRODUCTION

Currently, most polymer composites utilize petroleum-based materials that are nondegradable and difficult to recycle or incur substantial cost for disposal. Green composites can be used in nondurable limited applications. The development and use of

biodegradable plastics in packaging for environmental protection has been stimulated by public concerns and interest. Polymer-composites are usually prepared from materials with dissimilar properties. Most polymer composites are difficult to recycle or incur substantial cost for disposal. Green composites use agricultural-based polymers and biodegradable plant-based fillers.¹ Poly(lactic acid) (PLA) is prepared from agriculture by-products using lactic acid fermentation followed by polymerization. In addition to being biodegradable, PLA is comparable to petroleum-based polymers and can be extruded and injection molded, but is more expensive.^{2,3} The use of renewable and biodegradable plant fillers is desirable to provide cost-competitive polymer composites. PLA has been blended with reinforcing fibers,^{3,4} polymers including starch,^{5–10} and

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inorganic fillers.^{11–12} In recent work, sugar beet pulp, a coproduct of sugar refining, was blended with PLA.^{13–14}

Cuphea (*Lythraceae*) is an oil seed native to the tropics and subtropics of the Americas and is being commercially produced in the United States (Minnesota and North Dakota). The seeds yield oil rich in saturated medium-chain fatty acids such as capric acid. Medium-chain fatty acids are used in soaps, detergents, cosmetics, lubricants and food.¹⁵ Lesquerella (*Brassicaceae*), a native U.S. plant, is currently being developed for commercial industrial applications in Arizona and Texas. It produces seed containing a hydroxy vegetable oil. The seed contains around 30% protein and 25–30% oil, of which 55–60% is lesquerolic acid, a hydroxy fatty acid (HFA) analogous to ricinoleic acid from castor oil. HFAs are important industrial feedstocks and are used in lithium greases, coatings, food grade lubricants, polyurethanes and cosmetics. The current source of HFAs is from imported castor oil. Milkweed (*Asclepias*) is a new industrial crop whose fiber (floss) is in the market as a component of hypoallergenic pillows and comforters. Its seed oil contains linoleic and oleic acids.^{16–17} Industrial oils made from these oilseed crops are valuable to the United States because they may replace imported oils such as castor, palm kernel, and coconut oil. To improve the economical success of new oilseed crops, an effort is being made to use the biomass coproducts in other value-added products such as biodegradable composite materials.

In the work presented here, PLA-Cuphea and lasquerella composites were processed with three separate thermal or mechanical treatments [extrusion, pelletization, and injection molding (IM)].^{13,14} When quenched below glass transition temperature, polymer chains are not in equilibrium and will, in time, relax towards equilibrium. This process is called enthalpic relaxation and it is thermodynamically driven.^{10,18} The occurrence of the enthalpic relaxation phenomena causes changes in the mechanical properties of the polymer where the polymer become brittle with reduced elongation to break, a process called physical aging.¹⁹ The aging process can be determined by storing the polymer below its glass transition temperature for specific period. Enthalpic relaxation is a nonlinear process over time. It describes the relaxation of a wide range of molecules that have different molecular weights and relax at different times.

The objective of this research is to evaluate Cuphea and lasquerella as low-cost fillers for PLA to produce green polymer composites with suitable mechanical properties for lightweight construction materials or automotive interior panels. Since PLA will become brittle when stored below its glass tran-

sition temperature, this work will focus on determining the enthalpic relaxation of the composites. Enthalpic relaxation can predict the magnitude of aging effect on the polymer.

EXPERIMENTAL

Material

Poly(lactic acid) (PLA), provided by Dow Cargill (Minneapolis, MN), contained over 90% L-lactide with an average molecular weight \approx 150,000. The glass transition (T_g) and melting temperature (T_m), of PLA as determined by Differential scanning calorimetry (DSC), was 61 and 151°C, respectively. Cuphea seeds (PSR-23, *viscosissima*) were provided by the USDA-ARS in 2004. Lesquerella seeds (*fendleri*) were provided by the U.S. Water Conservation Laboratory (USDA-ARS, Phoenix, AZ). Oil was extracted by pressing the oilseeds with a pilot scale expeller (French, Model L250). After removal of oil, Cuphea and lesquerella, press seed cake retained \sim 8 and 7% residual oil, respectively. The protein content of the pressed seed cake was 20 and 31% respectively. The moisture content was 5 and 9% respectively. The pressed seed cake was ground and passed through a 300-mesh sieve.

Extrusion processing

PLA and biomaterials were blended at 85 : 15 and 70 : 30 weight fractions. Blending was performed using a Werner-Pfleiderer ZSK30 corotating twin-screw extruder (Coperion Corp., Ramsey NJ). The barrel was comprised of 14 barrel sections giving a length/diameter ratio of 44 : 1. The screw speed was 130 RPM. PLA was fed into barrel section 1 using a gravimetric feeder (Model 3000, AccuRate, White-water, WI). After melting the PLA, biomaterials were fed into barrel section 7 using a loss-in-weight feeder. The barrel was heated using eight heating zones. The temperature profile was 135°C (Zone 1), 190°C (Zone 2) and 177°C (Zone 3-8). A die plate with two holes (4-mm diameter) was used. The melt temperature of the exudates at the die was \sim 160°C. Residence time was \sim 2.5 min. Die pressure and torque were allowed to stabilize between formulations before sample was collected. Strands were pelletized using a Laboratory (2 in.) Pelletizer (Killion Extruders, Cedar Grove NJ).

Injection molding

An ACT75B injection molder (Cincinnati Milacron, Batavia, Ohio) was used to injection mold ASTM D638-99 Type I tensile bars (Master Precision Mold,

Greenville, MI). Barrel temperature profiles had to be adjusted to help forward material by cooling the feed section. The cooling time was increased as the samples with high weight fractions of biomaterial did not extrude as well as neat PLA. The shot size had to be increased slightly as the material density decreased with increased pulp content. Packing pressures were inverted for PLA-biomaterial composites with over 15% biomaterial due to extreme flashing characteristics. Other conditions included a hot sprue bushing (D-M-E, Madison Heights, MI) temperature of 177°C, and maximum injection pressure of 12,000 PSI.

Deferential scanning calorimetry

Samples were analyzed using TA Instrument Modulated DSC™ Q1000 equipped with a refrigeration cooling system. The samples (50 mg) were loaded and sealed in high volume stainless steel pans (TA Instruments Thermal Analysis and Rheology, New Castle, DE 19720). Samples were run at 10°C/min ramp speed from 0 to 200°C, isotherm for 1 min, cooled at 10°C/min back to 0°C, isotherm for 1 min. The DSC was calibrated against an indium standard. A nitrogen flow rate of 24 cm³/min was maintained during the run to purge the DSC cell as specified by the manufacturer. The DSC parameters, such as ΔH and temperatures were calculated using TA instrument software, where the onset, peak, and end temperatures of transition were determined, and the area under the curve was used as the ΔH value. This method was developed in our lab after consulting the PLA certificate of analysis provided by Cargill Dow LLC. Since PLA melting temperature (180°C) is higher than both biomaterials (bio-fillers), the glass transition (63°C), it was used as the upper limit of heating.

Aging study

Neat PLA, extruded (EX), extruded injection molded (EXIM), and EX and EXIM PLA- Cuphea or PLA-lesquerella composites at PLA:biomaterial 85 : 15 or 70 : 30) were prepared for aging study as follows: First they were melted by heating in the DSC pan up to 200°C and then quench cooled by immersion in liquid nitrogen. Samples were then stored in the DSC pan until further analysis. The aging study was performed at 0, 7, 15, and 30 days storage at room temperature. The extent of the aging process was measured by the magnitude of enthalpic relaxation (ER).

Thermogravimetric analysis

Thermo gravimetric analysis (TGA) measurements were taken using a TGA 2050 Thermogravimetric Analyzer. Composites were ground into powder using a Brinkmann/Retsch high-speed shaker mill. Samples (~ 10 mg) were heated from room temperature to 800°C at 10°C/min and held at an isotherm for 3 min. The TGA data were plotted as temperature versus weight %, from which onset and final decomposition temperatures were obtained. The TGA data were also plotted as temperature versus derivative of weight %, from which peak decomposition temperatures were obtained.

TGA was also used to determine the degradation kinetics of neat PLA or composites. Each sample was heated at three different heating rates: 10, 15, and 20°C/min in two atmospheres, nitrogen and air. After analysis, kinetics data was obtained using the TA Specialty Library software, with reported activation energies at 50% conversion. The three heating rates were used to calculate the Activation Energy of degradation (E_a) using the equation known as Flynn and Walls.²⁰

Enzyme degradation

Samples of EXIM PLA/SBP or Apple composites were cut to similar dimensions (10-mm wide × 10-mm long × 3.5-mm thick).¹⁹ For neat PLA and EX PLA-SBP samples, four pieces of each sample were used. Enzyme buffer was prepared (0.05M Tris-HCl, pH 8.6, or dissolve 0.91 g Tris in 150 mL Millipore water) the pH was adjusted to 8.6 using 1N HCl. Proteinase K enzyme (60 mg contain 7.5 unit/mg solid), and 30 mg sodium azide were added in 150 mL buffer. Each sample was immersed in 5 mL of enzyme buffer and stored at 37°C with occasional shaking. After 24 h, the enzyme solution of each sample was replaced with fresh buffer. After 72 h storage, samples were rinsed with distilled water, and dried under vacuum for 24 h. The difference in weight before and after enzyme treatment was record and the percent weight loss calculated. The enzyme-treated samples were used for SEM analysis. The Scanning Electron Microscopy (SEM) was performed using a scanning electron microscope model JXM 6400 (JEOL, Tokyo, Japan) at accelerating voltages 10 KV. Briefly, after enzyme treatment, samples were mounted on specimen stubs using silver paint (Fullman, Latham, NY) and coated under vacuum with gold-palladium at ~ 200/min.

Statistics

Single-factor, mixed model Analysis of Variance (ANOVA) was used to examine the percent weight

loss differences, resulting from enzymatic degradation, between composites for each extrusion treatment. The fiber ratios were used as replications in the analyzes. If the composite effect from an ANOVA *F*-test statistic was significant at $P < 0.05$, differences of Least Squares Means were used to determine which composites were different from the others. Determination was also made whether any weight loss estimate for a particular composite was significantly different from 0 for each extrusion treatment (i.e., if % weight loss not significantly different from 0, then no weight loss occurred). All analyzes were performed using PROC MIXED in SAS[®] PC for Windows Version 9.1.3.

The DSC data of the composites was analyzed using Multiple Regressions. The experiment consisted of 2 PLA composites: PLA/SBP and PLA/Apple, 3 fiber ratios: neat (0), 15, and 30, 4 ages: 0, 7, 15, and 30 days, and two Extrusion methods: extruded and extruded-injection molded. Five dependant variables (Y_i) were examined: TgMidt (T_g middle temperature), T_g , ΔC_p (J/g/°C), EX ER ΔH (enthalpic relaxation of extruded), CRY ΔH_c (crystallization value J/g), MELT ΔH_m (melting value J/g). Each PLA composite, 40 regression equations of the dependent variables as a function of fiber ratio were obtained [$5 (Y_i) \times 4 (Ages) \times 2 (extrusion\ methods)$], for a total of 80 equations. Predicted values of the dependent variables were obtained to compare neat (0) and fiber ratio 15 and 30, for each composite, age, and extrusion method combination using 95% confidence intervals. If the confidence intervals for predicted values overlap, then the value is not significantly different from one another. All analyzes were performed using Table Curve 2D v5.00, AISN Software, 2000.

RESULTS AND DISCUSSION

Neat PLA thermal analysis revealed a glass transition followed by crystallization and an immediate melting. These three events continue to appear on the PLA composites analyzed here and were used as guideline to determine the thermal properties of the composites compared to the neat PLA. Composites analysis using DSC provided information essential for determining: (1) glass transition (T_g); (2) crystallization and melting temperatures and ΔH ; (3) percent crystallinity; and (4) Enthalpic Relaxation (ER). Since polymers and biomaterials composites have the tendency to phase-separate, these parameters were measured at different storage times (aging). Tables I–IV list the analyzed data for both composites including fiber levels (0, 15, and 30%), and aging time (0, 7, 15, and 30 days) for both cuphea and lesquerella fibers. The data was analyzed using multiple regressions. The T_g temperatures of PLA or

TABLE I
Effect of Cuphea Level and Storage on the Dependant Variables

Cuphea (%)	T_g (°C)	ΔC_p (J/g/°C)	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0 Days				
0	60.27 a	0.47	0.00	0.65 b
15	53.98 b	0.45	23.77	24.3 a
30	51.75 c	0.41	25.31	24.3 a
7 Days				
0	59.10 a	0.53 a	1.19 b	0.57 b
15	55.99 b	0.50 b	2.42 a	23.80 a
30	54.71 c	0.48 c	2.42 a	23.81 a
15 Days				
0	59.82 a	0.54 a	1.20 b	– ^a
15	59.95 b	0.52 b	24.62 a	26.2
30	55.84 c	0.49 c	24.63 a	21.27
30 Days				
0	60.52	0.53 a	1.22 b	0.00
15	58.72	0.52 b	24.15 a	23.54 a
30	56.86	0.50 c	24.15 a	25.37 a

T_g , crystallization, and melting temperature of extruded PLA-cuphea blends.

The table is based on regression analysis where values within the column followed by the same letter are not significantly different based on non-overlap of 95% confidence intervals.

Means within column and storage days with no letters are not significantly different (a > b > c).

^a Unobtainable estimate.

composites were mutually affected by process type, extrusion or IM (EX or EXIM) in addition to the presence of fiber. Higher cuphea content in the EX composite, significantly decreased T_g temperature, while ΔC_p was not affected (Table I). The longer storage time did not change this trend except after 30 days aging, where the increase in cuphea showed no significant effect on the T_g temperature. The ΔC_p was significantly lowered by extended storage time of the cuphea composite. Except at zero storage time, the effect EX PLA in the cuphea composite significantly increased the ΔH of crystallization and melting (Table I). The effect of EXIM on the thermal properties of the cuphea composites was mixed, where the T_g temperature was significantly lowered only after 7 and 30 days storage (Table II). The ΔC_p was significantly decreased except at zero storage time. Apart from the effect of processing-type, the presence of cuphea in the composite had a moderate impact on the thermal properties of PLA. The storage time and level of cuphea had no significant effect on the ΔH of crystallization or melting indicating a prominent effect of IM over storage time and the levels of cuphea (Table I and II).

Unlike cuphea, lesquerella significantly reduced the T_g temperature and ΔC_p of the EX composites after 15 days storage (Table III). The ΔH of crystallization was significantly increased at 15 and 30%

TABLE II
Effect of Cuphea Level and Storage on the
Dependant Variables

Cuphea (%)	T_g (°C)	ΔC_p (J/g/°C)	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0 Days				
0	60.69	0.45	– ^a	–
15	53.61	0.45	26.69	26.71
30	50.39	0.35	22.04	22.00
7 Days				
0	58.44 a	0.53 a	–	–
15	56.82 b	0.01 b	26.04	26.25
30	54.09 c	0.42 c	21.50	21.93
15 Days				
0	59.43	0.52 a	–	–
15	57.05	0.52 a	26.42	26.38 a
30	54.57	0.44 b	21.86	21.74 b
30 Days				
0	60.07 a	0.546 a	–	–
15	57.71 b	0.535 b	26.22	26.44
30	55.52 c	0.455 c	22.24	21.80

T_g , crystallization, and melting temperature of extruded-injection molded PLA-Cuphea blends.

The table is based on regression analysis where values within the column followed by the same letter are not significantly different based on non-overlap of 95% confidence intervals.

Means within column and storage days with no letters are not significantly different (a > b > c).

^a Unobtainable estimate.

lesquerella after 15 days of storage, while the ΔH of melting showed no significant effect at both lesquerella levels and all storage times (Table III). This is indicative of the effect of temperature on the interaction between the two polymers. As listed in the materials and methods section, the protein content of cuphea was 20% and Lesquerella 31%. The difference in the protein content could be the cause of the significant effect of lesquerella on the T_g and the crystallization of PLA. The T_g temperature of the EXIM PLA-lesquerella composites was significantly reduced at higher lesquerella content just past 30 days storage (Table IV). The ΔC_p exhibited a significant drop except during the first seven aging days, which is similar to the effect of cuphea indicating physical change in the amorphous structure of the composite i.e., less compact (looser) structure that allows easier molecular mobility. The ΔH of crystallization within column and storage days for all days (Table IV) exhibited significant increase except on the 30 days, where the effect was mixed. The ΔH of melting significantly increased throughout the storage time and lesquerella level (Table IV).

The percent crystallinity of the PLA in the composites was calculated by subtracting the enthalpy of crystallization (ΔH_c) from the enthalpy of fusion (ΔH_f) and divided by the ΔH_f of 100% PLA crystals, which is reported in the literature to be 93.6 J/g²¹

(Table V). The crystallinity of unprocessed PLA sample used here was 22.7% and dropped to 0.75% and 4.31% after EX and EXIM, respectively. The drop in the percent crystallinity is due to the processing conditions, extrusion and IM, such as shear, temperature, and most importantly, the cooling rate immediately after processing. The trend of lower PLA crystallinity continued in the presence of cuphea and lesquerella, but with higher deficit than neat PLA. For example, the % Crystallinity was 1.18 in the presence of 15% Cuphea in the EX composite and 3.47 at 30% (Table V). The EXIM samples exhibited higher crystallinity compared to EX due to differential in the injection molding temperature and the slower cooling rate after process possibly resulting from the compacted structure, which allows slow heat dissemination. Overall, higher %crystallinity was observed in the presence of lesquerella, possibly due to the higher protein content. Aging time has decreased the % crystallinity of PLA in the presence of both Cuphea and Lesquerella.

The aging process of PLA was observed by measuring the Enthalpic Relaxation (ER), which is an endothermic transition under the glass transition profile.²¹ The ER has steadily increased with aging (storage) time at room temperature. Since ER is a time dependent process, it has no value at zero storage time. The ER of neat EX PLA has increased

TABLE III
Effect of Lesquerella Level and Storage on the
Dependant Variables

Lesquerella (%)	T_g (°C)	ΔC_p (J/g/°C)	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0 Days				
0	60.3	– ^a	–	–
15	54.56	0.44 a	15.34	15.7
30	51.99	0.39 b	23.61	24.0
7 Days				
0	–	0.53	–	–
15	56.27 a	0.0	15.7	15.23
30	54.59 b	0.48	23.2	24.55
15 Days				
0	59.89 a	0.543 a	1.19 c	–
15	57.67 b	0.539 a	17.56 b	17.55
30	55.44 c	0.511 b	24.34 a	25.50
30 Days				
0	–	0.534 a	1.77 c	–
15	58.38 a	0.526 b	15.17 b	15.55
30	56.78 b	0.504 c	24.57 a	24.90

T_g , crystallization, and melting temperature of extruded PLA-lesquerella blends.

The table is based on regression analysis where values within the column followed by the same letter are not significantly different based on non-overlap of 95% confidence intervals.

Means within column and storage days with no letters are not significantly different (a > b > c).

^a Unobtainable estimate.

TABLE IV
Effect of Lesquerella Level and Storage on the Dependant Variables

Lesquerella (%)	T_g (°C)	ΔC_p (J/g/°C)	Crystallization ΔH (J/g)	Melting ΔH (J/g)
0 Days				
0	60.78	0.442	3.15 b	2.63 b
15	54.12	0.442	25.53 a	25.25 a
30	51.36	0.391	25.53 a	25.25 a
7 Days				
0	58.50	0.532 a	3.095 b	2.64 b
15	55.39	0.518 b	25.95 a	26.22 a
30	54.11	0.492 c	25.95 a	26.22 a
15 Days				
0	59.36	0.526 a	3.23 b	2.60 b
15	56.71	0.526 a	25.86 a	25.3 a
30	55.58	0.456 b	25.86 a	25.3 a
30 Days				
0	59.99 a	0.546 a	30.70 a	2.74 b
15	57.83 b	0.542 a	27.90 b	26.72 a
30	55.82 c	0.514 b	25.35 c	26.72 a

T_g , crystallization, and melting temperature of extruded-injection molded PLA-lesquerella blends.

The table is based on regression analysis where values within the column followed by the same letter are not significantly different based on non-overlap of 95% confidence intervals.

Means within column and storage days with no letters are not significantly different (a > b > c).

significantly from 0.00 to 0.068, 0.446, and 1.27 (J/g) after storage for 0, 7, 15, and 30 days respectively, (Fig. 1), while lower ER for the EX neat PLA was observed for aging up to 15 days. As observed, the effect of process type (EX or EXIM) on PLA crystallinity, the presence of 15% cuphea showed unchanged ER between 15 and 30 aging days (Fig. 1), while EXIM exhibited steady increase by aging time. After 30 days aging, the most ER was noted at 15% cuphea or lesquerella and the lowest value at

30% for both composites. Generally, lesquerella progressively increased ER as a function of aging time. The higher ER-trend of PLA as a function of aging time was reported in the literature to reach a plateau after 6 days storage, while our data trend was steady increase past the 30 days storage.²¹ This could be due to the process type and PLA molecular weight and cooling rate, beside other factors such as instruments sensitivity.

The Activation Energy (E_a) of degradation was determined using TGA in both, air and nitrogen, according to the method based on different heating rates.²⁰

$$\log \beta \cong 0.457 \left(-\frac{E_a}{RT} \right) + \left[\log \left(\frac{AE_a}{R} \right) - \log F(a) - 2.315 \right] \quad (1)$$

where, β is the heating rate, T is the absolute temperature, R is the gas constant, a is the conversion, E_a is the activation energy, $F(a)$ is the function of conversion, and A is the pre-exponential factor. According to this equation, at the same percent-conversion, E_a can be obtained from the slope of the plot of $\log \beta$ versus $1000/T$ (K). The E_a was obtained by means of the software provided by TA Instruments (DSC manufacturer) and was determined for all samples at each heating rate, and the percent conversion per minute was reported. The E_a of the composites reached the peak at 20% conversion [Fig. 2(A)] and started decreasing as the %conversion increased. Passed 60% conversion, the E_a of neat-unprocessed PLA reached a plateau, while the E_a of the processed continued dropping off [Fig. 2(B)]. The degradation E_a of neat-unprocessed PLA under air was significantly lower than that under nitrogen,

TABLE V
Degradation E_a (in air and nitrogen), %Crystallinity, and %Weight loss After Enzymatic Treatment of Neat PLA and PLA-CUPHEA and Lesquerella Composites

Sample	Ratio ^a	Process	E_a (air) ^b J/g	E_a (N2) ^c J/g	%Crystallinity	%Weight Loss ^d
N. PLA	0	Unprocessed	143.0	218.3	22.7	7.0
Ex. PLA		Extruded	195.7	183.1	0.75	0.5
Mo. PLA		Injection Molded	165.0	163.5	4.31	1.4
PLA/Cuphea	15	Extruded	319.2	86.3	1.18	2.4
		Injection Molded	287.9	209.9	2.62	0.8
	30	Extruded	215.9	124.6	3.47	5.5
PLA/Lesquerella	15	Injection Molded	231.5	186.9	1.71	1.5
		Extruded	144.7	125.7	5.50	3.5
	30	Injection Molded	211.1	108.9	3.95	1.4
		Extruded	307.4	180.8	2.67	5.6
		Injection Molded	203.0	157.8	3.47	1.8

^a Ratio of PLA : fiber.

^b E_a , degradation activation energy in air.

^c E_a , degradation activation energy in nitrogen.

^d Weight loss after enzymatic treatment.

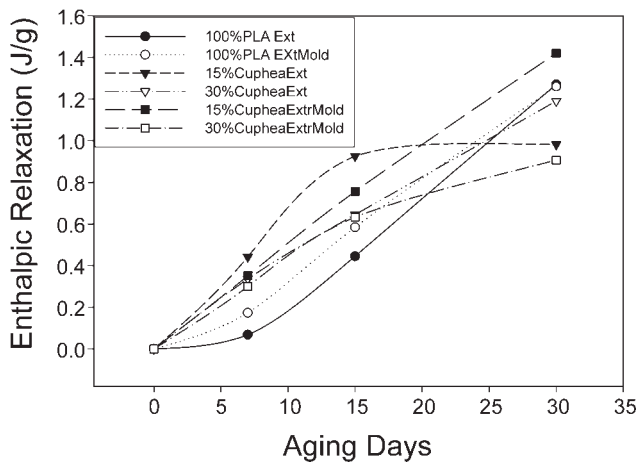


Figure 1 Effect of aging on the enthalpic relaxation of extruded and extruded-injection molded PLA-cuphea composites.

indicating the influence of oxygen on PLA degradation (Table V), while the EX or EXIM, exhibited similar E_a values in air or nitrogen. The presence of cuphea and lesquerella has increased E_a significantly, whereas the E_a values under oxygen continue to give results higher than nitrogen. The composites degradation in the presence of cuphea required higher E_a in air than lesquerella, except at the 30% lesquerella. In nitrogen, the process type, EX versus EXIM, affected the E_a value for both fibers, where the E_a of Ex lesquerella was significantly higher than cuphea. The EXIM cuphea exhibited E_a higher than lesquerella (Table V). The plot of E_a as a function of percent of degradation conversion was used as a predictor of the degradation mechanism, i.e., one-step or more degradation.²⁰ The degradation mechanism of neat PLA in air came to completion in three steps in [Fig. 2(B)], while cuphea composite exhibited a minimum of two steps for the 15 and 30% contents and for both air and nitrogen, except 15% cuphea in nitrogen, which was a one step mechanism [Fig. 2(A)]. The E_a values for the remaining composites are listed in Table VI. Cuphea-composites degraded in air within more than one mechanism steps (Table VI), whereas lesquerella mostly degraded in one-step. In nitrogen, the degradation mechanism was not as noticeable, except for injection-molded cuphea. Overall, multi step mechanism was observed in the injection-molded composites degraded in air versus extruded degraded in nitrogen (Table VI).

The morphological differences between the EX and EXIM was obvious from the SEM profile shown in Figure 3. The smoother surface of the EXIM in Figure 3(B), separates the EX on the left [Fig. 3(A)] from the EXIM. The difference in morphology continued on to the 30% lesquerella composite showed in Figure 3(C,D) and the enzymatically treated com-

posite in Figure 3(E,F). The enzymatic degradation of PLA is affected by the morphology of the material and thus with the fiber content in the composites. The EXIM specimens were covered with a film of PLA and fiber and mostly accessible to the enzyme only from the cut edges. Thus, the weight loss of these samples was much lower than the extruded (Table V and Fig. 4). Generally, the weight loss of the composites containing lesquerella was higher than cuphea due to the higher protein content of lesquerella (31%) versus 20% for cuphea, which can be easily attacked by the degrading enzyme. There were significant differences between % weight loss of the blends for both the extruded and the EXIM treatments ($P = 0.0147$ and $P = 0.009$, respectively). In the course of extrusion metering out, the weight loss of the composites were not significant, $P = 0.214$ and $P = 0.177$, for cuphea and lesquerella, respectively. Throughout the injection-molding process, PLA/cuphea, and PLA/lesquerella blends showed significant weight loss at $P = 0.0616$ and $P = 0.0286$, respectively. The weight loss in the extruded cuphea composites steadily increased with the percent cuphea as a function %crystallinity (Fig. 4). This data is consistent with what has been stated

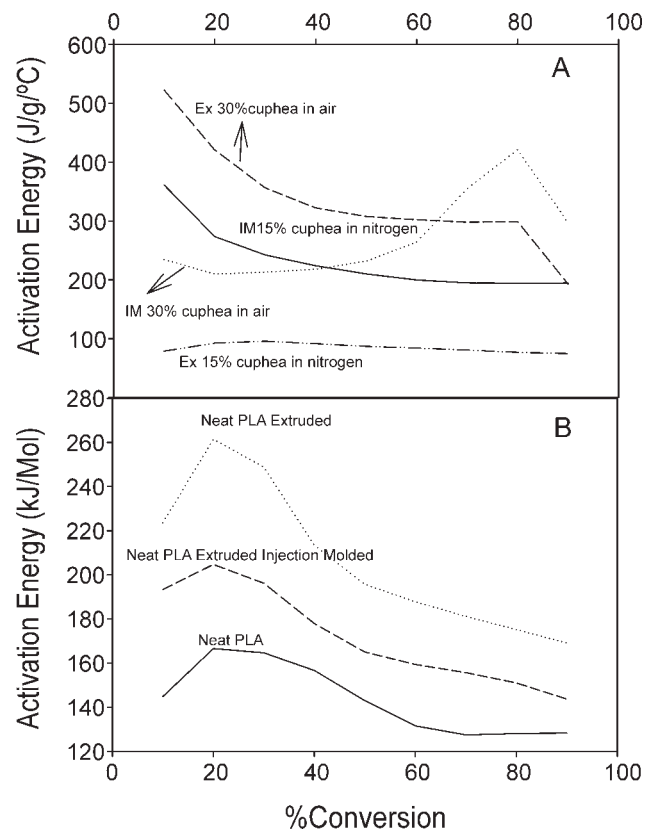


Figure 2 TGA degradation-Activation Energy of unprocessed, extruded, and extruded-injection molded: A cuphea (in air and nitrogen) and B neat PLA (in air) as a function of %conversion in nitrogen.

TABLE VI
TGA Degradation E_a of PLA Composites Listed in %Conversion for all Composites Extruded and Extruded-Injection Molded in Air and in Nitrogen

PLA	Ratio ^c	Process	TGA degradation (%)								
			10 ^d	20	30	40	50	60	70	80	90
PLA ^a	0	As is	289.8	261.8	244.2	229.7	218.3	209.2	201.8	196.7	194.5
PLA ^a		Extruded	207.9	200.6	193.6	188.3	183.1	179.2	174.9	171.4	168.8
PLA ^a		Injection Molded	160.6	171.5	176.2	171.0	163.5	154.0	144.1	136.9	133.6
PLA : Cuph ^a	85 : 15	Extruded	78.8	92.4	95.5	91.3	86.9	83.9	80.5	76.5	74.5
PLA : Cuph ^a		Injection Molded	361.0	273.4	242.2	223.8	209.9	199.6	194.7	193.9	194.4
PLA : Cuph ^a	70 : 30	Extruded	170.1	143.1	134.3	127.8	124.6	121.0	116.5	114.9	169.2
PLA : Cuph ^a		Injection Molded	200.7	195.0	191.5	187.5	186.9	189.0	196.0	221.1	255.5
PLA : Lesqu ^a	85 : 15	Extruded	109.1	115.6	119.6	122.1	125.7	132.7	139.4	145.9	146.8
		Injection Molded	113.9	115.1	111.8	109.7	108.9	109.8	112.1	115.6	119.7
	70 : 30	Extruded	218.5	193.7	185.8	181.6	180.8	184.5	192.9	205.9	238.0
		Injection Molded	138.7	137.0	145.4	152.3	157.8	161.4	165.9	172.1	189.5
PLA ^b	0	As is	144.9	166.6	164.7	156.1	143.0	131.6	127.5	128.1	128.4
		Extruded	223.6	261.4	248.8	213.4	195.7	187.8	181.2	175.2	169.1
		Injection Molded	193.3	204.7	196.2	177.9	165.0	159.4	155.7	151.0	143.7
PLA : Cuph ^b	85 : 15	Extruded	351.7	309.7	307.5	313.2	319.2	321.5	328.1	340.2	376.6
		Injection Molded	430.3	509.5	456.4	364.0	287.9	240.8	215.2	212.9	270.0
	70 : 30	Extruded	183.6	203.1	213.5	216.4	215.9	215.7	226.4	279.3	56.8
		Injection Molded	234.4	209.5	212.9	217.8	231.5	264.1	354.8	242.9	296.9
PLA : Lesqu ^b	85 : 15	Extruded	116.0	139.8	148.1	145.5	144.7	143.9	146.2	151.4	162.7
		Injection Molded	127.3	172.8	232.5	224.6	211.1	208.2	204.5	199.5	210.4
	70 : 30	Extruded	522.3	420.6	356.0	322.1	307.4	302.0	297.9	298.9	142.8
		Injection Molded	156.3	187.2	206.7	216.0	203.0	195.9	193.1	203.8	197.8

^a TGA test in nitrogen.

^b TGA test in air.

^c Ratio, PLA : fiber.

^d The percent degradation conversion PLA and cuphea or lesquerella composites in °C; 10, 20, 30, 40, 50, 60, 70, 80, and 90 are given in percentage (%).

before regarding higher crystallinity in the EXIM samples, which indicates, more compact structure, allowing only limited enzymatic activity, thus lower weight loss (Fig. 4).

Thermomechanical properties and intermolecular force parameters that affect polymers miscibility can be correlated based on DSC measurements, which include estimates of the degree of intermolecular interactions between mixture components.²² Generally, polymer-miscibility can be measured by the occurrence of a single T_g or a shift in T_g .²³ Model equations, such as the Gordon-Taylor (GT) equation,²⁴ have been proposed to predict the glass transition dependence of polymer composites from the experimental data of the neat polymers and the composites. The Gordon-Taylor equation for blends of PLA/fiber composites is represented as

$$T_g^b = \frac{W_1 T_{g1} + K W_2 T_{g2}}{W_1 + K W_2} \quad (2)$$

where, T_g^b = composites glass transition, W_1 and W_2 = weight fraction of cuphea (or lesquerella) and PLA respectively, T_{g1} and T_{g2} = glass transition of cuphea and PLA respectively, and K = adjustable fitting parameter related to miscibility i.e., the strength

of the interaction between the composite-components. The value of the parameter K in eq. (2) is unique for each composite ratio.

For blends of PLA/fiber composites, the Gordon-Taylor equation can be used in the following form:

$$T_g^b = \frac{W_1 T_{g1} + K(1 - W_1) T_{g2}}{W_1 + K(1 - W_1)} \quad (3)$$

where, $W_1 = (1 - W_2)$ is weight fraction of cuphea in the blend; $T_{g1} = T_{g\text{cuphea}}$, $T_{g2} = T_{g\text{pla}}$

To estimate the degree of intermolecular interactions between mixture components, the Gordon-Taylor equation [eq. (3)] was modified by Kwei²⁵ as follows:

$$T_g^b = \frac{W_1 T_{g1} + K(1 - W_1) T_{g2}}{W_1 + K(1 - W_1)} + q W_1 (1 - W_1) \quad (4)$$

where, the parameter q , is the coefficient of the interaction term, is regarded as a measure of the intermolecular interaction between components W_1 and W_2 when $W_2 = (1 - W_1)$. Both parameters, K and q , are used to fit eq. (4) to the experimental DSC data. The sign (positive or negative) of the value of the fitted

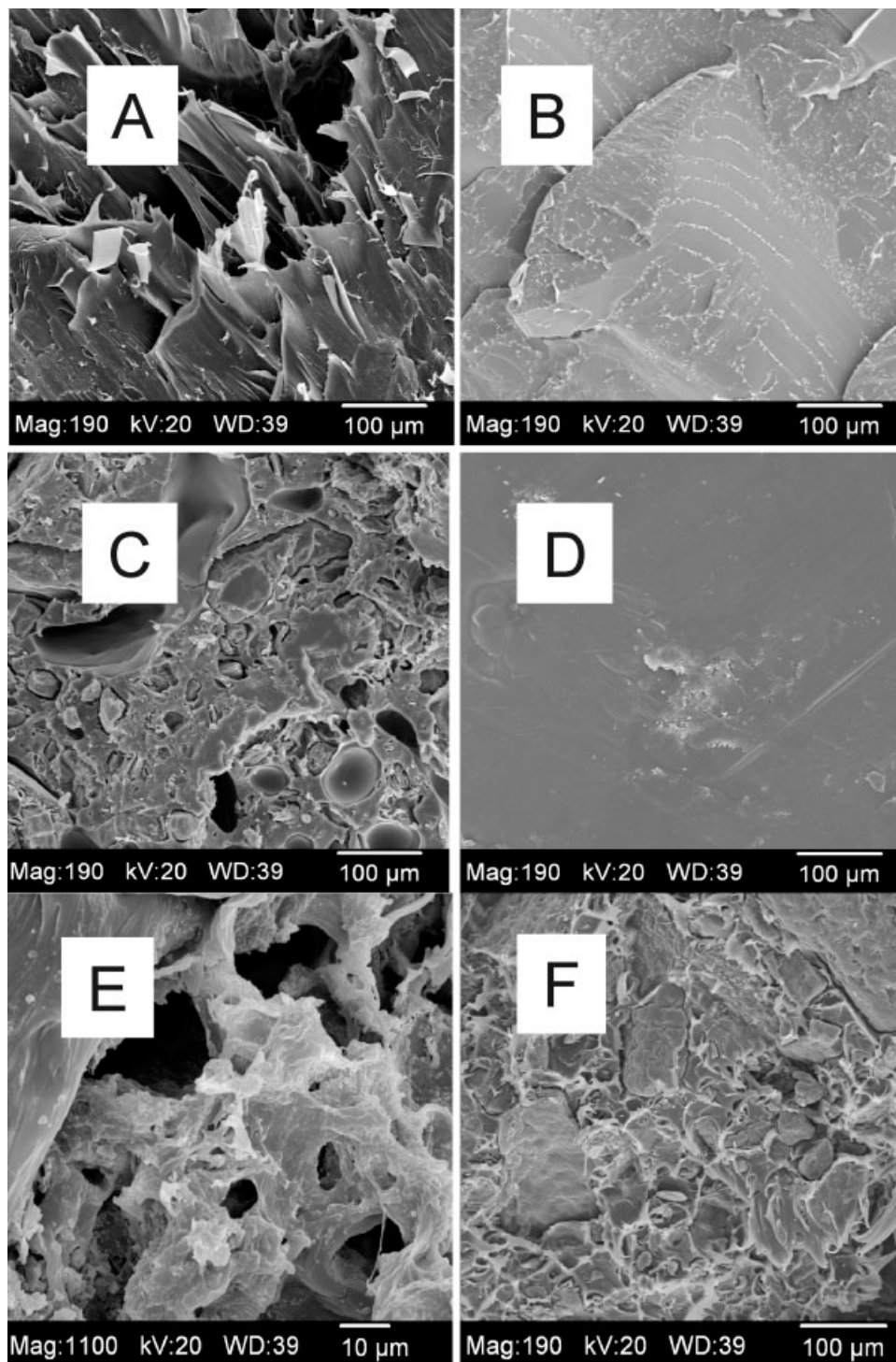


Figure 3 Scanning Electron Micrograph of enzymatically treated neat PLA, and PLA-lesquerella composite. A: EX neat PLA; B: EXIM neat PLA; C: EX 30% lesquerella; D: 30% EXIM lesquerella; E: enzymatically treated EX 30% lesquerella; F: enzymatically treated EXIM lesquerella.

parameter q , indicates the direction of the net change (increase or decrease) in the weight average of T_{g1} and T_{g2} produced by the molecular interaction. The magnitude of the fitted parameter q indicates the strength of the net effect on T_g^b due to various modes of intermolecular interaction.^{25g}

The Kwei modification (GTK), eq. (4), was fitted to the T_g^b for the composites studied in this work. Seven data points were plotted using T_g^b values from five composite ratios and the glass transition temperatures of the two neat polymers, T_{g1} and T_{g2} as experimental DSC data. Results of all three data set are

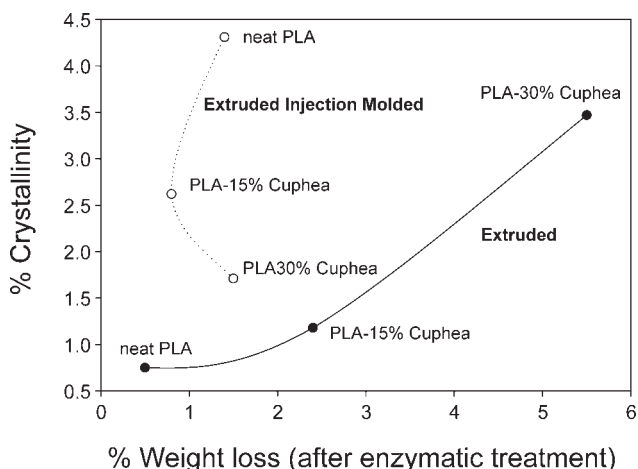


Figure 4 Effect of %crystallinity on the weight loss of neat PLA and PLA-cuphea composites subsequent to enzymatic treatment.

shown in Figures 5 and 6. The first set represents the experimental data, as is, T_g values taken from the DSC, the second set is prediction based on the experimental data and as a continuation of the set, and the third set is the predicted data using the K and q values. The computed K and q values are listed in Table VII with the correlation coefficients R^2 of the best fit for each composite.

The results in Table VII indicated that the best fit ($R^2 = 0.803$) with the GTK equation [eq. (4)] was obtained for EX PLA-lesquerella composite, which gave $K = 0.108$ and $q = -17.688$. Compared to the other three composites, this showed the largest value of q , which indicated that, intermolecular interaction was strongest between lesquerella and PLA extruded materials possibly due to the higher protein content. Results also indicated that intermolecu-

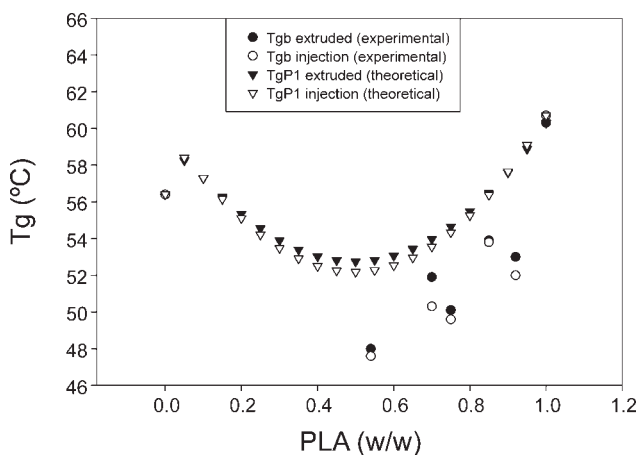


Figure 5 T_g versus composition in PLA-cuphea composite. The predicted T_g values of by Gordon-Taylor-Kwei equation using K and q values listed in Table VII. Unlike Gordon Taylor-Wood equation where one T_g value is fixed, the Kwei method uses both T_g values for the best fit.

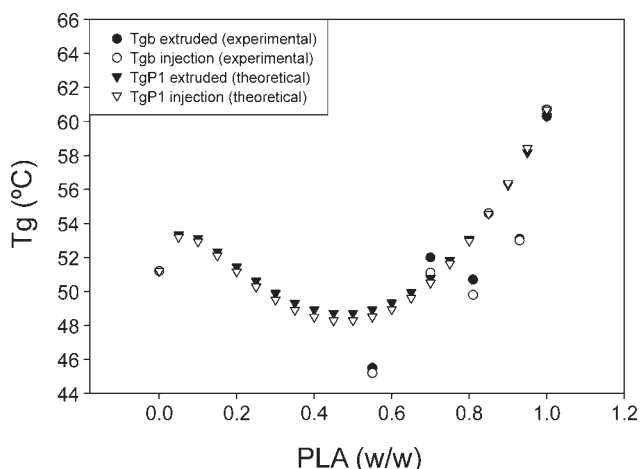


Figure 6 T_g versus composition in PLA-lesquerella composite. The predicted T_g values of by Gordon-Taylor-Kwei equation using K and q values listed in Table VII. Unlike Gordon Taylor-Wood equation, where one T_g value is fixed, the Kwei method uses both T_g values for the best fit.

lar interaction was least strong ($q = -33.9156$) in the EXIM PLA-cuphea. Although the q values of both cuphea composites were significantly lower than those of the lesquerella samples, this greater effect of extrusion over IM on intermolecular interaction was also seen in the q value of the EX and EXIM samples. The negative signs of the q values indicate the intermolecular interaction was strong enough to drive the glass transition temperatures of the blends to T_g^b values below the T_{g1} and T_{g2} of the neat polymers in all composites tested.¹⁰

CONCLUSIONS

Extrusion and injection molding has been found to affect the aging process of biopolymer composites. Enthalpic relaxation steadily increased with the storage (aging) time. IM or the presence of fibers enhanced the percent crystallinity of composites as well as the neat PLA. The activation energy of degradation has increased relative to the neat PLA, while a plot of activation energy as a function of percent conversion indicated more than one-step of degradation mechanism. Enzymatic degradation rate was decreased with the IM compared to the extruded composites. Extruded PLA-lesquerella

TABLE VII
Computed K and q Values from T_g^b Data with Best Fit Correlation Coefficients R^2

Blend	K	q	R^2
PLA-Cuphea (extruded)	0.0100	-30.0635	0.91620
PLA-Cuphea (injection)	0.0100	-33.9156	0.92448
PLA-Lesquerella (extruded)	0.1084	-17.6880	0.80399
PLA-Lesquerella (injection)	0.0910	-19.4938	0.83305

composite showed the largest q value compared to the other three composites, this indicated, stronger intermolecular interaction between the extruded lesquerella and PLA materials, possibly due to the higher protein content.

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