

The Effect of Citrate Ester Plasticizers on the Thermal and Mechanical Properties of Poly(DL-lactide)

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ABSTRACT: Citrate esters triethyl citrate, tributyl citrate, and acetyl tributyl citrate were used as plasticizers for amorphous poly(D,L-lactide) (PDLLA). The resultant compositions were analyzed by means of differential scanning calorimetry (DSC), dynamic mechanical thermal analysis, and tensile testing to investigate the properties of the blends. Glass transition temperatures (T_g s) obtained by DSC were also compared to theoretically calculated T_g s. Increasing plasticizer content decreased the resultant T_g of the blend with plasticizer efficiency enhanced as the molecular weight of the citrate ester increased. However, in blends with high plasticizer content, a lack of miscibility also occurred with increased molecular weight. Theoretical results were comparable with those obtained experimentally at compositions, which were miscible. Increasing plasticizer content increased the ductility and decreased the strength of the polymer. The addition of 10 wt % plasticizer to PDLLA decreased tensile strength by over 50% with the deterioration larger at higher concentrations of plasticizer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: thermal properties; mechanical properties; polyesters; additives; biomaterials

Received 30 November 2011; accepted 24 February 2012; published online

DOI: 10.1002/app.37600

INTRODUCTION

Of the many polymeric materials that are biodegradable, the α -hydroxy acid polylactide (PLA) is among the most extensively investigated. This is due to its proven biocompatibility and good material properties. PLA can exist in three stereochemical forms: poly(L-lactide) (PLLA), poly(D-lactide) (PDLA), and poly(DL-lactide) (PDLLA). Because of the stereo regular chain microstructure, PLLA and PDLA are semicrystalline. The polymerization of a racemic mixture of L- and D-lactides (a 50 : 50 mixture of L and D isomers) leads to the synthesis of PDLLA, which is amorphous¹ and is the type of material used in the work reported here. PLA possesses good mechanical properties and generally has an elastic modulus and tensile strength in the ranges of 3.2–3.7 GPa and 55–60 MPa, respectively.² In the unplasticized form, it has a glass transition temperature (T_g) greater than 37°C, causing PLA devices to possess brittle characteristics in physiological conditions.

The aim of this research work was to attempt to develop a resorbable bone substitute based on PLA. However, brittleness is a major drawback for many biomedical applications, and PLA devices tend to be susceptible to fracture when subjected to ten-

sion or load-bearing stresses during use.³ To modify its properties, PLA has been blended with other polymers such as poly(ethylene oxide),⁴ poly(vinyl acetate),⁵ and poly(methyl methacrylate).⁶ Another option is the use of a low-molecular weight compound that acts as a plasticizer, examples of compounds used with PLA include glycerol,⁷ triactine,⁸ polyethylene glycol,⁹ and citrate esters.¹⁰ An effective plasticizer for PLA is expected to reduce the glass transition of the amorphous phase and depress the melting point of the crystalline region.²

There are several important considerations when choosing a plasticizer for PLA for biomedical applications. It should be a nontoxic substance miscible with the polymer, thus creating a homogeneous blend. Also, the plasticizer should not be prone to migration as this would cause the material to regain the brittleness of pure PLA.¹¹ Citrate esters are used as plasticizers with a variety of different polymers such as poly(methyl methacrylate)¹² and cellulose acetates.¹⁰ They are nontoxic and approved for use as additives in food, personal care products, and in medical plastics.¹²

Labrecque et al.¹⁰ studied the effect that citrate esters had on the thermal and mechanical properties of semicrystalline PLA

and found that all plasticizers were miscible with PLA (a composition range of up to 30% plasticizer was analyzed). The reason for good solubility of PLA in citrate plasticizers is due to the polar interactions between the ester groups of PLA and the plasticizer.¹³ However, quantitative information on the effects of citrate ester plasticization of PDLLA is not readily available, and, so in this study, amorphous PDLLA was blended with three different citrate esters; triethyl citrate (TEC), tributyl citrate (TBC), and acetyl tributyl citrate (ATBC) and the resultant thermal, dynamic mechanical, and tensile properties were analyzed. The results found experimentally by differential scanning calorimetry (DSC) are also compared to theoretical results calculated for the various plasticized polymer compositions following the methods of Fox.

MATERIALS AND METHODS

Blending

The PDLLA investigated in this report supplied by Boehringer Ingelheim (Germany), had an equimolar mixture of D and L isomers and an average molecular weight of 2.028×10^5 Da as determined by gel permeation chromatography using THF as a solvent with a polystyrene calibration applied. Plasticizers TEC, TBC, and ATBC supplied by Sigma Aldrich (Ireland) had molecular weights of 276, 360, and 402, respectively, as reported by the supplier. The polymer was first ground to a fine powder before use and sample compositions consisted of PDLLA combined with 10–30 wt % plasticizer. All samples were prepared by heating to $\sim 150^\circ\text{C}$ in a beaker while being continuously stirred before being transferred to hot molds to be pressed.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Pyris 1 DSC. Plasticized samples (5–6 mg) were heated from -60 to 100°C at a rate of 10°C per minute under nitrogen atmosphere. PDLLA samples containing all three plasticizers ranging from 10 to 30 wt % content were analyzed. DSC was also performed on each plasticizer within a temperature range of -150 – 50°C under helium atmosphere. The glass transition temperature (T_g) was taken as the midpoint of the specific heat increment at the glass transition.

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) scans were carried out on PDLLA samples containing only plasticizer TBC using a Rheometric scientific mark 3 DMTA. Analysis was carried out on specimens measuring $10\text{ mm} \times 4\text{ mm} \times 2\text{ mm}$ in tensile mode with a temperature profile ranging from -60 to 120°C at a 2°C per minute heating rate with a frequency of 1 Hz. T_g was taken as the peak in the $\tan \delta$ curve accompanied by a step reduction in the storage modulus.

Tensile Testing

Tensile tests were performed using an Instron 4301 series tensile testing machine. Specimens were dogbone shaped with a gauge length of $\sim 13\text{ mm}$, a width of 3.5 mm and thickness of 3 mm prepared after ASTM standard D638-08. All samples were tested with the same crosshead speed of 10 mm/min using a 1 kN load cell. Tensile testing was performed on PDLLA samples containing 10, 20, and 30 wt % of all three plasticizers.

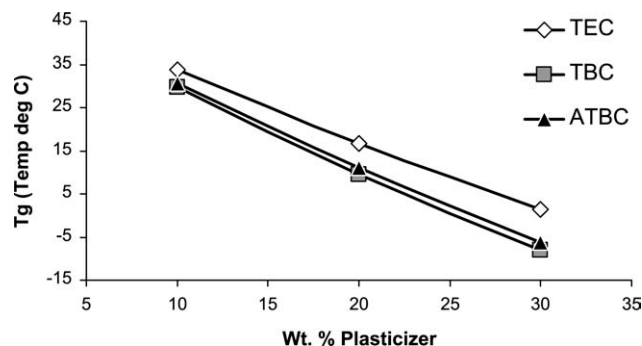


Figure 1. Theoretical T_g as a function of plasticizer content.

RESULTS AND DISCUSSION

Theoretical T_g

There are several equations reported in literature that enable the glass transition temperature of copolymers and polymer blends to be expressed as a function of their composition. Equation (1) was proposed by Fox for the T_g dependence of a binary system:

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}}, \quad (1)$$

where subscripts 1 and 2 refer to plasticizer and polymer, respectively, and ω is the weight fraction.¹⁴ This equation was applied to the various compositions of PDLLA with each plasticizer using the T_g obtained for PDLLA and each citrate esters by DSC. Figure 1 illustrates the theoretical T_g s calculated as a function of plasticizer content. Calculated theoretical T_g s are also listed in Table I.

Differential Scanning Calorimetry

Figure 2 illustrates the heat cycle differential scanning calorimetry (DSC) thermoscans for PDLLA and the polymer plasticized with different quantities of each plasticizer. The resultant T_g for all samples analyzed is listed in Table I. The glass transition is evident in the pure PDLLA material as a distinct peak whilst in the polymer–plasticizer blends, it is apparent as a significant change in slope. The very small event occurring at 20°C in all scans is an instrumental artifact.

As expected, by increasing plasticizer content, a decrease in T_g occurs, which is true for all three plasticizers analyzed. The low-molecular size of the plasticizer allows it to occupy intermolecular spaces between polymer chains, reducing the energy for molecular motion and the formation of hydrogen bonding between the polymer chains, which in turn increases free volume and molecular mobility.¹⁵

Figure 3 illustrates the effect all three plasticizers have on the T_g of the PDLLA as a function of plasticizer content analyzed by DSC in this study. The magnitude of the T_g change in the plasticized polymer is a good indicator for the plasticization efficiency of the plasticizer compound.¹⁶ The most effective plasticizer to decrease T_g was generally ATBC, followed by TBC and last TEC. By increasing the molecular weight of the plasticizer, the effectiveness of the citrate plasticizer to reduce the T_g of the PDLLA is generally enhanced.

Table I. T_g Values for Various Blends of Polymer and Plasticizer Found Experimentally and Theoretically

PDLLA	Theoretical (T_g)			DSC (T_g)			DMTA (T_g)
	TEC	TBC	ATBC	TEC	TBC	ATBC	TBC
	-			53.1			74.3
Plasticizer (wt %)	TEC	TBC	ATBC	TEC	TBC	ATBC	TBC
10	33.8	29.8	30.6	32.5	29.0	27.9	68.2
20	16.7	9.6	11.0	17.8	8.9	5.7	50.4
30	1.4	-8.1	-6.2	-0.5	-1.4	4.4	36.1
100	-	-	-	-72.7	-88.8	-85.7	-

TEC, the least effective plasticizer, only differs structurally from TBC in the number of carbons in its ester chain; TEC containing two carbons while TBC having four (see Table II). Both plasticizers have three ester functionalities, potentially acting as a hydrogen bond acceptor sites and a tertiary hydroxyl group, which has both hydrogen bond donating and accepting character.¹⁷ Interactions may occur between the hydroxyl groups of TEC/TBC and the hydrogen bond acceptor ester groups of PDLLA. TBC is most likely more effective as a plasticizer due to its larger nonpolar aliphatic segments. These segments shield dipoles on the PDLLA polymer chains from interacting with ad-

jacent polymer chains, pushing them apart, and increasing mobility, thus reducing the T_g more effectively than TEC.

ATBC and TBC structurally differ only by the acetylation of the tertiary hydroxyl group in ATBC. ATBC is exclusively a hydrogen-bond acceptor, while TBC having a hydroxyl group has both hydrogen bond donating and accepting character and has potential to form strong hydrogen bonds with the ester groups of PDLLA. These strong bonds between TBC and the polymer may result in a decrease in polymer chain mobility and flexibility,¹⁶ causing PDLLA plasticized with TBC to have a higher T_g than PDLLA plasticized with ATBC. ATBC having an extra acetyl group also has an increased associated free volume; the acetyl group may also further shield dipoles on the PDLLA chains, further pushing the polymer chains apart and increasing mobility.

These results found for amorphous PLA are similar to that of Labrecque et al.¹⁰ who reported that with increasing citrate plasticizer content, the T_g of semicrystalline PLA decreased. They also found that the lower the molecular weight of the plasticizer, the less efficient it was at lowering the T_g of the PLA.¹⁰

Only one glass transition was noted for each sample of PDLLA blended with TEC, which indicates that this plasticizer was miscible with the polymer for all compositions. Whereas a second slight endothermic shift in the specific heat occurring at the glass transition temperature of PDLLA was noted to occur in samples containing 20% ATBC, 30% ATBC, and 30% TBC. The miscibility of plasticizers and polymers can be estimated by comparing their solubility parameters. The solubility parameters for PDLLA and all three plasticizers are quite similar indicating good compatibility (see Table II). However, the difference between their solubility parameters increases with increasing

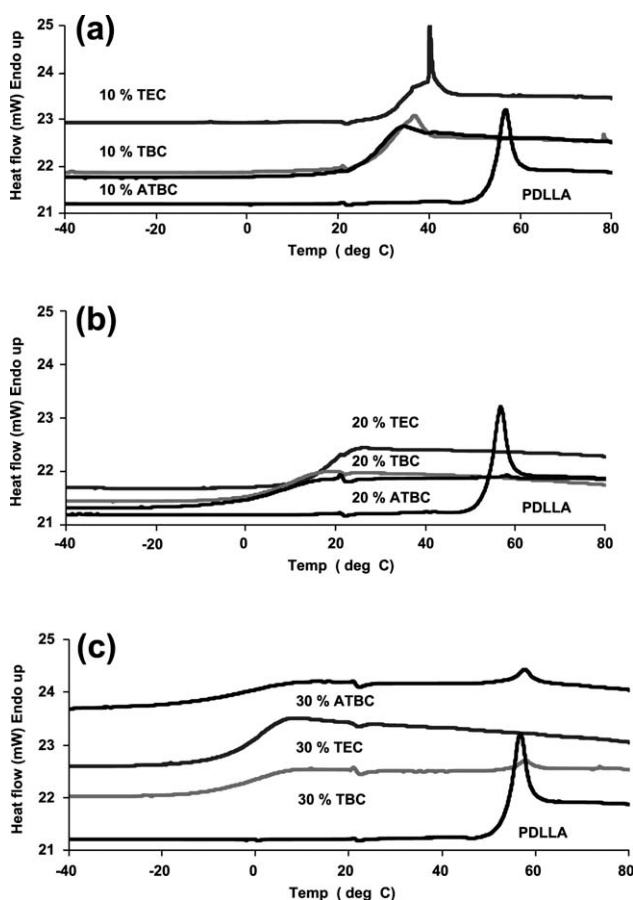


Figure 2. DSC thermographs of neat PDLLA and PDLLA samples plasticized with (a) 10, (b) 20, and (c) 30 wt % citrate ester. [Color figure can be viewed in the online issue, which is available at www.onlinelibrary.com.]

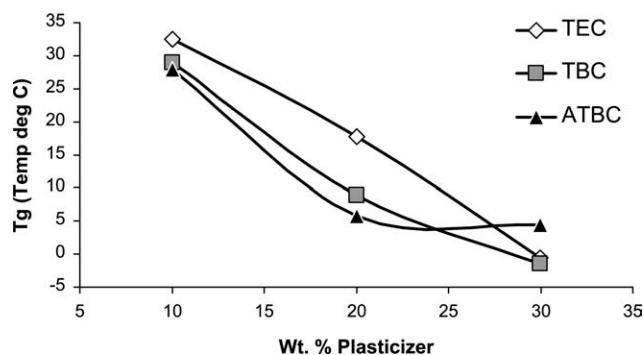
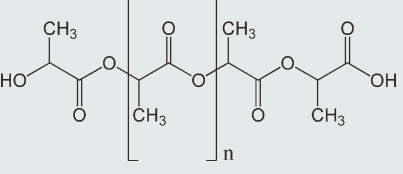
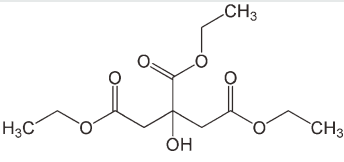
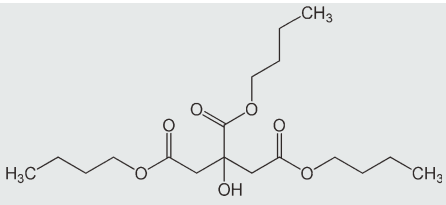
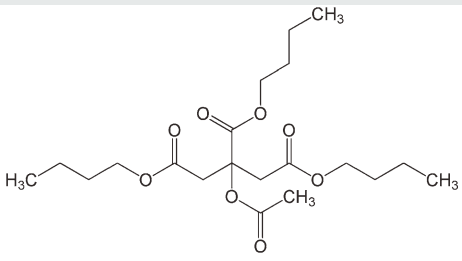


Figure 3. Experimental T_g as a function of plasticizer content obtained by DSC.

Table II. Structure of PDLLA and Each Citrate Ester Plasticizer and Their Corresponding Solubility Parameters as Reported by Ljungberg et al.⁸

Plasticizer	Structure	Solubility parameter δ (J cm ⁻³) ^{1/2}
PDLLA		20.1 ^a
TEC		19.7 ^a
TBC		19.6 ^a
ATBC		18.0 ^a

^aCalculated with group molar attraction constants from the Hoy series.

molecular weight of the plasticizer, resulting in a decrease in solubility and compatibility, which may explain the presence of two T_g s in compositions with higher molecular weight plasticizer contents. The lack of miscibility between PDLLA and ATBC at higher concentrations can be seen clearly in Figure 3. The T_g of PDLLA plasticized by 20% ATBC is 5.7°C; with the addition of a further 10% ATBC, the T_g only decreases slightly to 4.4°C. This differs with work completed on semicrystalline PLA by Baiardo et al.,² who reported that the solubility limit of ATBC in PLLA was 50 wt %.²

Dynamic Mechanical Thermal Analysis

Figure 4 shows the $\tan \delta$ and storage modulus curves obtained from dynamic mechanical analysis of PDLLA and PDLLA plasticized with 10–30 wt % TBC. Table I indicates the glass transition temperatures for each sample. With increasing plasticizer content, a decrease in T_g is obtained and the height of the $\tan \delta$ peak also decreases and broadens.

As seen in Figure 4(b), at temperatures above the T_g , the storage modulus of each sample drops dramatically due to the softening of the polymer specimens. With increasing plasticizer content, there is a decrease in storage modulus values below T_g as the plasticizer continues to increase the mobility of the polymer chains.

These results for amorphous PLA are similar to those obtained by Ren et al.¹³ who plasticized semicrystalline PLA with low-molecular weight triacetin and oligomeric poly(1,3-butylene glycol adipate). Increasing plasticizer content decreased the peak of the $\tan \delta$ curve while also making them shorter and broader. The storage modulus values were also similar, and a decrease could be seen with increasing plasticizer content.¹³

T_g of samples—DMTA versus DSC versus theoretical

Table I lists the T_g values for PDLLA plasticized with TBC obtained by dynamic mechanical thermal analysis (DMTA) and

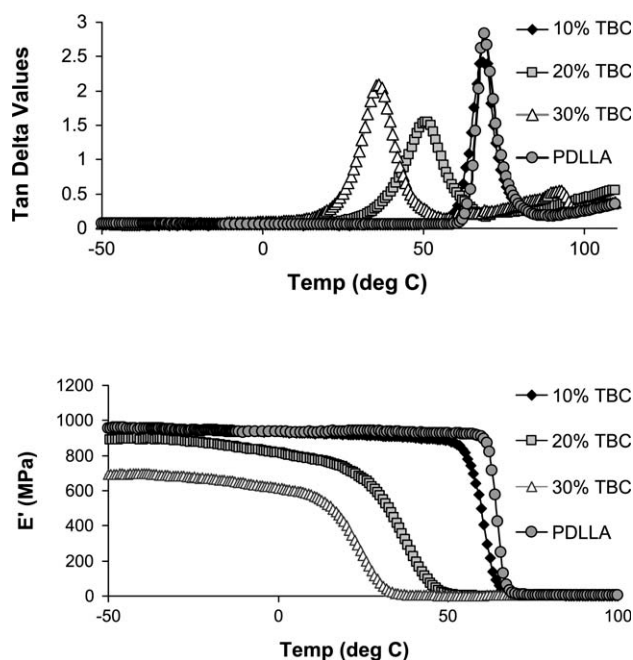


Figure 4. (a) $\tan \delta$ and (b) storage modulus curves obtained by DMTA for PDLLA and PDLLA samples plasticized with TBC.

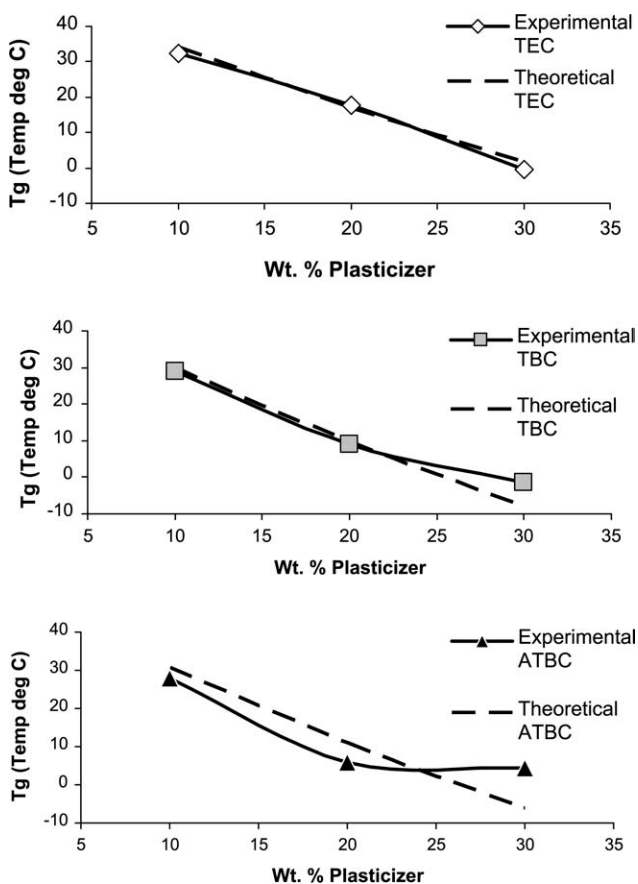


Figure 5. Theoretical versus experimental T_g of samples plasticized with (a) TEC, (b) TBC, and (c) ATBC as a function of plasticizer content.

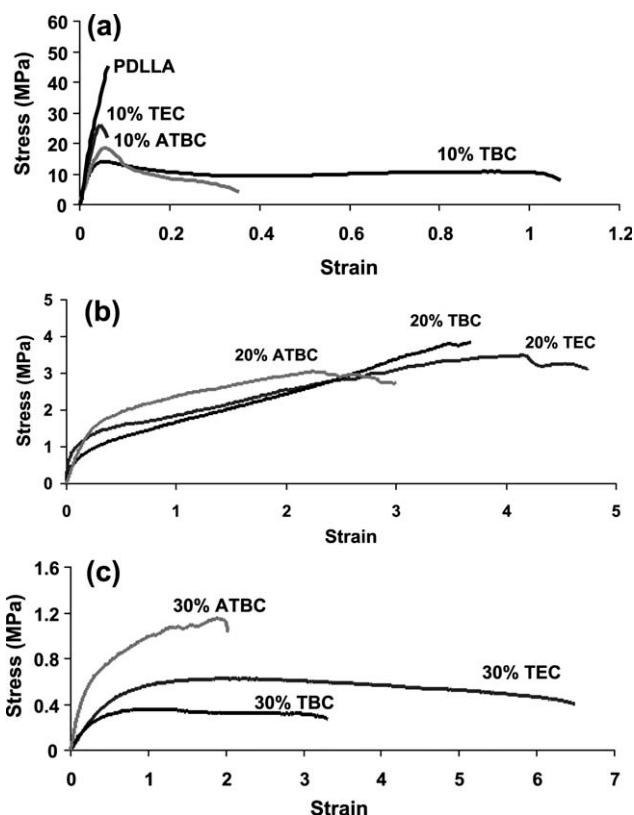


Figure 6. Stress–strain curves of neat PDLLA and PDLLA samples plasticized with (a) 10, (b) 20, and (c) 30 wt % citrate ester. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

differential scanning calorimetry (DSC). Because the glass transition is a kinetic process, it is affected by the rate at which the sample is heated, and different experimental techniques lead to different T_g values.¹⁸ This is due to different time responses in the motions of side or main-chain polar groups and mechanical or thermal stimulation of the motion.¹⁴ The T_g values for PDLLA plasticized with TBC obtained by DMTA are higher than that obtained by DSC. According to Averous et al.,¹⁹ differences in the temperature corresponding to transitions observed by DMTA and DSC are attributed to the frequency of the analysis method. A clear indication of the glass transition temperature range is more easily observed through DMTA, and this result may suggest that the segmental motion of the plasticized PDLLA has only been partially relaxed at the T_g as indicated by DSC.

Figure 5 compares the theoretical results calculated for plasticized PDLLA with those found experimentally by DSC. The theoretical results are in good agreement with those obtained experimentally for TEC [Fig. 5(a)] and TBC [Fig. 5(b)] at compositions that seemed to be miscible. At a composition of 30% TBC, which showed two separate T_g 's, the experimental result was slightly higher than that of the theoretical result calculated most likely due to lack of homogeneity in the sample tested. The results obtained experimentally for ATBC are lower than the theoretical results at compositions of 10 and 20 wt % ATBC

Table III. Tensile Testing Results

		Tensile strength (MPa)	Std dev (\pm)	Elongation to break (%)	Std dev (\pm)	Young's modulus (MPa)	Std dev (\pm)
PDLLA (wt %)		41	6	9	21	870	86
10	TEC	29	3	78	22	727	39
	TBC	15	1	171	10	325	84
	ATBC	18	1	46	17	525	26
20	TEC	4	0.3	319	224	25	0
	TBC	4	0.4	138	145	15	15
	ATBC	3	0.9	315	23	11	8
30	TEC	0.6	0.1	595	201	1	0
	TBC	0.4	0.07	337	48	1	0
	ATBC	1.2	0.2	225	63	4	1

[Fig. 5(c)]. He et al.²⁰ report that the differences between experimental and predicted T_g values are sometimes considered as a measure of the strength of interactions between the blend components. Glass transition temperatures found experimentally that are lower than those predicted may be attributed to weak specific interactions between the blends.²¹ At a composition of 30% ATBC, the measured value was higher than that of the theoretical result, which may also be due to lack of homogeneity in the sample.

Tensile Testing

Figure 6 illustrates the stress–strain curves of PDLLA samples unplasticized and plasticized by the three different citrate esters. Average Young's modulus, tensile strength, and percentage elongation at break for all samples tested are listed in Table III.

At 10 wt % plasticizer content [Fig. 6(a)], samples plasticized with TEC had the greatest stiffness and strength followed by ATBC-plasticized samples and last TBC-plasticized samples. TBC-plasticized samples also had the greatest elongation at this plasticizer concentration. These results do not fully correlate with the experiment T_g measurements, as it would be expected that the samples containing 10% ATBC, which had the lowest T_g would also have the lowest stiffness and strength and the greatest elongation. However, the results do correlate with the theoretical T_g s calculated, which predicted samples plasticized with 10 wt % TBC to have the greatest chain mobility at that plasticizer content (see Fig. 1).

As already stated, the T_g found experimentally for PDLLA plasticized with ATBC was lower than those predicted, which may be attributed to weak-specific interactions between ATBC and PDLLA. This may have resulted in the migration of the plasticizer ATBC causing the material to regain some of the rigidity of pure PDLLA. TEC-plasticized samples displayed the greatest elongation as the weight percentage content of plasticizer increased to 20 and 30% while TBC and ATBC were not as effective. The larger nonpolar aliphatic segments of ATBC and TBC may have shielded dipoles on the PDLLA polymer chains from interacting with adjacent polymer chains, and this disruption to the polymer system may have caused a decrease in elongation compared to samples plasticized by TEC.

Unplasticized PDLLA is quite brittle as seen in Figure 6(a) and fractured without yielding. The 10% TEC plasticized sample was less brittle than pure PDLLA and had some necking, while 10% TBC and ATBC-plasticized samples were more ductile than the 10% TEC sample with necking and further extension occurring at lower stress, occurring more so in the TBC plasticized sample than the ATBC-plasticized sample.

Figure 6 shows that with the increase in plasticizer content, there is a general increase in ductility and decrease in strength. Percentage elongation at break increases at the expense of Young's modulus and tensile strength. At compositions above 10 wt % plasticizer, both the stiffness and strength of the samples drop dramatically and at compositions of 30 wt % plasticizer, these properties are very low. These results for amorphous PLA are similar to those reported by Labrecque et al.¹⁰ who found that the addition of 10% citrate esters to semicrystalline PLA decreased tensile strength by $\sim 50\%$ with the deterioration larger at higher concentrations of plasticizer.

CONCLUSION

Plasticizing amorphous PLA with citrate esters results in a decrease in T_g with increasing plasticizer content. By increasing the molecular weight of the plasticizers, their effectiveness in reducing the T_g of the PDLLA is generally enhanced, but miscibility is decreased. The work is in good agreement with work previously completed on semicrystalline PLA, apart from the resultant solubility limits of the plasticizers within the amorphous polymer, with higher limits previously reported for the semicrystalline PLA form.

DMTA of TBC-plasticized PDLLA indicates that a decrease in T_g is obtained with increasing plasticizer content, and the decrease in storage modulus values below T_g shows that there is no low-temperature antiplasticization effect. The T_g values obtained by DMTA are higher than that obtained by DSC, which is a time-temperature effect. Theoretical T_g results for plasticized PDLLA are in good agreement with those obtained experimentally for TEC and TBC at compositions, which were miscible. Weak-specific interactions between ATBC and PDLLA may account for differences in experimentally observed and theoretical calculated T_g s.

As expected with the addition of a plasticizer, there is a general increase in percentage elongation at the expense of Young's modulus and tensile strength. The addition of 10% citrate esters to PDLLA decreases Young's modulus and nearly halves the tensile strength, with the deterioration larger at higher concentrations of plasticizer. Migration/retention of plasticizer as a function of time should be quantified, as this is likely to be significant at these plasticizer concentrations.

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