Materials Engineering

PLASTICIZING OF POLYLACTIC ACID (PLA) BIOPOLYMER WITH CITRATE ESTERS

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Abstract. Triethyl citrate (TEC) and acetyl tributyl citrate (ATBC) were used as plasticizer for Polylactic acid (PLA). The treated and plasticized PLA at various concentrations were analyzed by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), melt flow index (MFI) and thermogravimetric analysis (TGA). Differential scanning calorimetry was used to evaluate the crystallinity and thermal property of all the samples. It was found that the glass transition temperature (T_g) and the melting temperature (T_m) decreased as the amount of citrate esters increased. Additionally, the presence of TEC or ATBC tended to increase the crystallinity of PLA. This result was supported by x-ray diffraction. DMA of plasticized PLA indicates that a decrease in T_g is obtained with increasing plasticizer content, Plasticizing effect was also shown by decrease in the dynamic storage modulus and viscosity of plasticized mixtures compared to the treated PLA. The TGA results indicated that ATBC and TEC promoted a decrease in thermal stability of the PLA.
Keywords: Polylactic acid (PLA); Plasticizer; Citrate esters; Crystallinity, Triethyl citrate (TEC), acetyl tributyl citrate (ATBC).

INTRODUCTION

Polylactic acid (PLA) is a biodegradable thermoplastic that can be produced from renewable recourses because of its good mechanical properties, processibility and biodegradability [1, 2]. For these reasons PLA is an interesting candidate for producing biodegradable packaging materials and hygiene products [3, 4]. PLA is a rather brittle and rigid polymer. Plasticizers are widely used in the plastics industry to improve processability, and ductility of glass polymers [5]. In the case of semicrystalline polymers like PLA, an efficient plasticizer is expected not only to reduce the glass transition of the amorphous domains, but also to depress the melting point of the crystalline phase [6, 7]. The choice of polymers or plasticizers to be used as modifiers for PLA is limited by the requirements of the application. Only non-toxic substances approved for food contact can be considered as plasticizing agents in food packaging materials. For a low molecular weight plasticizer an important demand is that it should be miscible with PLA, thus creating a homogeneous blend. The plasticizer should not be too volatile so as not to evaporate at the elevated temperatures used during processing. Nor should the plasticizer be prone to migration as this would be a source of contamination of the food or beverage in contact with the plasticized PLA. Migration would also cause the blended material to regain the brittleness of neat PLA. Considerable effort has been made to improve the mechanical flexibility of PLA by reducing film tearing and cracking, which are caused by stresses during manufacturing or use. These efforts were made either by modifying PLA with biocompatible plasticizers or by blending PLA with other soft polymers [8–10]. PLA blends with various low molecular weights liquid plasticizers, such as including polyethylene glycol (PEG), citrate esters, such as triethyl citrate (TEC), tributyle citrate (TBC) and acetyl-tri-n-butyl citrate (ATBC), dioctyl adipate (DOA), glucose monoesters, oligomeric lactic acid, and glycerol, were reported to improve the ductility and impact resistance of the PLA significantly [11–17]. Citrate esters have been investigated as plasticizers for PLA [18]. Low molecular weight plasticizers, such as triethyl citrate, glyceryl triacetate, tributyl citrate and acetyl tributyl citrate, interacted well with PLA and improved crystallization rates and mechanical properties.

Labrecque et al. [14] compared the plasticizing effect of different citrate esters (triethyl citrate, tributyle citrate, acetyl triethyl citrate, and acetyl tributyl citrate) and found that these substances efficiently reduced the T_g and improved the elongation of PLA films. Similar results were obtained by plasticizing PLA with triacetin and tributyl citrate [16]. 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 [19]. Two biodegradable, nontoxic plasticizers that have been successfully blended with PLA are triethyl citrate (TEC) and acetyl tributyl citrate (ATBC). At the concentrations used (up to 30%) these esters were shown to be compatible with PLA and to generate significant decrease in T_g, thereby enhancing the ductility of the material. The aim of this study is to investigate the effects of triethyl citrate (TEC) and acetyl tributyl citrate (ATBC) on thermal, dynamical, structural properties and the opacity of films destined to food packaging.

EXPERIMENTAL

Materials and methods
Materials
Poly (lactic acid) (PLA 2002D, extrusion grade, MFI: 5-7 g 10 min at 210 °C, 2.16 kg) was provided by Cargill-Dow (USA).the melting temperature (T_m) was 180 °c and the glass transition temperature (T_g) was 60 °C, acetyl tributyl citrate (ATBC) and triethyl citrate (TEC) were purchased from sigma Aldrich (France).

Sample preparation
Before processing by melt-blending PLA was dried for 24 h at 60 °C, PLA was blended with the plasticizers in a Brabender plastograph. The temperature was 190 °C and the blending time 7 min, and blend rotation speed was 30 rpm. The plasticizers TEC and ATBC were blended to PLA at 5, 10, 15, 20 and 30% weight.

THEORETICAL

Characterization
Differential scanning calorimetry (DSC)
Differential scanning calorimetry (DSC) was conducted on a TA instruments DSC Q10. All samples were exposed to consecutive heating and cooling programs to eliminate their thermal history: first heating from 25 °C to 220 °C, isothermal for 3 min, cooling from 220 °C to –50 °C, isothermal for 3 min, and second heating from –50 °C to 220 °C. The heating and cooling rates were 10 °C min^{-1}.

Dynamic mechanical analysis (DMA)
Measurements were carried out with a dynamic mechanical analyzer (RSAII) at a frequency of 1 Hz. All films $30 \times 7 \times 0.5$ mm^3) were tested at a strain of 0.01% using a 3°C min^{-1}, temperature ramp from –50 to 120°C.

Melt flow index (MFI)
Melt flow index (MFI) is the mass flow rate index, expressed in grams, extruded isothermally 10 min under constant load through a die of standard dimensions was measured by using Melt Flow Indexer (MFI Controlab Melt flow rate apparatas model 5) at 190 °C and 2.16 Kg.

Thermogravimetric analysis (TGA)
Thermogravimetric analysis (TGA) of the samples was studied by using TA instrument Q100 (TA). The samples were heated from 30 to 500 °C with the heating rate of 10 °C min^{-1} under nitrogen atmosphere at the flow rate of 20 ml min^{-1}.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC)
During the last heating scan the glass transition, cold crystallization and melting temperature of the material were determined. The degree of crystallinity (X_c) was calculated from the DSC data using the following relationship:

$$X_c\,(\%) = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f \Delta X_{PLA}} \times 100 \qquad (1)$$

where ΔH_m, ΔH_{cc} and X_{PLA} are the enthalpy of melting, enthalpy of cold crystallization and weight fraction of PLA respectively, ΔH_f is the heat of fusion defined as the melting enthalpy of 100% crystalline PLA, which is 93 J.g^{-1} [20].

The differential scanning calorimetry (DSC) results (last scan) for the treated and plasticized PLA in Brabender plastograph are shown in figure 1 and summarized in Table 1.

The plasticizers decreased the glass transition temperature (T_g) of treated PLA from 60.42 °C to 10.29 °C and to 12.21 °C with addition 30% of TEC and ATBC respectively. As expected, by increasing plasticizer content, a decrease in T_g occurs, which is true for the TEC and ATBC. 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. By increasing the content of the plasticizer, the effectiveness of the citrate plasticizer to reduce the T_g of the PLA is generally enhanced [21].

The addition of TEC or ATBC to the PLA affects the cold crystallization temperature (T_{cc}). The T_{cc} observed in treated PLA at 130.94 °C is depressed to 71.72°C and to 69.26 °C with addition of 30% of TEC and ATBC respectively. The decreasing of T_g, T_{cc} and melting temperature (T_m) were enhanced with a higher plasticizer content as a result from the enhanced chain mobility [22].

The decrease of T_g, T_{cc}, T_m and the increase of degree of crystallinity as show in Table 1 was seen to depend on the plasticizer content. The percentage of crystallinity of the plasticized PLA is higher than that the treated PLA. For the plasticized PLA with TEC, greatest crystallinity is observed with addition of 30% for a value of 8.58%, and a rate of 9.07% for the plasticized PLA/ATBC. This increase indicates that the crystallization of the PLA becomes easier with the mobility of the chains caused by the citrate ester.

Dynamic mechanical analysis (DMA)

Variation of loss factor (tan δ) with temperature for treated and plasticized PLA with TEC and ATBC is presented in Figure 2A and B, respectively. As shown in Figure 2, tan δ decreased with the addition of citrate esters, which indicates that the T_g was significantly decreased for all the plasticized PLA. The T_g decreases with the increase of plasticizer content in the PLA. For example at 30% of TEC and ATBC, the glass transition of PLA decreased from 62.23°C to 17.49°C and to 26.91°C, respectively. These values of T_g obtained by DMA have the same tendency of the results found by DSC, where T_g decreased with the addition of plasticizer.

Melt flow index (MFI)

The variation of melt flow index (MFI) with the addition of TEC and ATBC was illustrated in Figure 3 respectively. MFI data show that all formulations have higher MFI than of treated PLA (4.6 g per 10 min). The addition of a plasticizer increases the polymer chain mobility which implies a reduction in viscosity and increase of MFI of plasticized PLA [23]. When lower quantity of citrate esters is added in PLA, the small citrate molecule can penetrate PLA matrix and then make PLA matrix slip and flow easier. With the addition of citrate increased large amounts of citrate molecule gathered with each other and surrounded the PLA matrix, which can resist slipping and flowing the PLA molecule chain. When the composition of the plasticizer increases, more molecules of the TEC or ATBC surround the PLA, which becomes more fluid and slippery. The melt index is in good correlation with the results of DSC and DMA.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an effective approach evaluating the thermal stability of polymeric material. Figure 4A and Figure 4B shows the TG and DTG curves of the neat PLA and plasticized PLA with TEC and ATBC respectively.
TGA were carried out on the different formulations reveals that the initial decomposition temperature of plasticized PLA with different concentrations of citrate esters is lower compared to neat PLA. While the kinetics of degradation shows that the plasticized PLA are stable within the range of interest (130 °C). However, the initial decomposition temperature of PLA shifts systematically to lower temperature when citrate esters are added. This shift is globally more important when the amount of plasticizer is higher. For example, a shift from 295 °C to 141 °C and to 146 °C is observed for the initial decomposition temperature of the plasticized PLA with 30% of TEC and ATBC respectively. The thermal stability of plasticized PLA with ATBC is greater than those with TEC. The T_{max} of the plasticized PLA with ATBC is higher than the treated PLA. The presence of hydroxyl end groups in the PLA oligomer chains was found to be critical for degradation, initiating the chain-scission and decreasing the thermal stability [24, 25]. The range temperature between 284 and 335 °C corresponds to evaporation of plasticizer components, that's where the boiling point of TEC and ATBC is 127 °C and 173 °C respectively, where they appear clearly in DTG of plasticized PLA with 30% of TEC or ATBC.

TABLES

TABLE 1. Thermal properties and crystallinity of treated and plasticized PLA with TEC and ATBC at various concentrations.

Formulation	T_g (°C)	ΔH_{cc} (J/g)	T_{cc} (°C)	ΔH_m (J/g)	T_m (°C)	X_c (%)
Trt PLA	60.42	4.986	130.94	5.240	151.90	0.27
PLA – TEC5	50.48	19.15	120.27	18.46	147.89	0.78
PLA – TEC10	41.20	10.62	114.77	11.46	149.04	1.00
PLA – TEC15	31.21	21.35	104.39	22.48	145.90	1.42
PLA – TEC20	23.56	19.38	91.73	23.07	143.55	4.95
PLA – TEC30	10.29	16.63	71.12	22.22	143.27	8.58
PLA – ATBC5	52.94	22.53	116.03	24.71	146.91	2.46
PLA – ATBC10	44.22	21.33	108.29	24.24	150.04	3.47
PLA – ATBC15	36.67	21.09	101.10	24.73	148.14	4.60
PLA – ATBC20	27.02	20,63	89.03	24.46	146.80	5.14
PLA – ATBC30	12.21	13.97	69.26	19.88	138.41	9.07

T_g: glass transition temperature; T_m: melt temperature; T_{cc}: cold crystallization; ΔH_m: melting enthalpy; ΔH_{cc}: enthalpy of the cold crystallization; X_c: crystallinity.

TABLE 2. Glass transition temperature and FWHM of the treated PLA and plasticized PLA with TEC and ATBC determined by DMA.

Formulation	T_g (°C) from tan δ curve	FWHM (°C)[a]
Trt PLA	62.23	6.48
PLA-TEC5	54.26	6.75
PLA-TEC10	45.91	7.90
PLA-TEC15	38.71	8.70
PLA-TEC20	31.86	18.02
PLA-TEC30	17.49	20.88
PLA-ATBC5	55.24	7.02
PLA-ATBC10	50.08	9.24
PLA-ATBC15	40.84	10.66
PLA-ATBC20	35.69	51.18
PLA-ATBC30	26.91	61.45

[a](FWHM): Full-width half-maximum measured from the tan δ curve.
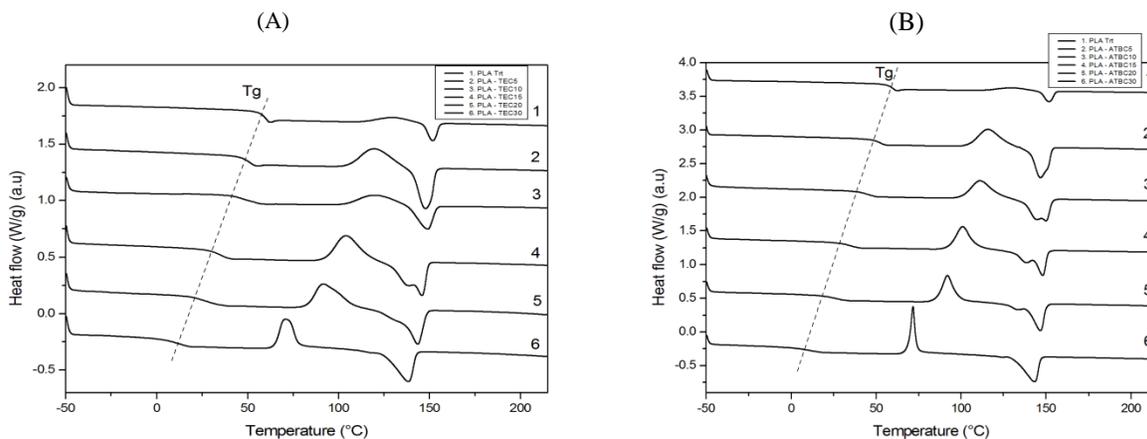
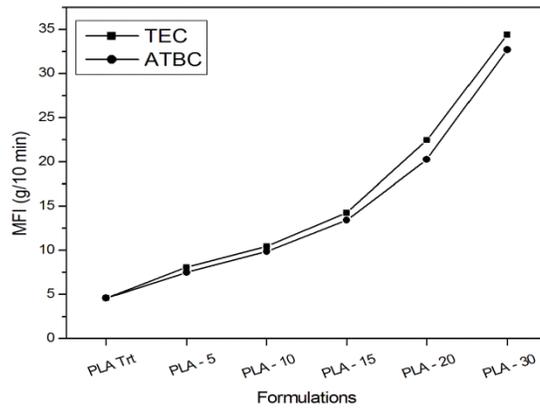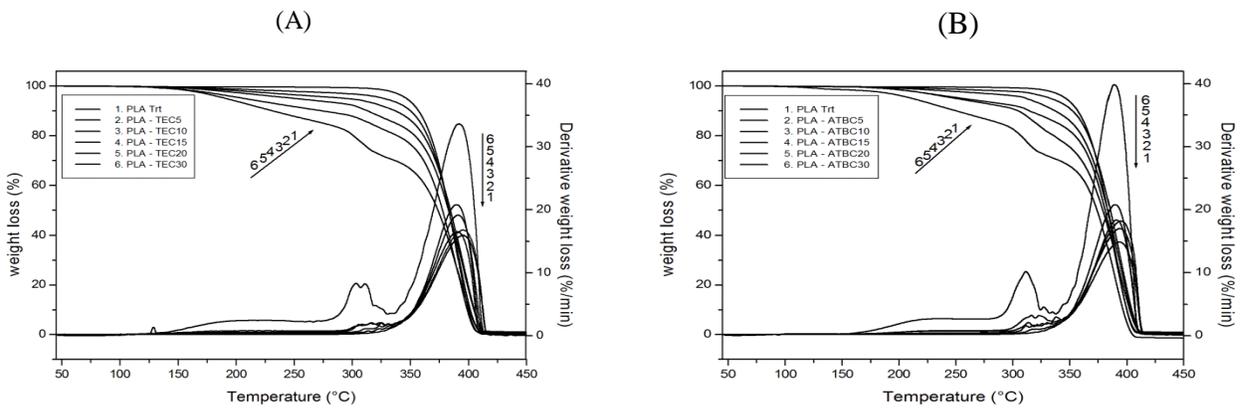# Figures

FIGURE 1. DSC diagrams of treated PLA and plasticized PLA with: (A) - PLA/TEC, (B) – PLA/ATBC at various concentrations.
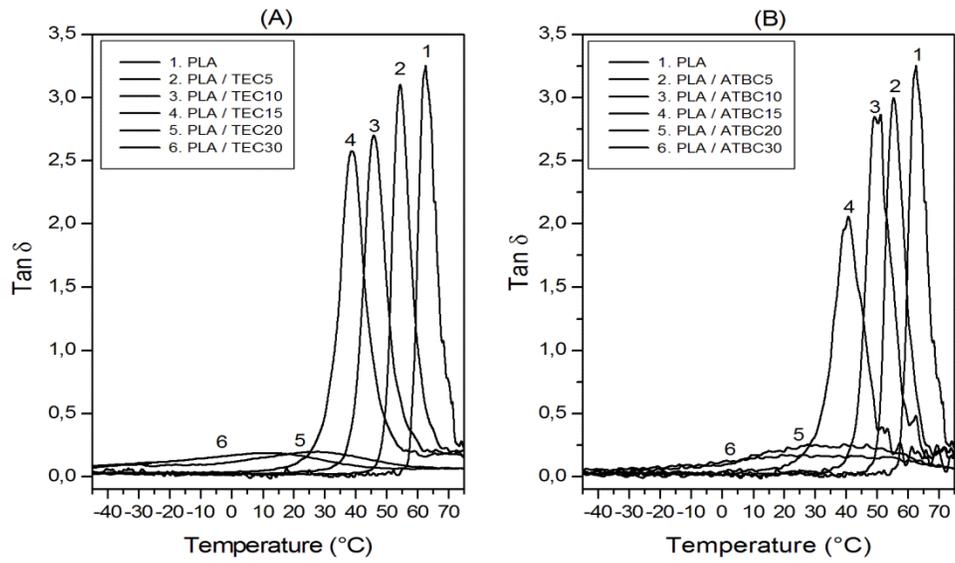
FIGURE 2: Variation of loss factor (tan δ) with temperature of the treated poly (lactic acid) (PLA) and plasticized PLA with: (A) triethyl citrate (TEC) and (B) acetyl tributyl citrate (ATBC) at various concentrations.

FIGURE 3. Variation of MFI of treated PLA and plasticized PLA with various concentrations of TEC and ATBC.

(A)   (B)

FIGURE 4. TGA/DTG thermograms of treated PLA and plasticized PLA with: (A) TEC; (B) ATBC at various concentrations.

CONCLUSIONS

In this study, the characterization of plasticized PLA with TEC and ATBC by using the simple melt blending method was reported. The thermal properties of plasticized PLA shows that TEC and ATBC are effective in lowering the glass transition temperature (T_g), the melting temperature (T_m) and the cold crystallization temperature (T_{cc}) of the PLA. In addition, its crystallinity increases with increasing content of plasticizer. The evaluation of the influence of the type and plasticizer content on the viscoelastic properties of PLA with DMA indicates a decrease in the storage modulus is observed for plasticized PLA, indicating the flexibility and mobility of the amorphous phase of PLA caused by TEC and ATBC. The value of the melt flow index (MFI) was observed for all samples are higher than those of neat PLA. The TGA results indicated that the TEC and ATBC promote a decrease in thermal stability of the PLA.

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