

# Poly(lactic Acid and Poly(Butylene Adipate-Co-Terephthalate) Blends Plasticised with Lactic Oligomers and Epoxy Reactive Plasticizers

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Poly(lactic acid (PLA) is a compostable and sustainable polymer, derived from renewable resources, with high elastic modulus and high transparency. By the way PLA has even some limitations such as low glass transition temperature, low thermal stability, high brittleness, and low crystallization rate. To increase flexibility of PLA based materials it is possible to add low molecular weight plasticizers or prepare blends with another flexible polymer, such as poly(butylene adipate-co-terephthalate) (PBAT). Even the use of a compatibilizer may allow a modulation of mechanical properties thanks to the achievement of a phase morphology characterized by a lower dimension of the dispersed PBAT phase and an increased adhesion. In the present study, blends of PLA and PBAT were prepared by adding different plasticizers combinations based on an oligomer of lactic acid, a polyester of adipic acid and 1,2-propane diol, and an epoxy functionalised resin. All the plasticizers were effective in providing flexibility to the blends, with higher efficiency from the epoxy functionalised plasticizer, and the polyester of adipic acid. Fox's equation showed that all plasticizers have the tendency to disperse more in the amorphous PBAT matrix than in the PLA one.

## 1. Introduction

Environmental concern on plastic waste management is raising, inducing academic and industrial search for valuable materials with sustainable end of life scenario (Cinelli, 2018). World plastic consumption is characterized by a strong growth rate (9% per year) but more negatively by a huge wasting (40% of packaging in EU) and a mismanagement of the produced waste (39% of landfills in EU). There is, thus a high interest to replace the conventional non-biodegradable petro-based plastic, with compostable and possibly carbon dioxide neutral plastics. Commodity plastics have been traditionally preferred for packaging production since they present good mechanical performances (tensile and tear strength), heat stability, good barrier properties, high availability and a relative low cost. Nevertheless, their end-life management is raising problems because only a limited fraction (less than 30%) is collected and recycled, mainly for single materials packaging.

Poly lactic acid (PLA) has attracted the interest of packaging producers being one of the cheapest and most available bio-based, compostable polymers in the market (Cinelli, 2017). PLA is produced from renewable resources, is recyclable (Seggiani, 2016) and industrially compostable (Auras, 2004) and presents relatively high tensile strength and elastic modulus values, whereas the elongation and flexibility are low.

PLA mechanical properties can be tuned by addition of low molecular weight plasticizers such as lactic acid oligomers (Burgos, 2013), additives (Cicogna, 2017) or by blending with a more flexible polymer such as poly(butylene adipate-co-terephthalate) (PBAT) (Mallegni, 2018). It is valuable to consider that even for PBAT, researches on its production by renewable resources are advanced, and the industrial synthesis of its monomers is almost achieved.

In view of their complementary properties, blending PLA with PBAT becomes a natural choice to improve PLA properties without compromising its biodegradability (Jiang, 2006). Use of compatibilizers was demonstrated to allow for a better modulation of properties thanks to the achievement of a phase morphology characterized by a lower dimension of the dispersed PBAT phase and an increased adhesion (Signori, 2009).

## 2. Experimental

Poly (lactic acid) (PLA) containing 4.5% of D-lactic acid units, was PLA INGEO™ 2003D from Natureworks LLC, (Minnetonka, MN, USA) having a nominal average molecular weight  $M_w = 199,590$  and a density of  $1.24 \text{ g/cm}^3$ . Poly (butylene adipate-co-terephthalate) (PBAT) was the product F Blend C1200 purchased from BASF, Ludwigshafen (GE). Polypropyleneglycol diglycidyl ether (EJ) (Figure 1) used as reactive plasticizer was EJ-400 Glyether® Resin purchased from Jsi Co., Ltd., Pyeongtaek, Gyeonggi, Korea.

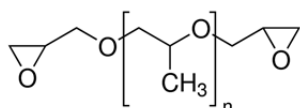


Figure 1. Structure of Polypropyleneglycol diglycidyl ether (EJ400),

OLA 2 is a low molecular weight modified PLA having a  $M_w = 1200$ , density  $1.10 \text{ g/cm}^3$  ( $25^\circ \text{C}$ ) (Figure 2), while Glyplast®206/3NL is a polyester of adipic acid and 1,2-propane diol low molecular weight ( $M_w = 3400$ ) () both produced by Condensia Quimica SA, Spain.

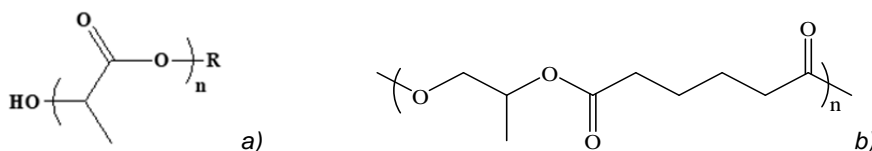


Figure 2. Structure of a) Oligomeric lactic acid OLA2, and b) Glyplast 206/3NL

Blends based on PLA-PBAT with reactive e non-reactive plasticizer were extruder using a MiniLab II HAAKE™ Rheomex CTW 5 conical twin-screw extruder (Thermo Fisher Scientific, Waltham, MA, USA). Previous studies outlined a good performance of epoxy plasticizer EJ400. When used in low amount, they allowed the reduction of non-reactive plasticizers amount such as 206NL and OLA2, which are significantly cheaper but easier to migrate and leach (Cicogna 2007, Mallegni 2008). Main compositions of the produced blends are reported in Table 1.

Table 1: Blends composition as percentage by weight (%wt)

Blend	Matrix wt%	EJ400	OLA2	206/3NL
PBEO5-10	[PLA(67%wt.)+PBAT(18%wt.)]	85	5	10
PBEN5-10	[PLA(67%wt.)+PBAT(18%wt.)]	85	5	-
PBEO10-5	[PLA(67%wt.)+PBAT(18%wt.)]	85	10	5

The blends were extruded at  $180^\circ \text{C}$  with a screw speed of 60 rpm, extrusion time was 60 s. During the extrusion the value of torque was recorded, taking a measure every 10 s, on a total mixing time of 60s.

After extrusion, the molten materials were transferred through a preheated cylinder to the HAAKE™ MiniJet II mini injection moulder, with mould at  $60^\circ$  for 20s (Thermo Fisher Scientific, Waltham, MA, USA), to obtain Haake Type 3 dog-bone tensile bars, in accordance with the ASTM D638 V. The dimension of the dog-bone tensile bars was: width in the larger section: 10 mm, width in the narrow section: 4.8 mm, thickness 1.35 mm, length 90 mm. Stress-strain tests were carried out at room temperature, with an Instron 5500R universal testing machine (Canton, MA, USA) equipped with a 10 kN load cell and interfaced with a computer running the Testworks 4.0 software (MTS Systems Corporation, Eden Prairie MN, USA), at a crosshead speed of 10 mm/min. At least five replicates for each sample were carried out at room temperature.

The thermal analysis was performed using Differential scanning calorimetry (DSC) Q200 differential scanning calorimeter from TA Instruments—Waters LLC, New Castle, DE (USA), equipped with RSC cooling system and a nitrogen gas purge set at 50 mL/min flow rate was used for all of the calorimetric measurements. The sample masses varied from 11 to 15 mg. The following thermal procedure was used: ramp 10 °C/min from -30 °C to 220 °C, isotherm at 220 °C for 3 min, ramp 10 °C/min from 220 °C to -75 °C, isotherm at -75 °C for 3 min, ramp 10 °C/min from -75 °C to 220 °C.

Melt processing and mechanical properties of blends containing coupled plasticizers, selected for further industrial exploitation, were investigated, while for the study of the solubility of the plasticizers in respectively PLA and PBAT, PLA/PBAT blends with single plasticizers were analyzed.

### 3. Results

#### 3.1 Melt processing of the blends

The values of torque during the melting of the blends allow the estimation of the blending ability, with the torque value directly connected to the viscosity of the molten material (Gu, 2008). In Table 2 are reported the values of torque for the studied blends.

Table 2: Torque values (Nm) in the selected blends

Time	0 s	10s	20s	30s	40s	50s	60s	Average
PBEO5-10	81	79	77	76	78	77	76	78
PBEN5-10	81	74	70	70	70	68	67	71
PBEO10-5	72	64	63	64	63	61	61	64

The blend with the combination of 5% OLA2 and 10% EJ400, presented relatively lower values of torque resulting more fluid than the other mixture with 5%EJ400 and respectively 10%OLA2 or 10% 206/3NL. Between OLA2 and 206/3NL, the last one presents lower values of torque, letting envisage a higher plasticising action.

#### 3.2 Mechanical properties

Both mixtures were processed in dog bone specimen used for the tensile tests. The results of mechanical properties are reported in Table 3.

Table 3: Mechanical properties of the selected blends

	E(GPa)	$\epsilon_Y$ (%)	$\sigma_Y$ (Mpa)	$\epsilon_B$ (%)	$\sigma_B$ (Mpa)
PBEO5-10	2.1±0.3	2.6±0.1	41.2±2	2.6±0.1	27.4±3
PBEN5-10	1.0±0.2	6.0±0.5	35.0±1	210.5±15	22.4± 2
PBEO10-5	1.5±0.2	3.0±0.1	34.3±2	111.0±23	23.5± 1

Y= Yield, B= Break

The blends containing 10% OLA2, and 5% EJ400 appear more suitable for semi-rigid materials and sheets, having a moderate elongation at break, and a relatively high modulus and strength, while for the blends with 10% 206/3NL and 5% EJ400, very high values of elongation at break are achieved, together with valuable tensile and modulus values, compatible for application in soft packaging. The mechanical properties confirm a highest effect of plasticisation in the blend with 10% of EJ400 and 5% OLA2 versus the reverse composition, with very high values of elongation at break achieved, and valuable values for modulus and strength. This formulation is also very interesting for the production of flexible items.

#### 3.3 Differential scanning calorimetry

Differential scanning calorimetry was performed on the polymeric blend PLA/PBAT and on the raw plasticizers OLA2, 2063NL and EJ400. In addition, blends PLA/PBAT with OLA2, or 2063NL or EJ400 were prepared and analysed in order to investigate the diffusion of single plasticizers in PLA or in PBAT. The blend of the polymeric matrix PLA/PBAT (78.8/21.2 by weight) confirmed the presence of immiscible phases, as reported in Figure 2. In the analysis the T<sub>g</sub> of PBAT can be observed near to -33 °C, while the T<sub>g</sub> of PLA is observed near to 60 °. The two distinct glass transition temperatures prove the immiscibility of the two polymers.

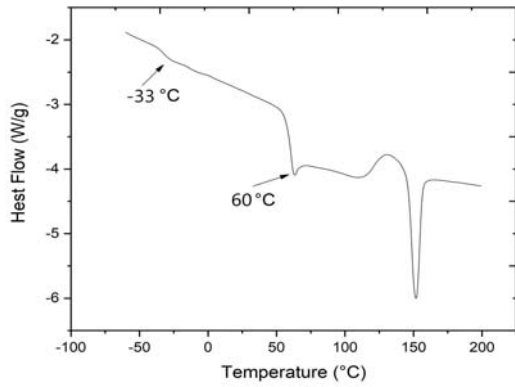


Figure 2. DSC analysis of PLA/PBAT blend

Figure 3 shows the DSC scan of the blend PLA/PBAT/OLA2 (70.5/19/10.5 wt%). A plasticizer percentage of about 10% was proved to be the amount required to produce a significant effect on the processing and mechanical properties. For this blend the glass transition temperature of PLA was 54 °C, evidencing a plasticizing effect. Figure 3 displays also the DSC curve of PLA/PBAT/2063NL (70.5/19/10.5 wt%). The  $T_g$  of this blend is 49 °C, as well as that of the blend PLA/PBAT/EJ400 (74.5,20,5.5 wt%). For both the blends, a significant plasticizer effect is observed.

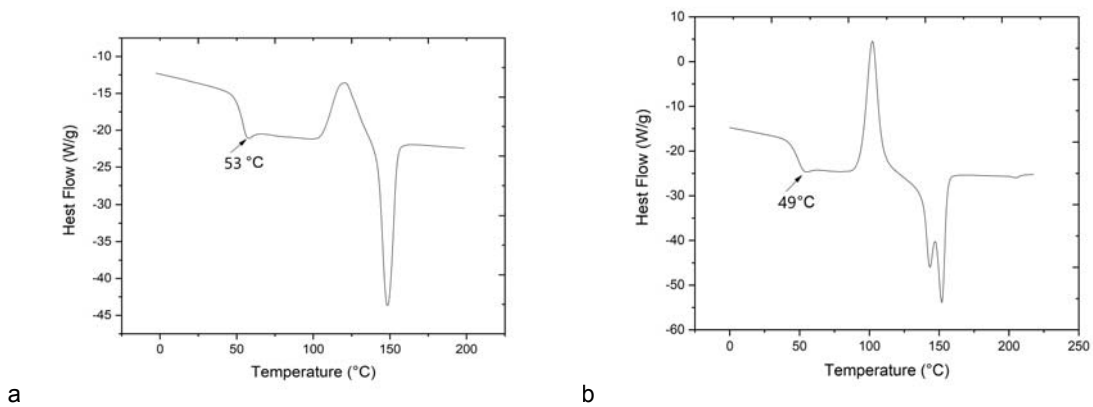


Figure 3. DSC analysis of PLA/PBAT/OLA2 and PLA/PBAT/2063NL blends.

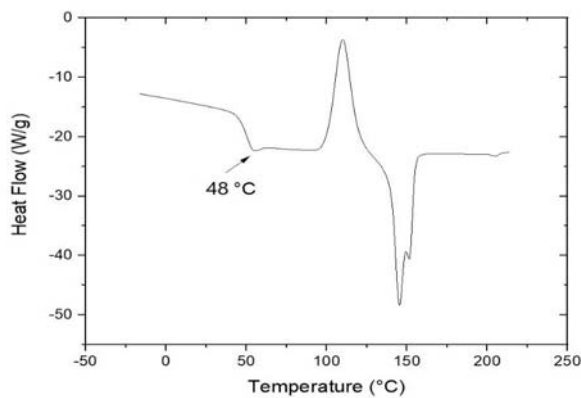


Figure 4 DSC analysis of PLA/PBAT/EJ400

Several equations were proposed to describe the  $T_g$  change in polymeric mixtures as a function of composition. One of the most used is the Fox's equation (Fox, 1956):

$$(1/T_g \text{ blend}) = (W_A/T_{gA}) + (W_B/T_{gB}) \quad (1)$$

where  $T_{gA}$  and  $T_{gB}$  are the glass transition temperatures of the two components, expressed in Kelvin, and  $W_A$  and  $W_B$  are the corresponding weight fractions. As PLA and PBAT are immiscible, the Fox equation was applied to evaluate the plasticizer percentage in the separate PLA, by taking into account the  $T_g$  depression of PLA.

*Table 4: Density, and glass transition temperature of mixture where fox's equation was applied*

	$\rho$ (g/cm <sup>3</sup> )	$T_g$ (K)
PLA	1.24	333
PBAT	1.26	240
OLA2	1.10	267
EJ400	1.14	266
206/3NL	1.09	268
PLA-PBAT-OLA2	-	327
PLA-PBAT-EJ400	-	322
PLA-PBAT-206/3NL	-	321

By means of the Fox's equation, percentages of 8 wt% of OLA2, 13 wt% of EJ400 and 15 wt% of 206/3NL were found dissolved in PLA. This means that all plasticizers disperse mainly in PBAT that is known to be an amorphous polymer. It is also interesting that the lower amount of EJ400, lowers the glass transition temperature of PLA in the blend more than the higher amount of OLA2, in agreement with what observed in the effect of EJ400 on the mechanical blends.

#### 4. Conclusions

Three different plasticizers were compared to improve process ability and tune mechanical properties in PLA/PBAT based blends. Both oligomeric lactic acid plasticizer OLA2, adipic acid derivatives (206/3NL) and epoxy plasticizer EJ400 resulted efficient in lowering glass transition temperature of PLA, in lowering viscosity of the molten material thus favouring process ability in the melt, as well as in providing flexibility in the produced materials.

The formula with higher content of OLA2 (10%) and lower content of EJ400 (5%) has properties more valuable for rigid packaging while blends with 206/3NL (10%) - EJ400 (5%) and with OLA2 (5%) - EJ400 (10%) is more valuable for flexible, soft packaging.

All the plasticizers have tendency to disperse in higher amount in the amorphous PBAT phase respect to the more crystalline PLA phase.

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#### References

- Auras R., Harte B., and Selke S., 2004, An Overview of Polylactides as Packaging Materials, *Macromolecular Bioscience*, 4, 835–864.
- Burgos N., Martino V.P., Jiménez A., 2013, Characterization and ageing study of poly(lactic acid) films plasticized with oligomeric lactic acid, *Polymer Degradation and Stability* 98, 651-658.
- Cicogna F., Coiai S., De Monte C., R. Spiniello, Fiori S., Braca F., Franceschi M., Cinelli P., Lazzeri A., Fehri S.M.K., Oberhauser W., Passaglia E., 2017, PLA plasticized with low molecular weight polyesters: structural, thermal and biodegradability features, *Polymer International*, 66(6), 762-769.
- Cinelli P., Coltelli M.B., Mallegni N., Morganti P.F. Lazzeri A. 2017, Degradability and sustainability of nanocomposites based on polylactic acid and nanochitin. *Chemical Engineering Transaction* 60, ISBN 978-88-95608-50-1, ISSN 2283-9216.

- Cinelli P., Coltelli M.B., Lazzeri A., 2018, Chapter.7, Biodegradable and Biobased Polymers: Definitions, Standards, and Future Perspectives, In *Bionanotechnology to Save the Environment; Plant and Fishery's Biomass as Alternative to Petrol*; Morganti, P., Ed.; MDPI: Basel, Switzerland, 105-124.
- Coltelli, M.-B.; Gigante, V.; Cinelli, P.; Lazzeri, A. 2018, Chapter 15 Flexible Food Packaging Using Polymers from Biomass. In *Bionanotechnology to Save the Environment; Plant and Fishery's Biomass as Alternative to Petrol*; Morganti, P., Ed.; MDPI: Basel, Switzerland, 272–296.
- Fox T.G., 1956, The viscosity of polymers and their concentrated solutions, *Bulletin of the American Physical Society*, 1, 123
- Gu S.-Y., Zhang K., Ren J., Zhan H., 2008, Melt rheology of polylactide/poly(butylene adipate-co-terephthalate) blends, *Carbohydrate Polymers*, 74, 79–85.
- Jiang L., Wolcott M.P., Zhang J., 2006, Study of biodegradable polylactide/poly(butylene adipate-coterephthalate) blends, *Biomacromolecules*, 7, 199-207.
- Mallegni N., Phuong T.V., Coltelli M.B., Cinelli P., Lazzeri A., 2018, Poly(lactic acid) (PLA) based tear resistant and biodegradable flexible films by blown film extrusion, *Materials*, Jan 17; 11(1), 148.
- Seggiani M., Cinelli P., Geicu M., Popa Mona E., Puccini M., Lazzeri A. 2016, Microbiological Valorisation of Bio-composites Based on Polylactic Acid and Wood Fibre, *Chemical Engineering Transaction* 49, 127-132.
- Signori, F.; Coltelli, M.B.; Bronco, S.; Ciardelli, 2009, F. Thermal degradation of poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) and their blends upon melt processing. *Polymer Degradation Stability* 94, 74–82.