Polylactides with "Green" Plasticizers: Influence of Isomer Composition

Veluska Arias, Anders Höglund, Karin Odelius, Ann-Christine Albertsson

Department of Fiber and Polymer Technology, KTH Royal Institute of Technology, 100 44, Stockholm, Sweden
Correspondence to: A.-C. Albertsson (E-mail: aila@polymer.kth.se)

ABSTRACT: Synthesized polylactides (PLA) with different D-isomer contents in the polymer chain were melt-blended with a series of "green" plasticizers by extrusion. Mechanical and thermal properties as well as the morphology of the plasticized materials were characterized to demonstrate how the combination of PLA with different D-contents and plasticizer controls the material properties. After addition of acetyl tributyl citrate (ATC), the elongation at break for PLA with a low D-isomer content was twice as high as that for PLAs with high D-isomer contents. Similar variations in the plasticization effect on the PLAs were also observed with the other plasticizers used, glyceryl triacetate (GTA), glycerol trihexanoate (GTH) and polyethylene glycol (PEG). In order to continue with the development of renewable polymers in packaging applications, the interrelation between a plasticizer and a specific polymer needs to be understood. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2962–2970, 2013

INTRODUCTION

One of the key steps in the development of industrial production of polylactide (PLA) was the introduction of some percentage of D-units in the poly(L-lactide) chain.[1–3] The mechanical properties of PLA mainly depend on the isomer composition and also on the processing conditions.[4] The small percentage of D-isomer increases the chain flexibility and lowers the glass transition temperature (T_g), resulting in a less brittle material. As a consequence, the melting temperature and the degree of crystallinity (necessary for physical cross-linking giving strength to the material) also decrease with increasing content of the D-isomer.[5–8] In addition, the degradation of industrial PLA with a small amount of D-units in the PLA-chain is significantly faster than that of laboratory-scale PLLA.[3]

A general approach to overcome the brittle nature of PLA includes copolymerization,[9–11] blending,[12–14] surface modification,[15,16] and plasticization.[17,18] Many different types of plasticizers have been used in the PLA matrix; but, they need to meet some specifications regarding the final application. In the case of food packaging, the plasticizer must be approved as non-toxic, should be miscible with the polymer and non-volatile at the processing temperature, and should furthermore not tend to migrate to the polymer surface. Citrate esters are promising candidates as "green" plasticizers for PLA, as they are derived from the natural compound citric acid, are non-toxic and have been approved in applications such as personal care and food

contact.[19–21] Glycerol and its derivatives are aliphatic alcohols that are known to be non-toxic.[22] Polyethylene glycol (PEG) is a polyether used in several fields due to its biocompatibility and water-soluble character. In addition, low molar mass PEG has been widely used as a plasticizer for PLA due to its miscibility and the fact that it is approved for food packaging applications.[23] However, previous work on plasticization of PLA was mainly done with solution-cast films and/or industrial PLA, no attention being paid to the amount of D-isomer in the material. Industrial PLA is actually a stereocopolymer where the percentage of the D-isomer improves the material properties and also facilitates processing. A similar strategy is well-known for poly(vinyl chloride) (PVC) that already in the 1920s was copolymerized with vinyl acetate for improved processability. More recently, it was demonstrated that the plasticizing effect of different phthalates was dependent on PVC stereoregularity.[24]

The aim of this study was to reveal the influence of stereoregularity of PLA on the plasticizing effect of a series of green plasticizers. Our hypothesis was that the choice of a plasticizer and its effect would be highly dependent on the content of D-isomer in the polylactide bulk. Herein, we demonstrate the importance of choosing a specific plasticizer adapted for a particular polylactide. To ensure full control over the material properties, polylactides with different D-isomer contents were synthesized. The materials were subsequently modified with a series of "green" plasticizers with some differences in their chemical structures. Low molar

Additional Supporting Information may be found in the online version of this article.

mass poly(ethylene glycol) (PEG) was chosen as a reference due to its extensive use as a PLA plasticizer. To resemble the polymer behavior in industrial processes, the plasticization was performed by extrusion and not solution-casting. Hence the results are transferable to either a pilot-plant or an industrial scale.

The results demonstrate that the effect of a given plasticizer on the material properties of PLA greatly depends on the D-isomer content in the polymer chain. For a specific PLA with a determine D-isomer content, a specific plasticizer was significantly better than the others.

EXPERIMENTAL

Materials

The monomers used were L-lactide (Boehringer Ingelheim, France) and D-lactide (Purac, The Netherlands) and they were purified by recrystallization in dry toluene. Ethylene glycol (EG) and stannous octoate (Sn(Oct)$_2$) were used as initiator and catalyst, respectively. The plasticizers acetyl tributyl citrate (ATC) (Sigma Aldrich, Sweden), glyceryl triacetate (GTA) (Sigma Aldrich, Sweden), glycerol trihexanoate (GTH; TCI, Belgium), and polyethylene glycol (PEG) with a number average molecular weight (M_n) of 1000 g mol^{-1} (Sigma Aldrich, Sweden; Figure 1) and the solvents hexane (Fisher Scientific, Sweden), methanol (LabScan, Ireland), toluene (Fisher Scientific, Sweden), and chloroform (Fisher Scientific, Sweden) were used as received. Hansen solubility parameters and boiling points for the plasticizers are shown in the Supporting Information Table S1.

Synthesis of Polylactide (PLA)

Polylactides (PLA) with different contents of D-isomer were synthesized by ring-opening polymerization of L-lactide and D-lactide monomers in bulk at 110°C during 72 h under continuous stirring according to a procedure described earlier.[25] The content of D-isomer in the monomer feed ratio was set to 0, 2.5, 5, 7.5, and 10% (mol/mol).

Materials Preparation

Extrusion. The PLA materials were blended with the plasticizers using a twin-screw mini-extruder (DSM Xplore 15 micro-compounder, Model 2005). The temperature gradient from the feed throat to the die was set to 168/168/170°C and the outlet temperature was 160°C. The screw speed was 80 rpm and the extrusion time was 3 min. A 10 g of material was pre-blended in 200 mL of chloroform using a plasticizer concentration of 10% (w/w). Blends with 5% (w/w) of ATC were also prepared. The solutions were cast in petri dishes and the solvent was allowed to evaporate for 1 week. The obtained films were thereafter cut into small pieces in order to fit in the extruder feeder. Before extrusion, the samples were pre-dried overnight at 40°C under vacuum in order to minimize degradation during processing. PLA without plasticizer was also processed as reference using the same conditions.

Melt-press. The extruded materials were melt-pressed into films using a hot press (Fontijne Presses). A 3 g of material was placed in a square mold with dimensions 15 cm × 15 cm. The temperature was set to 180°C and the melt-pressing was performed under a nitrogen atmosphere for 1 min with a pressing force of 200 kN.

Size Exclusion Chromatography (SEC)

The molar mass and the polydispersity index of the materials before and after processing were evaluated using a Verotech PL-GPC 50 Plus system with a PL-RI Detector and two Mixed-D (300 × 7.5 mm) columns from Varian. The samples were injected with a PL-AS RT Autosampler for PLGPC 50 Plus using chloroform as the mobile phase (1 mL min^{-1}, 30°C). Polystyrene standards with a narrow molar mass distribution in the range of 580–400,000 g mol^{-1} were used for calibration. Corrections for flow rate fluctuations were made using toluene as an internal standard. Cirrus^{TM} GPC Software was used to process the data.

Nuclear Magnetic Resonance (NMR)

The composition of the materials after extrusion was evaluated by ^{1}H NMR by comparing the peak intensities of the plasticizers and the PLA. ^{1}H NMR spectra were obtained using a Bruker Advance DPX-400 Nuclear Magnetic Resonance spectrometer operating at 400 MHz. The samples were prepared by dissolving
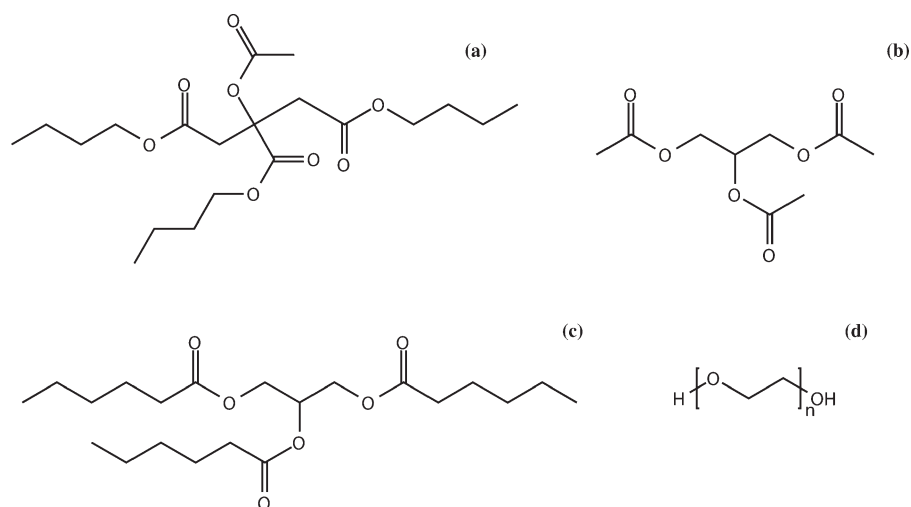

Figure 1. Molecular structures of the plasticizers used: (a) acetyl tributyl citrate (ATC), (b) glyceryl triacetate (GTA), (c) glycerol trihexanoate (GTH), and (d) polyethylene glycol (PEG).

15 mg of the material in 1 mL of deutero-chloroform (CDCl$_3$) in a 5 mm diameter tube. Non-deuterated chloroform was used as an internal standard (δ = 7.26 ppm).

^{1}H NMR (400 MHz, CDCl$_3$ δ): PLA: 5.13 (q, 3H, COCH$_2$ (–CH$_3$)O);[26] ATC: 2.07 (s, 3H, CH$_3$CO$_2$C[CO$_2$(CH$_2$)$_3$CH$_3$] [CH$_2$CO$_2$(CH$_2$)$_3$CH$_3$]$_2$);[27] GTA: 2.03 (s, 9H, (CH$_3$COOCH$_2$)$_2$ CHOCOCH$_3$);[28] GTH: 2.32 (td, 6H, [CH$_3$(CH$_2$)$_4$COOCH$_2$]$_2$ CHOCO(CH$_2$)$_4$CH$_3$);[29] PEG: 3.62 (s, 4H, H(OCH$_2$CH$_2$)$_n$OH).[26]

Polarimetry

The amount of D-isomer in the synthesized PLAs was determined using an AUTOPOL IV Automatic Polarimeter (Rudolph Research Analytical, New Jersey). The different PLA materials were dissolved in chloroform at a concentration of 1 g/100 mL. Sample solutions were transferred to 100 mm cells and analyzed at a standard wavelength of λ = 589 nm. The percentage of D-isomer was calculated using the following equation:

$$\%D = \frac{[\alpha]_{PLLA} - [\alpha]_{PDLLA}}{2[\alpha]_{PLLA}} \times 100 \qquad (1)$$

where $[\alpha]_{PLLA}$ is the specific rotation for PLLA and $[\alpha]_{PDLLA}$ is the specific rotation for the unknown sample.[30]

Differential Scanning Calorimetry (DSC)

The thermal properties of the plasticized materials were measured on a Mettler Toledo DSC 820 module. A 4–7 mg of polymer was weighed in 40 μL aluminum crucibles without pin. The temperature program used was: (i) heating from -20°C till 200°C, (ii) cooling from 200°C to -20°C, and (iii) heating from -20°C to 200°C. The heating and cooling rates were 40°C min^{-1} under a nitrogen atmosphere (50 mL min^{-1}). This cooling rate was selected due to that no crystallization peak was observed at a lower cooling rate (10°C min^{-1}). The glass transition temperature, T_g, was determined from the midpoint temperature of the glass transition of the first heating scan. The degree of crystallinity of the PLAs was calculated according to the equation:

$$w_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \qquad (2)$$

where w_c is the degree of crystallinity, ΔH_f is the heat of fusion of the sample and ΔH_f^0 is the heat of fusion of 100% crystalline PLLA (93 J g^{-1}).[31]

Tensile Testing

Tensile tests on the melt-pressed films were carried out using an INSTRON 5566 module according to the ASTM D638-10 standard. Strips with a width of 5 mm width and a length of 50 mm were cut from the melt-pressed films and eight specimens were tested for each material. The measurement was performed with a 500 N load cell at a strain rate of 20 mm min^{-1}. The samples were preconditioned at 23°C and 50% RH for 40 h according to the standard ASTM D618-08 prior to testing.

Scanning Electron Microscopy (SEM)

The morphology of the cross-section area of the polylactides was evaluated by means of a Hitachi S-4800 SEM using an acceleration voltage of 1.5 kV. The samples were mounted on metal studs and sputter-coated with platinum-palladium using a Cressington 208HR sputter coater unit.

RESULTS AND DISCUSSION

We here demonstrate the effect of a given plasticizer on polylactides (PLA) with different contents of D-isomer in the polymer chain. To enhance processability and improve the mechanical properties, we have applied a set of "green" plasticizers that have a low molar mass for better miscibility, and also have good availability. The choice of polyethylene glycol (PEG) as a plasticizer was based on the large amount of research that has been reported, and this enables comparison with previous work.

The characteristics of the different polylactides before and after extrusion were determined to confirm a non-destructive melt blending (Table I). The polymers described are named according to the percentage (mol/mol) of D-isomer in the initial feed. The number average molar masses of the synthesized polymers were all in the same range, and the polydispersity index was narrow in all the cases. All obtained polymers contained low amounts of remaining monomer after purification.

The content of D-isomer was lower than in the initial feed. One possible explanation is transesterification reactions between the polymer chains already formed and the monomers with opposite stereoregularity remaining in the mixture.[32] In addition, unreacted monomers cause a shift in the specific rotation and hence alter the D-isomer content measured by polarimetry. The specific rotation of lactide monomer at 25°C is ($[\alpha]^{25})_{LLA}$ = 285° compared to ($[\alpha]^{25})_{PLLA}$ = 156° for PLA, leading to an underestimation of the D-isomer content.[29] Nevertheless, the content of D-isomer in the PLAs increased in proportion to the amount of D-monomer in the feed. Thus, a representative series of PLA materials were obtained for further processing and analysis.

The M_n of each plasticized polylactide remained in the same range before and after extrusion (data shown in the Supporting Information Table S2). Only a slight increase in the molar mass of the neat PLAs was observed after extrusion (Table I). Thermal degradation of polymers occurs to some extent during processing, and this can lead to cross-linking reactions that may increase the molar mass.[31] In addition, reactions between the PLA and the plasticizer may induce chain coupling.

Thermal analysis of the neat materials showed as expected, that the degree of the crystallinity (w_c) and consequently the melting temperature, T_m, of the PLAs decreased with increasing D-isomer content (Table I). With more than 2.6% of D-isomer in the main chain, the polymers showed no crystallization. The samples PLLA, PDLLA2.5, and PDLLA5 could crystallize whereas samples PDLLA7.5 and PDLLA10 were amorphous (DSC thermograms are shown in the Supporting Information Figure S1). The relatively high T_g values of PDLLA 2.5 and PDLLA5 are probably due to the higher molar mass.

The plasticization of the synthesized polylactides was achieved by an extrusion process. The materials were extruded to avoid the drawbacks commonly associated with plasticized solution-cast films. The amount of plasticizer determined after processing

Table I. Properties of the Neat Polylactides Before and After Extrusion

	Properties before extrusion				Properties after extrusion				
	M_n (g mol^{-1})[a]	PDI[a]	D-content [%(mol/mol)][b]	Conversion (%)[c]	M_n (g mol^{-1})[a]	PDI[a]	T_g (°C)[d]	T_m (°C)[d]	w_c[d]
PLLA	125.2 ± 0.7	1.2 ± 0.001	–	97	146 ± 1	1.1 ± 0.01	53.08 ± 1	169.5 ± 0.04	45.8 ± 2
PDLLA2.5	124 ± 3	1.1 ± 0.04	0.8 ± 0.2	97	134.5 ± 0.7	1.2 ± 0.002	58.9 ± 0.3	158.8 ± 0.1	23.9 ± 3
PDLLA5	154.9 ± 0.7	1.2 ± 0.01	2.6 ± 0.4	99	193.8 ± 2	1.2 ± 0.01	56.8 ± 0.8	147.2 ± 0.1	0.8 ± 0.07
PDLLA7.5	116.5 ± 2	1.2 ± 0.01	3.4 ± 0.01	94	123.7 ± 0.1	1.2 ± 0.001	53.8 ± 0.1	–	–
PDLLA10	116.5 ± 0.7	1.3 ± 0.01	7.3 ± 0.07	99	144.8 ± 0.6	1.3 ± 0.01	50.8 ± 3	–	–

[a] Number average molar mass and polydispersity index determined by SEC before and after extrusion.
[b] D-isomer content in PLA calculated from Polarimetry.
[c] Monomer conversion determined by ^{1}H-NMR.
[d] Thermal properties determined by DSC.

was very close to the initial amount used (data shown in the Supporting Information Table S3).

Mechanical and Thermal Properties of the Plasticized Polylactides

Copolymers of L-lactide and D-lactide have lower glass transition temperatures than those of the corresponding homopolymers.[4] However, PDLLA2.5 and PDLLA5 had a slightly higher T_g than PLLA (Table II), presumably because the materials were quenched during the thermal analysis, leaving no time for a full crystallization of the L-isomer. The amorphous regions therefore contained more L-lactide units giving higher values for the T_g.

The plasticization effect on the thermal and mechanical properties was significantly different for the semi-crystalline and the amorphous PLA materials. In the case of the semi-crystalline PLAs the plasticization by a given additive was different for each material in this group.

An ideal plasticizer improves the ductility while maintaining the original strength of the polymer. The T_g decreased after the addition of plasticizers (Table II). In agreement with our results, it has been reported that a successful plasticization of PLA occurs when the T_g is shifted down to 35°C.[33] Thus, high values for the elongation at break were expected for all the plasticizers. GTA and GTH were the best plasticizers for PLLA, improving both the tensile strength and elongation at break (ε_b) (Figures 2 and 3). The rest of the plasticizers enhanced the tensile strength but had no significant effect on the elongation at break. PEG induced the lowest T_g value for PLLA (40.5°C).

This is comparable to the T_g of 38°C that previously has been found for PLLA plasticized via extrusion, i.e., not solution-cast films, by the addition of 10% (w/w) PEG ($M_n = 1000$ g mol^{-1}) and an elongation at break of about 3%.[23] Non-plasticized PLLA had a T_g of 53.1°C, and adding GTA or GTH decreased the T_g to 45.2°C and 45.0°C, respectively. GTA augmented the elongation at break of neat PLLA (ε_b of 2.4%) by 21 times its original value. GTH, ATC, and PEG improved the elongation at break by 10, 5, and 3 times respectively. This effect is a combination of the different factors related to the decrease in T_g including the solubility of the additive in the PLLA matrix.

The glass transition temperature of PDLLA2.5 was significantly decreased by all the plasticizers, the lowest T_g value (25.3°C) being obtained was with the addition of PEG. The best plasticizers were ATC and GTH with ε_b values of 1510 and 1060%, respectively, in comparison to neat PDLLA2.5 that showed an ε_b of 18%. In the case of PDLLA5, all the plasticizers decreased the T_g, the lowest value being obtained was with GTH (31.8°C). The elongation at break was also increased with good values for both GTH and PEG in the PDLLA5 polymer.

In the case of the amorphous formulations, PDLLA7.5 and PDLLA10, the glass transition temperature decreased in comparison with the neat samples after the addition of plasticizers (Figure 2). The T_g values were in the same range for all the plasticized PLAs in this group. The lowest value was achieved by the addition of PEG with a T_g of 31.7 and 31.2°C for PDLLA 7.5 and PDLLA10, respectively. The ε_b of the non-plasticized PDLLA7.5 and PDLLA10 was 6.3 and 5.7%, respectively. These

Table II. Thermal Properties of the PLAs with the Addition of Plasticizers

	T_g (°C)[a]	w_c[a]	T_m (°C)[a]
PLLA	53.1 ± 1	45.8 ± 2	169.5 ± 0.04
PLLA–ATC [5% (w/w)]	52.9 ± 0.1	54.9 ± 2	177.1 ± 0.1
PLLA–ATC [10% (w/w)]	47.6 ± 2	54.4 ± 0.001	177.5 ± 1
PLLA–GTA	45.2 ± 1	53.3 ± 0.5	175.1 ± 0.04
PLLA–GTH	45 ± 1	56 ± 0.8	181.2 ± 3
PLLA–PEG	40.5 ± 3	52 ± 5	183.3 ± 0.1
PDLLA2.5	58.9 ± 0.3	23.9 ± 3	158.8 ± 0.1
PDLLA2.5–ATC [5% (w/w)]	46 ± 2	33.5 ± 5	158 ± 2
PDLLA2.5–ATC [10% (w/w)]	33.5 ± 0.1	30.2 ± 0.1	156.1 ± 0.1
PDLLA2.5–GTA	36.2 ± 0.2	34.3 ± 0.1	153.7 ± 0.4
PDLLA2.5–GTH	32.9 ± 1	31.8 ± 1	155.9 ± 0.1
PDLLA2.5–PEG	25.3 ± 1	32.9 ± 0.4	158.7 ± 0.1
PDLLA5	56.8 ± 0.8	0.9 ± 0.1	147.2 ± 0.1
PDLLA5–ATC [5% (w/w)]	51.2 ± 3	5.8 ± 1	148.8 ± 2
PDLLA5–ATC [10% (w/w)]	41.2 ± 0.3	15.1 ± 1	147.6 ± 0.2
PDLLA5–GTA	41.3 ± 0.7	7.3 ± 1	144.4 ± 0.9
PDLLA5–GTH	31.9 ± 0.04	24.6 ± 0.3	147.5 ± 0.03
PDLLA5–PEG	34.7 ± 1	25.7 ± 2	150.1 ± 0.1
PDLLA7.5	53.8 ± 0.1		
PDLLA7.5–ATC [5% (w/w)]	40.6 ± 3		
PDLLA7.5–ATC [10% (w/w)]	34.7 ± 0.2		
PDLLA7.5–GTA	34.8 ± 4		
PDLLA7.5–GTH	32 ± 3		
PDLLA7.5–PEG	31.7 ± 0.3		
PDLLA10	50.8±3		
PDLLA10–ATC [5 % (w/w)]	38.8 ± 0.2		
PDLLA10–ATC [10% (w/w)]	32.7 ± 0.9		
PDLLA10–GTA	31.8 ± 1		
PDLLA10–GTH	31.5 ± 0.2		
PDLLA10–PEG	31.2 ± 0.9		

[a] Thermal properties determined by DSC analysis. The plasticizer concentration used was 10% (w/w). Samples with variation in ATC content are also shown.

values were surprisingly similar given that the respective amounts of D-isomer were 3.4 and 7.3%. The elongation at break was greater for all the plasticized formulations, where the best plasticizers were ATC and GTA. ε_b of 550 and 518%, respectively, were recorded for PDLLA7.5, and 520 and 580%, respectively, for PDLLA10.

Tensile strength of the polylactides was also studied and related to the degree of crystallinity of the materials under the plasticization effect. All the plasticizers increased the overall degree of crystallinity of the semi-crystalline polymers compared to the neat PLLA, which presented a value of 45.8% (Table II). This is probably due to an increased mobility of the chains that facilitates the crystallization.

The tensile strength of neat PDLLA2.5 and PDLLA5 was higher than that of PLLA, even though the degree of crystallinity was lower (Figure 3). This is probably due to an increase in the entanglement density with increasing amount of co-monomer providing certain toughness to the material.[34] The tensile strength of neat PLLA was very low due to the rapid cooling rate used during the extrusion process. This decreases the degree of crystallinity and therefore the strength of the material. The highest tensile strength values for PLLA were 30.9 MPa after addition of GTA and 31.7 MPa after addition of GTH corresponding to an increased in the w_c to 53 and 56%, respectively. ATC and PEG increased the tensile strength up to 32 and 19 MPa, respectively, and increased the w_c to 54 and 52%, respectively. This is in line with previous work on PEG as plasticizer
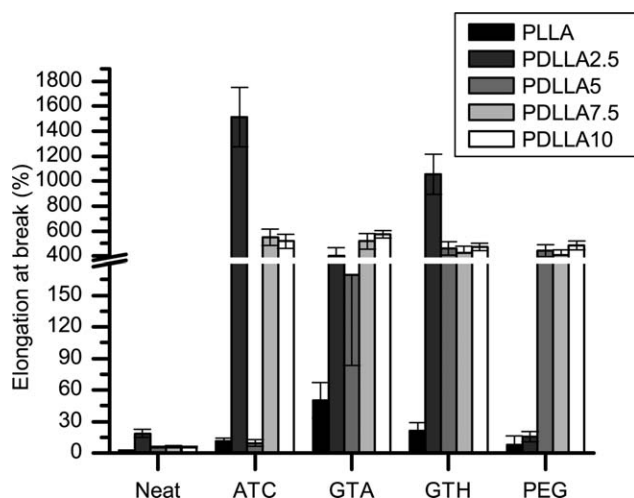
Figure 2. Elongation at break (ε_b) of the different polylactides with the addition of 10% (w/w) plasticizer.

for PLLA, where a higher strength was obtained than for neat PLLA due to a higher crystallinity.[23] In the case of PDLLA2.5, the tensile strength of all the plasticized materials was lower than that of the non-plasticized material. Plasticized PDLLA5 showed a lower tensile strength than that of the neat material, irrespective of which plasticizer was added. However, ATC decreased the tensile strength from 53.8 MPa to only 45 MPa.

As described before, the semi-crystalline polylactides had a degree of crystallinity dependent on the amount of D-isomer. In these polymers, crystalline domains act as physical crosslinks between the polymer chains, and these increase the material strength. The addition of D-units increases the entanglement density and this decreases the physical crosslinks and thus the strength. However, the elasticity of the semi-crystalline polylactides increases with these entanglements. The most favorable mechanical properties are obtained when there is a balance between semi-crystalline domains and entanglements regions.
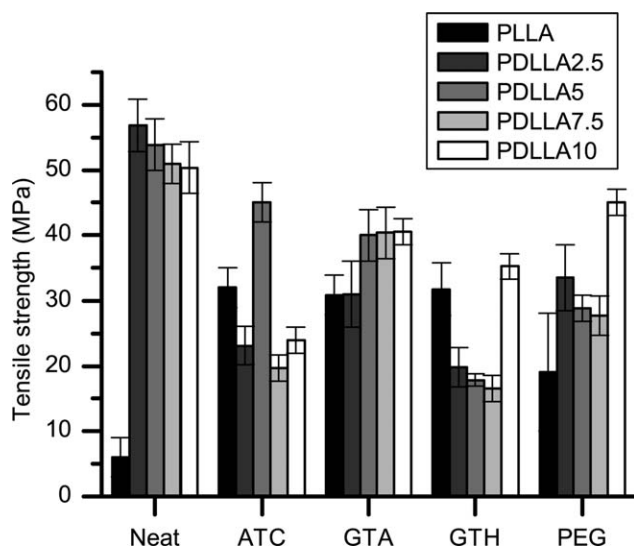

Figure 3. Tensile strength of the different polylactides with the addition of 10% (w/w) plasticizer.

The addition of plasticizers had a different effect in each of the semi-crystalline polylactides, which showed that is important to take the D- and L-isomer ratio into consideration when modifying PLA.

The tensile strength of the amorphous plasticized PLAs was also determined (Figure 3). PDLLA7.5 and PDLLA10 had similar values, 50.9 and 50.4 MPa, respectively. The plasticized materials, showed a behavior dependent on the plasticizer used. In the case of PDLLA7.5, GTA lowered the strength from 50.9 to 40.4 MPa whereas GTH lowered the tensile strength to 16.6 MPa. In the case of PDLLA10, PEG was the plasticizer that maintained the tensile strength closest to that of the non-plasticized material (45.1 MPa in comparison to 50.4 MPa). GTA lowered the strength to 40.5 MPa, while ATC lowered the tensile strength to 24 MPa. Despite these differences, the plasticization effect on the synthesized amorphous polylactides was less dependent on the D-isomer content than that on the semi-crystalline materials.

In conclusion, the addition of plasticizer lowered the tensile strength of all the PLAs containing D-isomer. Only for neat PLLA was the tensile strength improved. The elongation at break increased for all the formulations, and the glass transition temperature decreased for all the polymers with the addition of 10% (w/w) of plasticizer.

Morphology

The morphology of the cross-section area of the polylactides was also studied to evaluate the interaction between plasticizer and the polylactide bulk. Major differences in mechanical and thermal properties were seen for PDLLA2.5 after the addition of the different plasticizers and this material was also the one with the mostly improved elongation at break (Figure 2). Thus, the micrographics of these plasticized samples were selected to illustrate the plasticizing effect (Figure 4).

The morphology of neat PLLA is shown for comparison with the neat PDLLA2.5. As expected, neat PLLA had a rougher cross-section surface in comparison with PDLLA2.5 due to a higher degree of crystallinity.[35,36]

The cross-sections of the plasticized PDLLA2.5 materials showed no phase separation and thereby indicated miscibility between the plasticizer and the polymer matrix. Plasticization occurs when there is good solubility of the plasticizer in the polymer. Here the plasticization of PLA is due to polar interactions between the components. The Hansen solubility parameters of the materials used are for PLA $\delta = 20.1$ (J cm^{-3})$^{1/2}$,[37] for acetyl tributyl citrate (ATC) $\delta = 18.7$ (J cm^{-3})$^{1/2}$,[21] for glyceryl triacetate (GTA) $\delta = 20.2$ (J cm^{-3})$^{1/2}$,[38] for glycerol trihexanoate (GTH) $\delta = 19.27$ (J cm^{-3})$^{1/2}$,[39] and for PEG $\delta = 20.19$ (J cm^{-3})$^{1/2}$.[40] The solubility parameters of the plasticizers and the PLA are all in the same range and, they should hence be miscible.

It has been shown that there is a difference between the Hansen solubility parameters for pure poly(L-lactide) and for copolymers of poly(D,L-lactide). The solubility parameters for lactide-based polymers was investigated by Rissanen et al.,[41] who calculated the Hansen solubility parameters for poly(D,L-lactide) by the contribution method and obtained $\delta = 21.1$ MPa$^{1/2}$ and $\delta = 19.3$ MPa$^{1/2}$ for poly(L-lactide) by the intrinsic three-dimensional
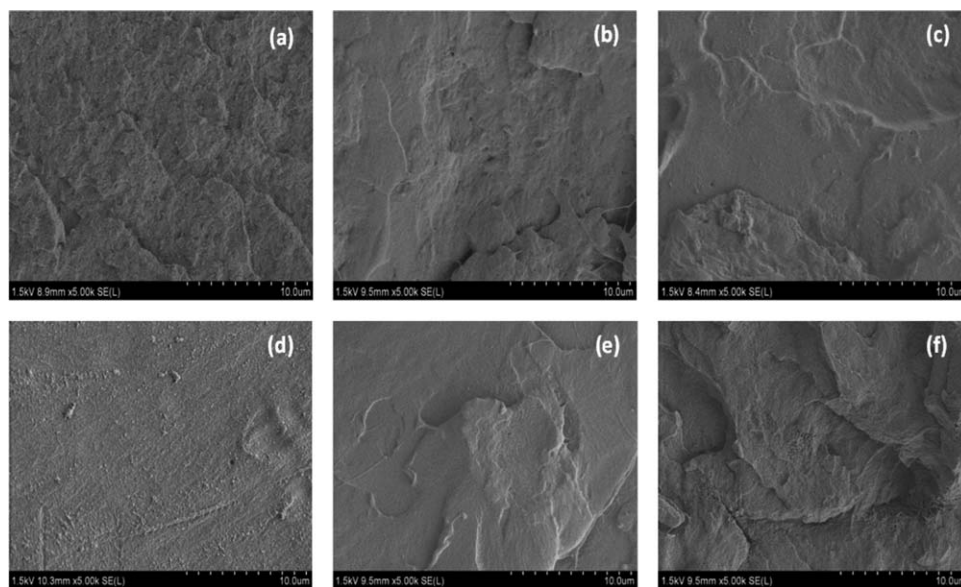
Figure 4. Morphology of the cross-section of: (a) neat PLLA, (b) neat PDLLA2.5, (c) PDLLA2.5 with the addition of 10% (w/w) of ATC plasticizer, (d) PDLLA2.5 with the addition of 10% (w/w) of GTA plasticizer, (e) PDLLA2.5 with the addition of 10% (w/w) of GTH plasticizer, and (f) PDLLA2.5 with the addition of 10% (w/w) of PEG.

viscosity method. The random copolymers of poly(D,L-lactide) are more easily dissolved than isotactic polymers from the pure enantiomers, due to less hydrogen bonding between the chains as a result of the disorder created by the D-isomer. In addition, the Hansen solubility parameters of polymers created from lactic acid or lactide monomers depend on their degree of crystallinity, molar mass, and on the monomer ratio in the polymer.[7]

In this sense, the cross-sections of the plasticized PDLLA2.5 materials were substantially different (Figure 4). PDLLA2.5 with the addition of ATC or GTH resulted in a relatively smooth cross-section whereas the addition of GTA and PEG resulted in a more granular and rough/porous structure respectively. These results are in accordance with the improved elongation at break

(Figure 2). PDLLA2.5 with the addition of 10% (w/w) ATC had a smoother cross-section than the neat PDLLA2.5, yet some crystalline regions are observed. This is in line with the high elongation at break (Figure 2) and the lower tensile strength (Figure 3) in comparison with the neat material.

The rougher cross-section of PDLLA2.5 after the addition of GTA and PEG is related to the increased degree of crystallinity (Table II). In contrast, the sample plasticized with GTH had the smoothest cross-section surface of all materials. This sample had a high elongation at break (Figure 2) but also the lowest tensile strength (Figure 3), the latter due to low amounts of crystalline regions. The morphologies of the cross-sections of the different plasticized PDLA2.5 confirmed the mechanical and thermal properties of the plasticized polylactides.

Variation in Plasticizer Content

To elucidate the amount of plasticizer needed to plasticize the PLAs the effect of plasticizer content on the material properties was determined. ATC contents [5 and 10% (w/w)] were used in combination with the PLA polymers. Analogous to the choice of plasticizer, the amount of plasticizer needed to improve the materials properties was also dependent on the D-isomer content in the PLA formulations.

The decrease in glass transition temperature of all the PLAs was greater with the addition of 10% (w/w) ATC than with 5% (w/w) ATC (Figure 5). This was more pronounced in the case of the semicrystalline polymers, i.e., PLLA, PDLLA2.5, and PDLLA5. In the case of PDLLA7.5 and PDLLA10, the T_g decreased in comparison with the neat sample, but the values with 5 and 10% (w/w) of plasticizer were quite close to each other. For the elongation at break, the major effect was observed with the addition of 10% (w/w) of ATC in PDLLA2.5, PDLLA7.5, and PDLLA10. In the case of PDLLA5, ATC did not change the ε_b in comparison with the neat material.
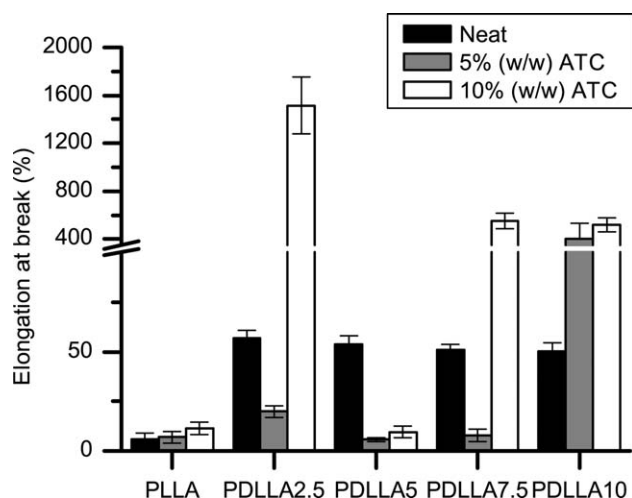

Figure 5. Elongation at break (ε_b) of the polylactides with different amounts of ATC plasticizer.
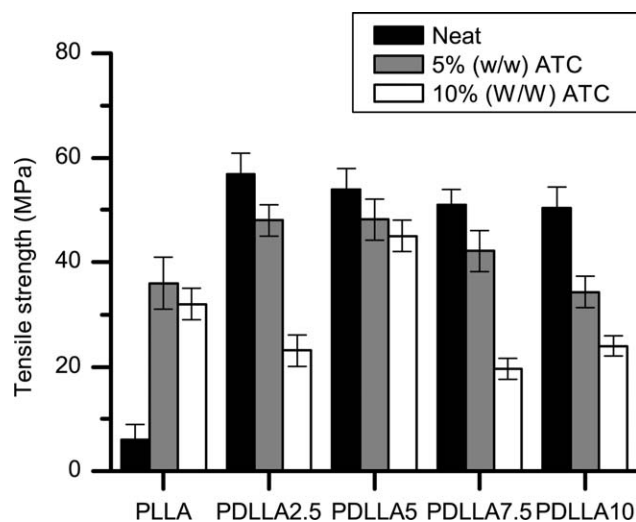
Figure 6. Tensile strength of the polylactides with different amounts of ATC plasticizer.

Different amounts of ATC influenced the tensile strength and the degree of crystallinity of the PLA samples to different extents (Figure 6). The tensile strength of plasticized PLLA was greater than that of the neat material, but no difference was observed between 5 and 10% (w/w) added plasticizer. In contrast, for the PLAs containing D-isomer, the tensile strength decreased with the addition of plasticizer. No significant difference in tensile strength was observed for PDLLA5 when plasticized with 5 and 10% of ATC. For the other PDLLAs, however, adding 10% (w/w) ATC decreased the tensile strength more than the addition of 5% (w/w) ATC. The degree of crystallinity of the plasticized PLLA was the same, regardless of plasticizer concentration (Table II). However, the w_c for PDLLA5 plasticized with 10% (w/w) ATC was approximately three times higher than that of PDLLA5 plasticized with only 5% (w/w) ATC. Thus, the influence of the added amount of ATC on the properties of polylactides was dependent on the content of D-isomer in the polymer.

CONCLUSIONS

The effect of a given plasticizer on the mechanical and thermal properties of polylactide (PLA) was greatly dependent on the D-isomer content in the main chain. For each synthesized PLA, each of the "green" plasticizers used had a different effect. The difference in plasticizer effect on the PLAs was more pronounced with the semi-crystalline than with the amorphous polylactides. Acetyl tributyl citrate (ATC) increased the elongation at break of PLA with 2.5% D-isomer content in the monomer feed (PDLLA2.5) from *ca.* 20 to *ca.* 1500%, whereas the PLA material with 5% D-isomer content (PDLLA5) was not significantly affected. Similarly, the other plasticizers used, GTA, GTH, and PEG, all had different effects on the PLAs. The morphology of the plasticized PDLLA2.5 materials confirmed the different effect obtained for a given PLA with each one of the plasticizers used. The influence of the amount of plasticizer was also dependent on the D-isomer content. For PDLLA2.5, 10% (w/w) of ATC was needed to improve the elongation at break,

whereas for PDLLA10, 5% (w/w) and 10% (w/w) of the same plasticizer had similar effects. The addition of a small amount of D-isomer provides more amorphous regions that enhance the flexibility of the polymer chain. The use of "green" plasticizers would broaden the range of application of polylactide products, since these plasticizers are non-toxic and hence maintain the non-toxic character of the PLA polymer. The importance of choosing the most suitable plasticizer for a particular polymer type was here proven. This constitutes a key issue when designing future renewable materials for packaging applications.

REFERENCES

1. Inkinen, S.; Hakkarainen, M.; Albertsson, A.-C.; Södergård, A. *Biomacromolecules* **2011**, *12*, 523.

2. Anderson, K. S.; Schreck, K. M.; Hillmyer, M. A. *J. Macromol. Sci., Part C: Polym. Rev.* **2008**, *48*, 85.

3. Höglund, A.; Odelius, K.; Albertsson, A.-C. *ACS Appl. Mater. Interf.* **2012**, *4*, 2788.

4. Kwon, M.; Lee, S.; Jeong, Y. *Macromol. Res.* **2010**, *18*, 346.

5. Grijpma, D. W.; Pennings, A. J. *Macromol. Chem. Phys.* **1994**, *195*, 1633.

6. Urayama, H.; Kanamori, T.; Kimura, Y. *Macromol. Mater. Eng.* **2001**, *286*, 705.

7. Urayama, H.; Moon, S.-I.; Kimura, Y. *Macromol. Mater. Eng.* **2003**, *288*, 137.

8. Södergård, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.

9. Chang, K.; Robertson, M. L.; Hillmyer, M. A. *ACS Appl. Mater. Interf.* **2009**, *1*, 2390.

10. Focarete, M. L.; Scandola, M.; Dobrzynski, P.; Kowalczuk, M. *Macromolecules* **2002**, *35*, 8472.

11. Dacko, P.; Kowalczuk, M.; Janeczek, H.; Sobota, M. *Macromol. Symp.* **2006**, *239*, 209.

12. Odelius, K.; Ohlson, M.; Höglund, A.; Albertsson, A.-C. *J. Appl. Polym. Sci.* **2013**, *127*, 27.

13. Wang, Y.; Chiao, S. M.; Hung, T. F.; Yang, S. Y. *J. Appl. Polym. Sci.* **2012**, *125*, E402.

14. Kowalczyk, M.; Piorkowska, E. *J. Appl. Polym. Sci.* **2012**, *124*, 4579.

15. Wu, F.; Ji, D.; Liu, Z.; Yang, W.; Yang, M. *J. Appl. Polym. Sci.* **2013**, DOI: 10.1002/app.38585.

16. Höglund, A.; Hakkarainen, M.; Edlund, U.; Albertsson, A.-C. *Langmuir* **2010**, *26*, 378.

17. Andersson, S. R.; Hakkarainen, M.; Albertsson, A.-C. *Biomacromolecules* **2010**, *11*, 3617.

18. Li, H.; Huneault, M. A. *Polymer* **2007**, *48*, 6855.

19. Höglund, A.; Hakkarainen, M.; Albertsson, A.-C. *Biomacromolecules* **2009**, *11*, 277.

20. Ljungberg, N.; Wesslen, B. *Polymer* **2003**, *44*, 7679.

21. Labrecque, L. V.; Kumar, R. A.; Dave, V.; Gross, R. A.; McCarthy, S. P. *J. Appl. Polym. Sci.* **1997**, *66*, 1507.

22. Ljungberg, N.; Andersson, T.; Wesslen, B. *J. Appl. Polym. Sci.* **2003**, *88*, 3239.

23. Sungsanit, K.; Kao, N.; Bhattacharya, S. N. *Polym. Eng. Sci.* **2012**, *52*, 108.

24. Gonzalez N.; Fernandez-Berridi, M.J. *J. Appl. Polym. Sci.* **2008**, *107*, 1294.

25. Odelius, K.; Plikk, P.; Albertsson, A.-C. *Biomacromolecules* **2005**, *6*, 2718.

26. Ren, J.; Hong, H.; Ren, T.; Teng, X. *React. Funct. Polym.* **2006**, *66*, 944.

27. Sakakura, A.; Kawajiri, K.; Ohkubo, T.; Kosugi, Y.; Ishihara, K. *J. Am. Chem. Soc.* **2007**, *129*, 14775.

28. Yuksel, N.; Baykara, M.; Shirinzade, H.; Suzen, S. *Int. J. Pharm.* **2011**, *404*, 102.

29. Ataide, T. d. R.; Ferreira, d. L. M. R.; Valentim, I. B.; Pinheiro, D. M.; Sant'Ana, A. E. G. *Int. J. Food Sci. Technol.* **2007**, *42*, 1504.

30. Feng, L.-D.; Sun, B.; Bian, X.-C.; Chen, Z.-M.; Chen, X.-S. *Polym. Test.* **2010**, *29*, 771.

31. Lim, L. T.; Auras, R.; Rubino, M. *Prog. Polym. Sci.* **2008**, *33*, 820.

32. Hirata, M.; K. Kobayashi; Y. Kimura. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, 794.

33. Kulinski, Z.; Piorkowska, E. *Polymer* **2005**, *46*, 10290.

34. Grijpma, D. W.; Pennings, A. J. *Macromol. Chem. Phys.* **1994**, *195*, 1649.

35. Liu, L.; Jin, T.; Coffin, D. R.; Liu, C.; Hicks, K. B. *J. Appl. Polym. Sci.* **2010**, *117*, 486.

36. Odelius, K.; Höglund, A.; Kumar, S.; Hakkarainen, M.; Ghosh, A. K.; Bhatnagar, N.; Albertsson, A.-C. *Biomacromolecules* **2011**, *12*, 1250.

37. Ljungberg, N.; Wesslén, B. *J. Appl. Polym. Sci.* **2002**, *86*, 1227.

38. Ren, Z.; Dong, L.; Yang, Y. *J. Appl. Polym. Sci.* **2006**, *101*, 1583.

39. Huynh, L.; Grant, J.; Leroux, J.-C.; Delmas, P.; Allen, C. *Pharm. Res.* **2008**, *25*, 147.

40. Prodduturi, S.; Manek, R. V.; Kolling, W. M.; Stodghill, S. P.; Repka, M. A. *J. Pharm. Sci.* **2005**, *94*, 2232.

41. Rissanen, M.; Puolakka, A.; Nousiainen, P.; Kellomäki, M.; Ellä, V. *J. Appl. Polym. Sci.* **2008**, *110*, 2399.