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Plasticization of poly(lactide) with blends of tributyl citrate and low molecular weight poly(D,L-lactide)-b-poly(ethylene glycol) copolymers

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ABSTRACT

Polylactide (PLA) is a potential candidate for the partial replacement of petrochemical polymers because it is biodegradable and produced from annually renewable resources. Characterized by its high tensile strength, unfortunately the brittleness and rigidity limit its applicability. For a great number of applications such as packaging, fibers, films, etc., it is of high interest to formulate new PLA grades with improved flexibility and better impact properties.

In order to develop PLA-based biodegradable packaging, the physico-mechanical properties of commercially available PLA should be modified using biodegradable plasticizers. To this end, PLA was melt-mixed with blends of tributyl citrate and more thermally stable low molecular weight block copolymers based on poly(D,L-lactide) and poly(ethylene glycol) of different molecular weights and topologies. The copolymers have been synthesized using a potassium based catalyst which is expected to be non toxic and were characterized by utilization of TGA, GPC and NMR techniques.

The effect of the addition of up to 25 wt% plasticizer on the thermo-mechanical properties of PLA was investigated and the results were correlated with particular attention to the relationship between properties and applications.

To confirm the safety of the catalyst used for the preparation of the copolymers, in vitro cytotoxicity tests have been carried out using MTS assay and the results show their biocompatibility in the presence of the fibroblast cells.

Compost biodegradation experiments carried out using neat and plasticized PLA have shown that the presence of plasticizers accelerates the degradation of the PLA matrix.

1. Introduction

Biodegradable polyesters have received much attention over recent decades. Because of their biodegradability and biocompatibility, they were first intensively investigated for biomedical applications. Poly(lactide) (PLA) is one of the most studied polymers of this family because it can be produced via fermentation of renewable resources, like sugar beets or corn starch [1–3]. PLAs were initially investigated for drug delivery, sutures and orthopaedic implant applications [4–12]. Recently, considerable efforts have been made to extend the application of PLA to the packaging field [13–18].

PLA represents a good candidate to produce biodegradable packaging because of its good mechanical properties and processability using most conventional techniques

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and equipment [19,20]. However, low elongation at break and high modulus have limited its application only to the rigid thermoformed packaging industry while for flexible packaging new grades of PLA with specific end-use performances are required. The most important requirements for packaging materials such as films include a high tensile strength, ductility and flexibility at room temperature, transparency, barrier properties, etc.

Attempts have been made to improve the mechanical properties of PLA by copolymerization with other monomers but none of these copolymerization processes is yet economically viable and none is known to produce copolymers on an industrial scale for packaging applications [21–24]. Blending PLA with other polymers/copolymers has also been investigated, however only moderate improvement in mechanical properties was achieved [25–34].

Another way to improve the processability, flexibility and ductility of PLA is the use of plasticizers as for glassy polymers in the plastics industry. The choice of plasticizers to be used as modifiers for PLA is limited by the requirement of the application. Only non toxic substances approved for food contact can be considered as plasticizing agents in food packaging materials. The plasticizer should be compatible with PLA and stable at the elevated temperature used during processing. The PLA/plasticizer blends should be stable over time because the migration of the plasticizer to the surface could be a source of contamination of the food or beverage in contact with the packaging or may possibly regain the initial brittleness of pure PLA.

In the past decade, a large amount of research was devoted to the plasticization of PLA to produce flexible films. Candidates included poly(ethylene glycol) (PEG), citrate esters, glyceryl triacetate, glucosemonoesters, (partially) fatty acid esters, lactide monomer, lactic acid oligomers, etc. have been widely attempted to plasticize PLA [35–48]. Plasticization by lactide monomer has shown a significant increase in the PLA thermal degradation during processing and a rapid migration to the end-product surface [35,48]. PEG was found to be a good plasticizer, but phase separation and its migration to the surface over time results in an unstable PLA/PEG blend [44–47]. Blending PLA with 20–25% of citrates resulted in a material with a glass transition temperature (T_g) well below room temperature and produced a higher elongation at break. For these materials the tensile strength was significantly decreased which makes the material unsuitable for the packaging applications where high stress performances are needed [37–40]. On the other hand, the processing conditions usually require an advanced thermal stability of the PLA-plasticizer compositions and in this context improved formulations are sought.

In the present work we report the plasticization of PLA by blends of tributyl citrate and low molecular weight poly(D,L-lactide)-b-poly(ethylene glycol) copolymers (PLA-b-PEG) of different structures. The effects of the blend composition, as well as copolymer structure/topology, on the thermal and mechanical properties of the final materials are investigated.

Selected examples illustrating the biodegradability of PLA and plasticized PLA compositions in a composting environment as well as the results of the cytotoxicity tests that have been carried out are presented and discussed.

2. Experimental

2.1. Materials

PLA was obtained from NatureWorks (USA). The characteristics of the sample of PLA are as follows: number average molecular weight (M_n) = 81,000, polydispersity index (PD) = 1.54 and L/D isomer ratio of 95/5. Toluene (99%, Aldrich) was refluxed over CaH_2 and distilled prior to use. D,L-lactide (Purac) was recrystallized from toluene just before use. Poly(ethylene glycol)350 methyl ether (PEG350), poly(ethylene glycol)750 methyl ether (PEG750), poly(ethylene glycol)400 (PEG400) and tributyl citrate (TBC) were purchased from Aldrich and used as received. Trimethylolpropane ethoxylate (three arm star poly(ethylene glycol), (TP200™)) and pentaerythritol ethoxylate (four arm star poly(ethylene glycol), (PP150™)) were a kind gift from Perstorp (Sweden) and were used as received. Potassium hexamethyldisilazide (Avocado) was used as received.

2.2. Synthesis of PDLLA-PEG diblock and PDLLA-PEG-PDLLA triblock copolymers

The structure of the copolymers synthesized and used in this study is shown in Fig. 1. The number between brackets shows the molar copolymer compositions used in the feed, e.g., PDLLA-PEG350 (10-4) means $[DLLA]_0/[PEG350]_0 = 10/4$, where DLLA and PEG350 units are considered as 144 and 350, respectively. All the polymerizations were carried out in toluene at room temperature in a glove box under an argon atmosphere using a new method developed recently by some of us [49]. The syntheses of PDLLA-PEG350 (10-4) (COPO1), PDLLA-PEG750 (10-4) (COPO2) and PDLLA-PEG400-PDLLA (10-2) (COPO3) are similar and as an example, the preparation of COPO1 is given here. In a typical experiment, $K[N(SiMe_3)_2]$ (0.042 g, 0.21 mmol) was added to PEG350 (2 g, 8.33 mmol) in 3 ml of toluene and stirred for 5 min. The solution of MeO-PEG350 and catalyst was added to D,L-lactide (3.0 g, 20.83 mmol) in 32.5 ml of toluene. The mixture was stirred for 20 min and the solvent was removed by evaporation under vacuum.

^1H NMR ($CDCl_3$): PLA ($\delta_{CH3} = 1.57$ ppm and $\delta_{CH} = 5.15$ ppm), PEG ($\delta_{CH2} = 3.61$ ppm), C(O)–O–CH_2– ($\delta = 4.25$ ppm), HO–CH(CH_3)– ($\delta = 4.35$ ppm), HO–CH(CH_3)– ($\delta = 1.45$ ppm), –OCH_3 ($\delta = 3.35$ ppm).

Molecular weight and thermal characterization are given in Table 1.

2.3. Synthesis of star-shaped copolymers based on poly(ethylene glycol) and poly(D,L-lactide)

The synthesis of *3-star*-[poly(ethylene glycol)-b-poly(D,L-lactide)] *3-star*-(PEG-PDLLA)(10-1.3) (COPO4) and *4-star*-[poly(ethylene glycol)-b-poly(D,L-lactide)] block copolymers *4-star*-(PEG-PDLLA)(10-1) (COPO5) was carried out using the same procedure used for the preparation

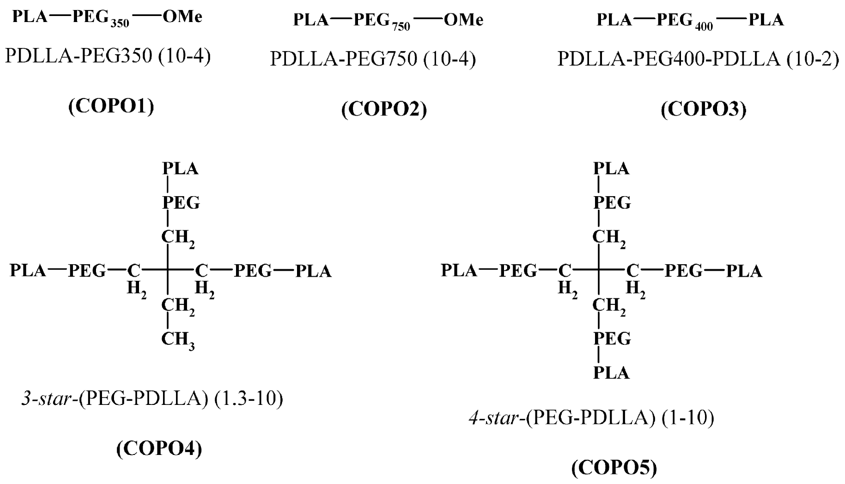

Fig. 1. Structures and compositions of PLA-b-PEG block copolymers synthesized and used as plasticizers for PLA.

Table 1
Polymerization of D,L-lactide in the presence of poly(ethylene glycol) of different structures and $K[N(SiMe_3)_2]$ as catalyst in toluene at 25 °C. $[\text{lactide}]_0 = 1.25$ M.

Copolymer	PEG Type	$[DLLA]_0/[PEG]_0$ [a]	Mn [b]	PD [c]	T_g [d] (°C)
COPO1	MeO-PEG350	10/4	650	1.3	−53
COPO2	MeO-PEG750	10/4	1000	1.2	−55
COPO3	PEG400	10/2	1050	1.1	−30
COPO4	TP200	10/1.3	1750	1.1	−33
COPO5	PP150	10/1	1750	1.1	−22

[a] D,L-lactide monomer to PEG molar ratio used in the feed. The molecular weights of MeO-PEG350, PEG400, MeO-PEG750, TP200 and PP150 were considered as given by the manufacturer 350, 400, 750, 1014 and 796 respectively.

[b] Molecular weight number average calculated by GPC using polystyrene calibration.

[c] Polydispersity index calculated by GPC analysis.

[d] Glass transition temperature determined by DSC.

of linear copolymers above and detailed previously [50]. The macroinitiators 3-*star*-PEG or 4-*star*-PEG were substituted for MeO-PEG or PEG.

The preparation of COPO4 is given here as an example. $K[N(SiMe_3)_2]$ (0.034 g, 0.17 mmol) was added to 3-*star*-PEG (1.86 g, 1.85 mmol) in toluene (5 ml) and stirred for 5 min. The solution of (TP200 and catalyst) was added to a solution of D,L-lactide (2.0 g, 13.8 mmol) in 20 ml of toluene. The mixture was stirred for 20 min and the solvent was removed under vacuum.

GPC and DSC characterization are given in Table 1. ^1H NMR analyses show the same signals for PLA and PEG units mentioned in case of linear copolymers in 2.2 except the absence of the OCH_3 end group signal.

2.4. Melt-blending procedure

Before processing, PLA was dried overnight at 80 °C under vacuum. PLA-plasticizer blends were obtained by melt-compounding PLA pellets with the plasticizer at 170 °C using a Brabender bench-scale kneader (model 50 EHT, 80 cm^3 free volume) equipped with cam blades for 3 min at 30 rpm, followed by 4 min at 70 rpm. Plates were then prepared by compression molding at 170 °C using an Agila PE20 hydraulic press (low pressure for 200 s with three degassing cycles, followed by a high-pressure cycle at 150 bars for 150 s and cooling by tap water at 50 bars). Specimens for tensile and impact testing were cut from plates by using either a milling-machine or by cutting in accordance to ASTM D638-02a (type V) and ASTM D 256-A norm, respectively.

The plasticizers used are: COPO1/TBC, COPO2/TBC, COPO3/TBC, COPO4/TBC and COPO5/TBC. The ratio of TBC to the copolymer was 1/1 (w/w). Four blends (polymer/plasticizer) were prepared from each plasticizer with the composition of polymer to plasticizer 90/10, 85/15, 80/20 and 75/25 (wt/wt). Blends of PLA/TBC (80/20) and PLA/Copolymer (80/20) have also been prepared. From each composition a minimum of five specimens were produced and used for mechanical characterization. Neat PLA was processed under the same conditions to serve as a reference.

2.5. In vitro cytotoxicity texts

In vitro cytotoxicity tests were carried out at the Histology Laboratory of University of Ghent, Belgium. The cell culture consists of fibroblasts from 7-day-old chicken embryos brought in culture with Hanks medium supplemented with 10% Foetal Calf Serum (FCS), 0.5% penicillin/streptomycin, 1% Fungizone and 2% glutamine. After confluence, cells are seeded in a 96 well plate (density: 40,000 cells/well) and kept in culture for 24 h with the culture medium. The tests were performed on PLA-b-PEG (20-1) using the MTS assay in accordance with the ISO 10993-1 guidelines. MTS assay is a laboratory tests and standard colorimetric assays (an assay which measures changes in color) for measuring the viability of cells. MTS represent the following reagent: 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium salt. Because the experiment requires films, PLA-b-PEG copolymers with low PEG content were used. Briefly, PLA-b-PEG (20-1) films were sterilized with ethylene oxide and the presence of toxic leachables in the samples was investigated by incubating the material in the culture medium for 8 days which is added to cell culture afterward. The extraction procedure was as follows: 1.5 g of the material is brought in a test tube and 1.5 ml phenol red free Dulbecco's Modified Eagle's Medium (DMEM) with 10% FCS, 0.5% penicillin/streptomycin and 1% Fungizone is added. The samples are sealed and incubated for 1 day or 1 week in the dark at 37 °C on a mechanical shaker. This culture medium is added to a primary fibroblast culture for 24 h. Cell viability in contact with the leachables is compared to cells in contact with culture medium, using the MTS assay.

2.6. Compost degradation tests

Composting degradation tests were carried out according to the established CEN standard procedures (ISO 14855) using cellulose as reference. Polymer films (2 mm thickness) were mixed in settled down compost (58 ± 2 °C and 50% humidity). The release of CO_2 was measured by infra red after calibration. At a determined time interval the molecular weight of the degraded samples was measured.

2.7. Characterization

2.7.1. NMR measurements

^{1}H NMR spectra were obtained at room temperature in $CDCl_3$ at resonance frequencies of 300 MHz using a Bruker AVANCE 300 NMR instrument.

2.8. Gel Permeation Chromatography (GPC) measurements

Number average molecular weights and molecular weight distributions of the copolymers were determined in THF at 35 °C using a Knauer size exclusion chromatograph equipped with a Knauer 2320 refractometer index detector and two PLGel columns (MIXED-D and 103A). Samples were dissolved in THF (5 mg/1 ml), 50 μL of the solutions were injected into the columns using a flow rate of 1 ml/min. Monodisperse polystyrene standards (Polymer Laboratories Ltd.) were used for the primary calibration.

2.8.1. Differential scanning calorimetry (DSC) measurements

Differential scanning calorimetry (DSC) measurements were performed by using a DSC 2920 from TA Instruments under nitrogen flow (first heating ramp of 10 °C/min from −80 to 180 °C to eliminate a different thermal history after the processing by compression molding, cooling ramp of 10 °C/min down to −80 °C to give to samples a similar thermal history, second heating with ramp of 10 °C/min from −80 to 180 °C to record the events of interest and to compare polymer crystallization properties). Glass transition temperature (T_g), crystallization temperature (T_c), enthalpy of cold crystallization (ΔH_c), melting temperature (T_m) and melting enthalpy (ΔH_m) were determined from the second heating cycle. The degree of crystallinity was determined by substracting ΔH_c from ΔH_m and considering a melting enthalpy of 93 J/g for 100% crystalline PLA as in previous work [52]. In the case of DSC measurements for pure copolymers and TBC the temperature range was between −100 °C and 80 °C.

2.8.2. Mechanical testing measurements

Tensile tests were performed with a Lloyd LR 10 K tensile bench in accordance with ASTM D638-02a norm (specimens type V, 3 mm thickness) at a rate of 10 mm/min using a distance of 25.4 mm between grips. Notched impact strength (Izod) measurements of selected compositions were performed by using a Ray-Ran 2500 pendulum impact tester and a Ray-Ran 1900 notching apparatus, in accordance to the ASTM D 256 norm (Method A, 3.46 m/s impact speed, 0.668 kg hammer, specimens of 60 × 12 × 2 mm).

For both tensile and impact tests, specimens were previously conditioned for at least 48 h at 20 ± 1 °C under relative humidity of 45 ± 5% and values were averaged over five measurements.

3. Results and discussions

3.1. Synthesis of copolymers

In previous papers concerning the preparation of block copolymers of different structures based on PLA and PEG we demonstrated the efficiency of a potassium compound as an alternative to the tin based catalyst for the ring opening polymerization of lactide [49,50]. Linear and star PLA-b-PEG block copolymers have been synthesized at room temperature in toluene using potassium hexamethyldisilazide as catalyst and PEG as macroinitiator. A wide range of copolymers with different compositions were prepared and fully characterized. The results show that the polymerization is very well controlled under the used experimental conditions. The polymerization is easy to control and capable of forming polymers of predictable number average molecular weight with a narrow polydispersity and complete absence of cyclic oligomers. The molecular weights calculated from the NMR spectra are in good agreement with the theoretical values [49,50]. The physical properties of the final copolymers depend on the copolymer compositions and thus can be used for different applications [49,50]. The use of these copolymers as plasticizers requires that the copolymers should be liquid or viscous. The synthesis of low molecular weight copolymers was achieved by using high content of PEG in the starting polymerization feed. Based on the previous results the copolymers synthesized in this work are designed to have the same PLA chain length with a degree of polymerization of 2.5 by adjusting the initial monomer to PEG molar ratio in the polymerization feed. The copolymers synthesized were characterized in terms of physicochemical properties by GPC, DSC and 1H NMR analyses. The molecular weights measured by GPC ranged from 650 to 1750 (Table 1). ^{1}H NMR analysis was used to determine the copolymer composition. The ^{1}H NMR spectra of the different copolymers are similar and as an example, the spectrum of COPO1 with detailed assignments is given here (Fig. 2). The absence of methine group signal around 4.98 ppm indicates the

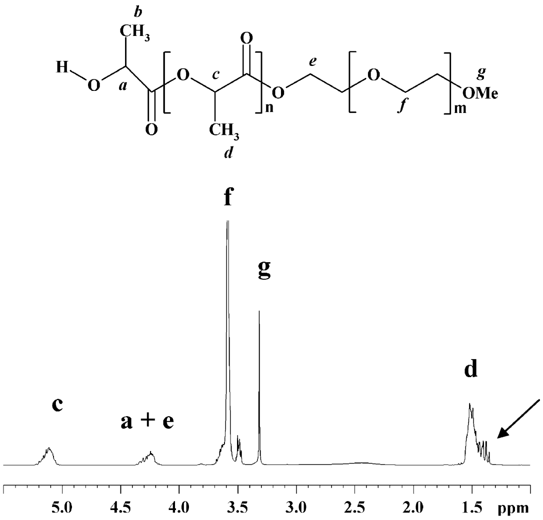

Fig. 2. ^{1}H NMR spectrum ($CDCl_3$) of PDLLA-b-PEG350 (10-4).

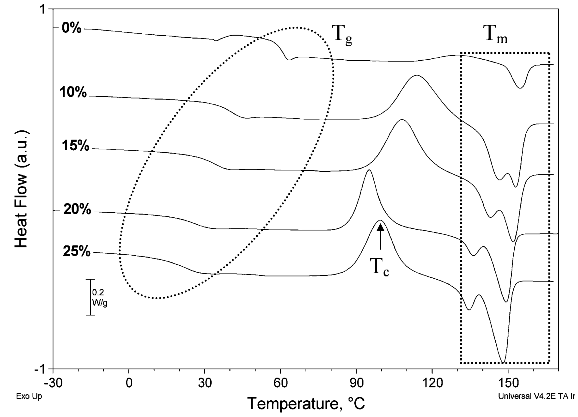

Fig. 3. DSC diagrams of neat PLA and PLA:(COPO4/TBC) compositions with different percentages of plasticizer (%, by weight).

complete conversion of the lactide monomer. The formation of block copolymers was discussed and confirmed in our previous work [49,50]. DSC analysis of the copolymers (Table 1) shows only one T_g which can attributed to the PLA segment because DSC analysis of the different PEG's used as macroinitiator does not reveal any glass transition in this temperature range (−100–80 °C). The difference in T_g observed for the different copolymers could be attributed to copolymer structure and the interaction between PLA and PEG segments effects.

3.2. Thermal characterization of PLA blends

To overcome some disadvantages of TBC (boiling point = 325 °C – source Acros Organics, but the results from TGA measurements show that is volatile) and PEG as plasticizers for PLA, this work is designed to investigate the plasticizing effect of the equigravimetric blends of TBC and block copolymers based on PLA and PEG on the thermo-mechanical properties of PLA. The use of PLA-b-PEG/TBC blends as plasticizer for PLA was approached for the following reasons:

(a) TBC will enhance the elongation at break whereas the combination with PLA-b-PEG copolymer will keep the tensile strength high enough to reach the requirements of the end-use applications.
(b) TGA analysis shows that TBC is less thermally stable with respect to the PLA-b-PEG copolymers (Fig. 3); in this context, it was predicted and experimentally confirmed, that the utilization of PLA-b-PEG/TBC blends will reduce more significantly the amount of volatiles/degradables than in the case of TBC alone as plasticizer.
(c) PLA-b-PEG copolymer should be more compatible than PEG with PLA because of the interaction of the esters groups of the both, the PLA matrix and copolymer. Thus a solution could be realised to the problem of the phase separation observed during ageing of PLA compositions with PEG as plasticizer.

Since the glass transition temperature (T_g) is an excellent indicator of chain mobility, plasticizing efficiency has therefore been evaluated by measuring the decrease of T_g as a function of plasticizer concentration. All the blends realized in this work show only one T_g in the DSC diagrams indicating a good miscibility between polymer and plasticizer (Fig. 4). The decrease of T_g highlights the effect of the plasticizer in PLA compositions with increasing molecular mobility [52]. The plasticizing effect is confirmed by the modification of T_g which is significantly decreased by comparison to the neat PLA matrix (T_g = 61 °C).

As far as T_g is concerned, addition of 20 wt% TBC leads to PLA composition characterized by a significant decrease of the T_g value (Table 2), more likely demonstrating good plasticizing efficiency with PLA, while for a similar percentage, COPO1 and COPO2 (diblock copolymers) leads to slightly higher T_g (Table 2). By considering the decrease of T_g, these copolymers (COPO1 and COPO2) seem to be slightly more efficient by comparing to triblock or star

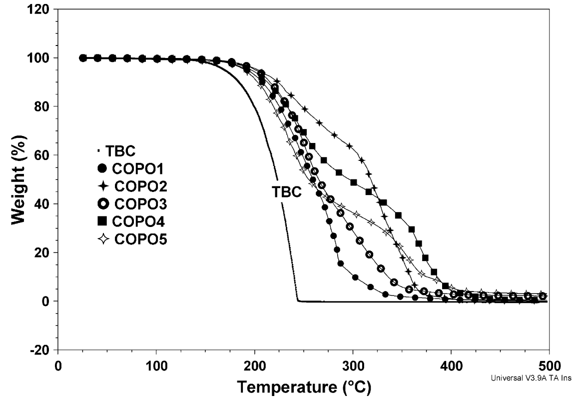

Fig. 4. TGA traces of TBC compared to PLA-b-PEG copolymers (under air flow, ramp 20 °C/min).

Table 2
Comparative DSC data of different PLA compositions with/without plasticizers (second heating with a ramp of 10 °C/min).

Blend (wt/wt)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	χ_c[*] (%)	T_m (°C)	ΔH_m[**] (J/g)
Neat PLA	61	131	3.1	3.4	155	5.1
PLA:TBC (80:20)	20	95	17.6	18.9	146	18.2
PLA:COPO1 (80:20)	29	101	24.3	26.1	151	25.7
PLA:COPO2 (80:20)	26	90	19.8	21.3	152	25.3
PLA:(COPO3) (80:20)	36	107	24.0	25.8	152	24.2
PLA:(COPO4) (80:20)	35	103	22.8	24.5	153	24.0

[*] χ_c – Increase of crystallinity due to cold crystallization.
[**] Initial crystallinity of the plasticized samples was less than 6% as calculated by substracting ΔH_c from ΔH_m.

copolymers COPO3 and COPO4, which lead to T_g higher than 35 °C (Table 2). In fact, by considering also the results of mechanical characterization-point 3.3, it is believed that the copolymers/plasticizers with a high level of branching lead to lower plasticizing effects as was ascribed elsewhere [54]. The blend PLA/COPO5 was supposed to be similar to PLA/COPO4 and was not realized due to the lack of product (COPO5).

On the other hand, by considering the PLA-b-PEG/TBC blends as plasticizers for PLA it should be noted that the decrease of T_g is quite well correlated with the plasticizer content, whereas in a similar correlation T_m slowly decreased with the amount of plasticizer (Table 3). Multiple endothermic peaks were found because of additional cold crystallization processes, the peak temperature of the largest endotherm was taken as the melting temperature and reported in Table 3.

On the other hand, DSC measurements performed using the described procedure, confirm the poor ability of neat PLA matrix (5% content of D isomer) to crystallize. Indeed, the initial crystallinity of neat PLA is about 2.2%, whereas the increase of crystallinity due to cold crystallization is about 3.4% only. Interestingly enough, in all cases, the addition of more than 10 wt% plasticizer in this matrix promotes an important crystallization exotherm (cold crystallization), that seems be more important for the synthesized copolymers or their blend with TBC, in comparison with the utilization of, even a high percentage of TBC, i.e., 20 wt% (Table 3). So, contrary to neat PLA, heating of plasticized compositions with COPO1-5 and/or TBC at approximately 90–120 °C promotes an important increase of crystallinity degree up to a maximum value of 30% (likely due to higher chain mobility) without an evident correlation with percentage plasticizer (Fig. 3). This increase of crystallinity represents a property of interest that can be made use of for film and fiber applications.

Finally, from DSC measurements it comes out that (co)addition of up to 25 wt% PLA-b-PEG/TBC blends into PLA can lead to a significant decrease of T_g with respect to the neat polyester matrix and therefore improved ductility/toughness can be expected.

It is important to point out that in the main goal of the improvement of thermal properties, the utilization of thermally stable polymeric plasticizers has been recently considered for plasticizing PLA [53]. In relation to the thermal stability of TBC in comparison with low molecular weight PLA-b-PEG copolymers (Fig. 4), the experimental strategy implies the partial/total replacement of TBC due to its potential volatility during the mixing process. Because TBC is ascribed with higher volatility compared to PLA-b-PEG, an increase in the thermal stability of PLA:(PLA-b-PEG/TBC) compositions can be assumed (this is confirmed by additional TG measurements of plasticized compounds, results not discussed here) and as consequence these blends could be recommended for applications where improved resistance at high temperature and/or long residence time in processing conditions is required.

3.3. Mechanical characterization of PLA blends

It is known that a low molecular weight plasticizer behaves like a solvent when mixed with a polymer and

Table 3
Comparative DSC data of different PLA compositions with/without blend of plasticizers (second heating with a ramp of 10 °C/min).

Blend (wt/wt)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	χ_c[*] (%)	T_m (°C)	ΔH_m[**] (J/g)
Neat PLA	61	131	3.1	3.4	155	5.1
PLA:(COPO1/TBC) (90:10)	42	115	24.3	26.1	153	25.4
PLA:(COPO1/TBC) (80:20)	24	91	27.4	29.5	149	29.2
PLA:(COPO1/TBC) (75:25)	15	83	19.3	20.8	146	24.5
PLA:(COPO2/TBC) (80:20)	26	100	19.9	21.4	150	21.1
PLA:(COPO3/TBC) (80:20)	25	101	22.6	24.3	149	23.4
PLA:(COPO4/TBC) (90:10)	41	114	24.7	26.6	153	26.6
PLA:(COPO4/TBC) (80:20)	27	95	19.4	20.9	150	22.0
PLA:(COPO4/TBC) (75:25)	23	98	23.0	29.1	150	27.1
PLA:(COPO5/TBC) (90:10)	47	123	14.0	15.1	151	15.8
PLA:(COPO5/TBC) (80:20)	28	103	19.4	20.9	150	20.1
PLA:(COPO5/TBC) (75:25)	23	99	24.0	25.8	148	29.4

[*] χ_c – Increase of crystallinity due to cold crystallization.
[**] Initial crystallinity of the plasticized samples was less than 6% as calculated by substracting ΔH_c from ΔH_m.

usually leads to a decrease of the macromolecular chain cohesion. From a molecular perspective, the plasticizer penetrates between the macromolecular chains and decreases the cumulative intermolecular forces along them [54,55]. In this context, by addition of plasticizer the stress developed is reduced because of the lower molecular adhesion. Since the ultimate mechanical properties (both impact and tensile testing) of a specimen can vary significantly as a result of their processing history, in the following discussion the samples are compared to neat PLA prepared under similar processing conditions.

Actually, the main goal of plasticizer addition into PLA matrix is to decrease its rigidity (i.e., Young's modulus) and to increase PLA ductility, while polymer tensile strength is maintained at the optimum level. It is worth noting that neat PLA at room temperature is characterized by low elongation (nominal strain at break = 6%) and low impact values, together with high tensile strength and Young's modulus (52 MPa and 1800 MPa, respectively – Table 4). Since the most important modifications of tensile properties by plasticization have been observed at relatively high percentage of plasticizer (10-20%), these effects are discussed here as result of their key-importance for further practical applications.

As summarized in Tables 4 and 5, addition of plasticizer leads to an expected decrease of tensile strength and Young's modulus explained by lower macromolecular chain cohesion, whereas the nominal strain at break is characterized by an important increase with respect to the neat polyester. The PLA studied has a maximum tensile strength of 51 MPa, while the plasticized compositions are characterized by a considerable reduction of tensile strength, and generally, this decrease is quite well correlated with the percentage of plasticizer.

The comparison of the plasticized compounds PLA/TBC (80/20) and PLA/(PLA-b-PEG) (80/20 by weight) confirms again an excellent plasticizing effect induced by the addition of TBC (Table 4, entry 2: nominal strain at break of about 320%, Young's modulus of 9 MPa), whereas the PLA-b-PEG copolymers generally lead to higher tensile strength values, i.e., between 21 and 30 MPa. In all cases addition of 20 wt% copolymer leads to an important increase in the nominal strain at break of PLA attesting for important plasticizing effects, while by considering both ultimate elongation and Young's modulus, the most interesting results are obtained using COPO1 (Table 4, entry 3) and COPO2 (Table 4, entry 4, values of 220% and 290 MPa were recorded, respectively).

Concerning the blends where plasticizer is a mixture of PLA-b-PEG and TBC (50:50 by weight), the stress–strain diagrams (not shown here) show that the great majority of specimens are characterized by brittle behavior at lower plasticizer percentage, i.e., 10 wt%, ascribed to some "anti-plasticizing" effects and ductility for higher percentages, e.g., 20 wt%, (Table 5).

Indeed, the association of TBC and PLA-b-PEG copolymers promotes a strong plasticizing effect at an amount of 20 wt% plasticizer, in all cases leading to significant increases of nominal strain at break (250–300% with respect to 6% for PLA) and an important decrease of Young's modulus (values of about 20 up to 400 MPa in comparison with 1800 MPa obtained for neat PLA).

On the other hand, to identify the most interesting system for plasticizing PLA it will be important to know the end-use performances required for the targeted application. When using the level of tensile strength as the selection criterion the blend TBC/COPO2 (Table 5, entry 5) seems to lead to more interesting results, i.e.; a tensile

Table 4
Mechanical properties of neat PLA and plasticized PLA compounds.

Entry	Blend (wt/wt)	Max. tensile strength (MPa)	Nominal strain at break (%)	Young's modulus (MPa)	Impact strength (kJ/m^2)
1	Neat PLA	52 (±2)	6 (±1)	1800 (±150)	2.6 (±0.2)
2	PLA:TBC (80:20)	20 (±1)	320 (±20)	9 (±1)	No break
3	PLA:(COPO1) (80:20)	21 (±1)	170 (±10)	790 (±180)	1.6 (±0.6)
4	PLA:(COPO2) (80:20)	25 (±1)	220 (±20)	300 (±50)	8.3 (±2.5)
5	PLA:(COPO3) (80:20)	30 (±1)	130 (±20)	1700 (±100)	1.9 (±0.6)
6	PLA:(COPO4) (80:20)	24 (±2)	170 (±10)	1150 (±150)	1.9 (±0.7)

Table 5
Mechanical properties of neat PLA and PLA plasticized with blends TBC/PLA-b-PEG copolymers.

Entry	Blend (wt/wt)	Max. tensile strength (MPa)	Nominal strain at break (%)	Young's modulus (MPa)	Impact strength (kJ/m^2)
1	Neat PLA	52 (±2)	6 (±1)	1800 (±150)	2.6 (±0.2)
2	PLA:(COPO1/TBC) (90:10)	40 (±2)	4 (±1)	2000 (±110)	2.7 (±0.2)
3	PLA:(COPO1/TBC) (80:20)	17 (±1)	260 (±20)	9 (±1)	6.4 (±1.9)
4	PLA:(COPO2/TBC) (90:10)	27 (±2)	140 (±20)	1480 (±80)	2.4 (±0.2)
5	PLA:(COPO2/TBC) (80:20)	24 (±1)	260 (±10)	19 (±5)	No break
6	PLA:(COPO3/TBC) (90:10)	37 (±1)	4 (±1)	1850 (±200)	ND*
7	PLA:(COPO3/TBC) (80:20)	16 (±1)	300 (±20)	16 (±7)	ND*
8	PLA:(COPO4/TBC) (90:10)	39 (±2)	4 (±1)	2000 (±100)	2.5 (±0.2)
9	PLA:(COPO4/TBC) (80:20)	22 (±1)	250 (±10)	150 (±65)	5.5 (±0.8)
10	PLA:(COPO5/TBC) (90:10)	37 (±1)	4 (±1)	1950 (±150)	2.5 (±0.2)
11	PLA:(COPO5/TBC) (80:20)	20 (±1)	260 (±20)	400 (±140)	3.8 (±1.1)

[*] Not determined.

strength of 24 MPa and evident improved ductility and lower rigidity, confirmed by both nominal strain at break and Young's modulus, respectively. In this context, these blends can be considered as more suitable for applications where good tensile strength properties are expected. Moreover, advanced plasticizing properties (e.g., Young's modulus of 16 MPa) are well evidenced for the blend TBC/COPO3 (entry 7) but this system has the disadvantage of conferring a lower tensile strength, i.e., of about 16 MPa.

Finally, for similar amount of plasticizer (20 wt%) the stress performances recorded using TBC/COPO4 and TBC/COPO5 blends can be also mentioned, these compositions being characterized by tensile strength of about 22 MPa, while the Young's modulus is higher by comparison to the utilization of the TBC/COPO1-3 blends as plasticizers.

Regarding the impact properties, it might be interesting to use PLA compositions in applications where medium to high impact values are sought and as consequence it is important to have information about their behavior at higher deformation rates applied during impact solicitation. Because some differences exist between tensile and impact procedures, in particular concerning the deformation rates, it has been found in some cases that materials with high elongation at break can be characterized by relatively weak impact values [40]. On the other hand, it is important to appreciate that for plasticized compositions with low content in plasticizer (e.g., less than 10 wt%) a decrease in impact strength has sometimes been reported [43,52]. For small amount of plasticizer, the plasticizer molecules may be totally immobilized by attachment to the polymer chains by various forces. These tend to restrict the freedom of motion of small sections of the polymer molecules necessary for the absorption of mechanical energy which leads finally to lower impact strength and higher Young's modulus, even than for a neat PLA matrix.

From the previous discussion it has been concluded that addition of 20 wt% TBC into PLA leads to stronger plasticizing effects within the polyester matrix (decrease of Young's modulus, high elongation at break, etc.). These improvements are also correlated with noticeable impact strength (Table 4, entry 2), i.e., addition of 20 wt% TBC results in samples that are not broken. The addition of 20 wt% copolymers into PLA (Table 4), the most important results are obtained again by using COPO2, which leads to an impact strength value of 8.3 kJ/m^2 (Table 2, entry 4), whereas at similar percentage, the other copolymers such as COPO1, COPO3 and COPO4 seem to decrease the impact properties of PLA (impact strength of 2.6 kJ/m^2).

Interestingly enough, especially at high amount of plasticizer (20 wt%), the TBC/COPO blends lead to plasticized PLA compositions that do show improved impact strength (Table 5, entries 3, 5, 9 and 11), assumed to be principally caused by TBC addition, but some synergies between components cannot be excluded (Table 5, entry 5).

Finally, a lower rigidity recorded by tensile testing is generally reconfirmed by impact testing, COPO2 alone or in blend with TBC leading to the most interesting results, that can be assumed to be due to a higher molecular mass of PEG, as was already reported in other experimental works [42].

From the results of mechanical characterization it comes out that the plasticizer structure could have an important effect on plasticizing efficiency. Indeed, by considering both Young's modulus and impact strength, the efficiency of PLA-b-PEG copolymers seems to decrease in the case of triblock and star-shaped copolymers. Clearly, many assumptions and correlations can be proposed to take into account the results obtained using these copolymers, including their molecular weights and structures, presence or not of catalysts, etc… A more detailed understanding of the action of the most effective copolymers is under current investigation and will be the object of a future contribution.

3.4. *In vitro biocompatibility*

The requirements needed for the plasticizing agents depend on a given application of the final material. In the case of the biodegradable food packaging, the biodegradability and biosafety should be added to the common requirements. Citrate esters are well known as food additive that can degrade under the same conditions as PLA. PLA-b-PEG copolymers are also well known as biodegradable and biocompatible. They have been investigated widely for biomedical applications. To confirm the biosafety of the novel catalyst for food packaging applications, in vitro cytotoxicity texts were carried out for PLA-b-PEG (20-1) using MTS assay. MTS is used to test the viability of cells when brought in contact with the material or extraction products of the material. The material is considered as non toxic when the cells viability is higher than 75% in comparison to the control. The dilutions are used to determine at which concentration the material became toxic. The copolymer tested is of low PEG content because relatively high molecular weight copolymer is needed for the formation of films which are needed for the tests. The results obtained indicate that the material does not show any toxicity towards the fibroblast cells (Fig. 5). Moreover, similar results have been recently reported for PLA and PLA-b-PCL prepared using the same catalyst [51].

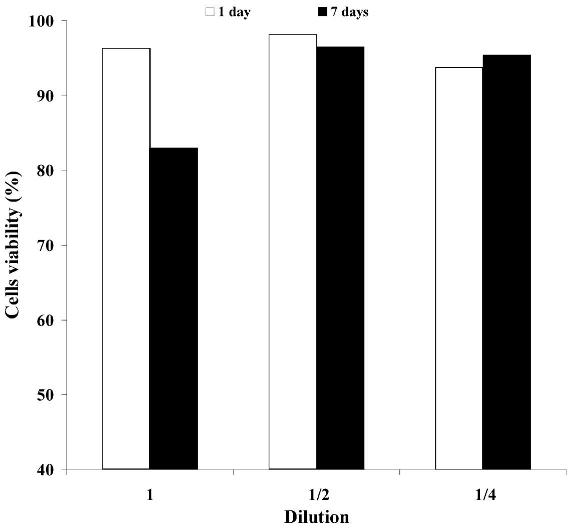

Fig. 5. Viability of fibroblast cells in the presence of PDLLA-PEG (20-1) copolymers.

3.5. Compost degradation tests

Compost degradation tests of neat and plasticized PLA were carried out using cellulose as reference. The degradation was monitored by measuring the CO_2 evolution. The results obtained showed that the plasticized PLA degrades faster than unplasticised material (Fig. 6). GPC analysis of samples aged for 54 days in the compost showed that the molecular weight of neat PLA has decreased from 78,000 (M_n after processing) to 21,000 whereas the selected plasticized composition (initial M_n = 75,000) showed after biodegradation a bimodal chromatogram with the molecular weights of 10,500 and 3800 (Fig. 7). The third peak corresponds to COPO5 used in the plasticizer blend. Comparing the results in terms of CO_2 evolution and the decrease of the molecular weight, the latter is faster because as known the biodegradation process of PLA starts first with the hydrolysis degradation and then followed by the microorganism attack.

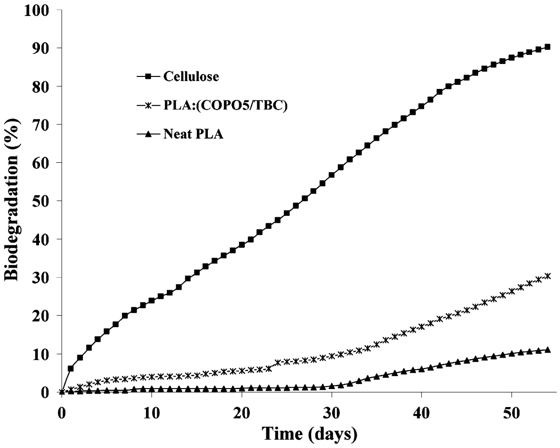

Fig. 6. Compost degradation of PLA and PLA:(COPO5/TBC) 80:20 (w/w) at 60 °C.

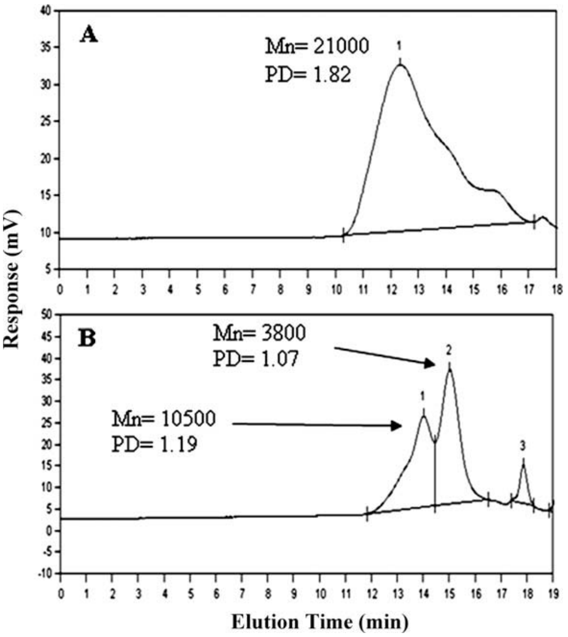

Fig. 7. GPC chromatograms of neat PLA100 (A) and PLA:(COPO5/TBC) 80:20 (B) after 54 days in the compost at 60 °C.

4. Conclusions

Low molecular weight PLA-b-PEG block copolymers of different structures/topologies have been synthesized using potassium based catalyst. The in vitro cytotoxicity tests showed that the copolymers prepared using this catalyst are not toxic at least towards the fibroblast cells.

The combination of more thermally stable PLA-b-PEG copolymers with TBC as plasticizers for PLA leads to an important improvement of the thermo-mechanical properties of the plasticized blends. The compositions containing 80 wt% PLA and 20 wt% blend of plasticizers show a T_g below 30 °C, high nominal strain at break (>220%) and interestingly enough tensile strength for application in packaging field (values up to 24 MPa). On the other hand, TBC in association with PLA-b-PEG has a beneficial effect in the increase of impact strength of PLA, the best results showing samples that are not broken during testing.

In addition to the physico-mechanical properties, it has been evidenced by biodegradation tests in compost conditions that the plasticizers investigated in this work enhance the degradation of the PLA matrix.

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