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Palm oil deodorizer distillate as toughening agent in polylactide packaging films

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Abstract

Poly(lactide) (PLA) is the most used biodegradable and biobased food packaging polymer for rigid containers and films. However, its low ductility is a hurdle for increasing its applications in flexible food packaging. A solution is the use of additives. Palm oil deodorizer distillate (PODC) is revealed to be an excellent additive promoting PLA ductility. PODC is a by-product of vegetable oil refining, which is available in stable quality and in sufficient amounts. Amorphous PLA/PODC blends had an elongation at break of around 130% and that of semi-crystalline blends was still around 55% compared to the initial 5% of neat PLA. At the same time the PLA rigidity and high glass transition temperatures were kept. PODC was also a very efficient processing aid, allowing for film blow extrusion. The blends were stable in properties during six months without exudation. They complied with legal norms of Food Contact Materials (EU 10/2011) and induced no sensorial alteration of packed food. Therefore PODC is a very interesting alternative to common plasticizers for the production of flexible PLA packaging films.

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Keywords: poly(lactic acid); PLA; ductility; food packaging; toughening agent; processing aid; biodegradation; oil refinery by-product; deodorizer distillate

INTRODUCTION

Food packaging represents some 30% of the volume of plastics produced worldwide. Considering this, the use of biobased and biodegradable polymers can be one of the contributors to enhancing environmental performance of the plastics sector and also of packed food. Among those polymers, polylactide (PLA) accounts for the largest volume today. Its major applications are in rigid and flexible food packaging.¹ PLA has a number of interesting properties for food packaging applications, such as stiffness, transparency, heat-sealing ability, printability, suitability for active food packaging^{2,3} and low aroma compound sorption.⁴ Its low ductility is a hurdle to numerous applications, however, in particular in the field of flexible films. Moreover, the poor melt strength of PLA compared to polyolefins makes it difficult to get a stable bubble during extrusion blowing.⁵

Generally, external plasticization with miscible liquids having a high boiling point or with ductile polymers is employed with the aim of enhancing the elongation at break of PLA.^{6,7} Most plasticizers have a petrochemical origin and are commonly added at weight contents from 10 to 30%. This reduces the biobased carbon content of the formulated material and may, in some cases, be the cause of failure of the product to comply with biodegradability norms. Besides, many plasticizers contain in their structure chemical moieties having toxicological alerts, so their employment in food contact materials is strictly regulated by legislators. Two types of regulations have been elaborated by the European (EU No. 10/2011) and the North American authorities. Consequently, developing a biobased and biodegradable additive suitable for

food contact materials, with a low cost and a stable sourcing, could be very attractive for the industrial development of PLA as food packaging. The vegetable oil mill industry is an interesting source of molecules with potential for increasing the ductility of PLA. For example, epoxidized soy bean oil has been investigated with some success.^{8,9} Another strategy is to use by-products of this industry. Deodorizer distillates are produced during oil refining by blowing steam through heated fat held under high vacuum.^{10,11} Today they are a waste stream of vegetable oil refining and most often used mixed with oil cake as animal feed. Therefore deodorizer distillates are possibly a price-competitive additive for PLA. Ruellan *et al.*¹²

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showed recently that the addition of 15 wt% palm oil deodorization condensate (PODC; or palm oil deodorizer distillate) allowed for an increase of PLA elongation at break up to 180%, while conserving PLA stiffness and glass transition temperature (T_g) higher than room temperature.

The goal of our study reported here was to assess the use of deodorizer distillate of vegetable oil refining as a biobased and biodegradable additive for food packaging. Therefore we investigated first the role played by the deodorizer distillate as a processing aid for cast and blow extrusion of PLA. Second, we created a prototype showing the permanence of the additive in structures during storage and the compliance with European regulations for food contact materials and biodegradable polymers.

EXPERIMENTAL

Materials

PLA was purchased from NatureWorks (USA). PLA 4060D contains $89 \pm 1\%$ L-lactide and $11 \pm 1\%$ D-lactide units (according to the datasheet), which frustrates crystallization under common processing conditions.¹³ Materials produced with this type of PLA were amorphous. PLA 4042D contains $96 \pm 0.5\%$ L-lactide and $4 \pm 0.5\%$ D-lactide (according to the datasheet). This product was used to produce semi-crystalline samples. T_g of both products obtained from DSC measurements are 57 and 59 °C (midpoint), respectively. PODC was supplied by ITERG (Bordeaux, France). The chemical composition of the palm oil condensate is given in the supporting information (S1).

Polymer processing

In order to remove water traces prior to the melt-blending process, PLA 4060D and PLA 4042D were respectively dried at 60 and 80 °C for 24 h under dried air using a Motan 100 L dryer. Melt blending of PODC with PLA 4060D or PLA 4042D was realized using a co-rotating twin-screw extruder (Dr Collin) with a screw diameter of 35 mm and a length-to-diameter ratio of 56:1. Liquid addition of PODC was carried out to reach 10 wt% in PLA using a Robatech PuMelt D280 pump heated at 70 °C. The twin-screw extruder temperatures were 180 °C for all extruder zones when processing neat PLA (introduction in the first zone of the extruder) and 60/180/180/180/180/180/170/170/160/160/150/140/140/140 °C along the extrusion flow when adding PODC (introduction in the ninth zone of the extruder). Feeding rates were 9 kg h⁻¹ for PLA and 1 kg h⁻¹ for PODC. The twin-screw rotation speed was 250 rpm. Cooling of the strands was done under air. The obtained pellets were stored in hermetic metalized sealed bags to avoid water uptake.

Two film extrusion processes were tested for PLA 4060D/PODC blends. Single-screw cast extrusions of neat PLA 4060D and PLA 4060D/PODC films were done using a Mapre E1 30 30D single-screw extruder. The temperature profile for PLA 4060D extrusion was 170/180/180/180/180/170/170 °C and that for PLA 4060D/PODC extrusion was 160/160/155/150/150/150/145 °C along the extrusion flow. A flat die of 550 μm in thickness and 200 mm in width was heated at 170 and 140 °C, respectively. Films were stretched and cooled with chill rolls rotating at a chosen speed, adjusting the final film thickness to about 30 μm. Film blowing of PLA 4060D/PODC was done with a Mapre E1 30 30D single-screw extruder using a temperature profile 140/145/150/150/150/150/155 °C along the extrusion flow, mounted with a film blowing device (Dr Collin) equipped with a

spiral die ending in an annular ring of 800 μm in thickness and 50 mm in diameter heated at 145 °C. A blowing ratio of about 2.5 was applied and the roll speed was adjusted to get a final film thickness of about 25 μm.

Crystallization of neat and formulated PLA 4042D samples was carried out using sheets of 1 mm in thickness obtained by thermo-moulding at 190 °C and 220 bar (22 MPa) (Laboratory Press Gibitre Instruments, 20 tons). For that, pellets were pre-melted at 190 °C without pressure during 180 s and then the heated plates were closed with a progressive increase in pressure during 120 s to eliminate air bubbles. Obtained sheets were quenched in cold water and subsequently annealed in an oven at 90 °C for 24 h.

Characterization

Composition of PODC

Glyceride composition of the PODC was determined according to both IUPAC 6.002 and EN 14105 standards using a Shimadzu GC-2010 Plus gas chromatograph equipped with a Zebron ZB 5 HT Inferno (15 m, 0.25 mm, 0.1 μm) column and a flame ionization detector set at 380 °C. The vector gas was hydrogen at a flow rate of 1.17 mL min⁻¹. The oven temperature was set to 60 °C for 3 min, then raised at 10 °C min⁻¹ to 370 °C and held at 370 °C for 12 min. Samples were injected on-column.

Fatty acid composition of the PODC was determined according to the ISO 12966-2 standard using a Shimadzu GC-2010 Plus gas chromatograph equipped with a BPX70 (50 m, 0.22 mm, 0.25 μm) column and a flame ionization detector set at 250 °C. The vector gas was hydrogen at a flow rate of 0.32 mL min⁻¹. The temperature programme consisted of an initial isotherm of 2 min at 60 °C, a heating ramp at 20 °C min⁻¹ to 170 °C and an isotherm at 170 °C for 25 min, a second ramp at 4 °C min⁻¹ to 230 °C and finally an isotherm at 230 °C for 10 min. The injector temperature was set at 250 °C and a split ratio of 200 was applied.

Water content of the PODC was measured using a Mettler Toledo HB43 S halogen moisture analyser set at 103 °C.

PODC content of formulated PLA blends

Thermogravimetric measurements were conducted using a TGA Q500 thermobalance (TA Instruments). Prior to experiments, weight calibration of the device was performed using calibration weights and temperature calibration by an external thermometer and the Curie point of nickel. Samples of about 3 mg were heated under nitrogen atmosphere (40 mL min⁻¹) between 25 and 500 °C at a heating rate of 10 °C min⁻¹. The chosen comparison temperature at which the PODC amount was estimated in formulated samples was 250 °C because measurements showed that a large amount of neat PODC was volatilized at that temperature while only a very low weight loss for neat PLA was observed (supporting information S2). Thus, the following calculation was applied to estimate the PODC content in samples:

$$\text{PODC wt\%} = \frac{(\text{PLA/PODC}_{\text{weight-loss}})_{(t)} - 0.9 (\text{PLA}_{\text{weight-loss}})_{(t)}}{(\text{PODC}_{\text{weight-loss}})_{(t)}} \times 100 \quad (1)$$

where PODC wt% is the PODC weight percentage in the formulation, and $\text{PLA/PODC}_{\text{weight-loss}}$, $\text{PLA}_{\text{weight-loss}}$ and $\text{PODC}_{\text{weight-loss}}$ are the relative weight losses of blend, neat PLA and neat PODC at 250 °C, respectively. Experiments were carried out in triplicate.

In order to validate concentration of PODC measured with the TGA method, about 6 g of material was cut in 0.5 cm² pieces and placed into a 125 mL Soxhlet apparatus with 200 mL of ethanol

boiled under reflux during 8 h. The extracted PLA samples were dried in an oven for 2 days at 40 °C under vacuum. Then, materials were weighed to determine the weight content of PODC. Analyses were done in triplicate.

Size exclusion chromatography

The average molecular weight and the dispersity of neat and formulated PLA samples were measured using SEC with a Waters Co. apparatus equipped with an isocratic pump (GILSON 307), a column oven (Waters Control Module II), a gel column (Styragel H5E 7.8 × 300 mm) having a separation range from 2000 to 1 000 000 g mol⁻¹, an autosampler (Waters 717 plus) and a refractive index detector (Waters 2414). Data acquisition and analysis were carried out with the help of Breeze software. The analyses were performed at 35 °C with tetrahydrofuran (THF) as eluent at a flow rate of 1 mL min⁻¹. The calibration was done prior to the experiments, based on polystyrene standards (Shodex Standard from Showa Denko, range 3070 to 778 000 g mol⁻¹). For sample preparation, neat and formulated PLA pellets were dissolved in THF (20 mg L⁻¹) on a shaker at 60 °C for 45 min. Analyses were done in triplicate.

Differential scanning calorimetry

Standard DSC analyses of neat PODC and PLA 4042D formulations were performed with a Mettler Toledo DSC1 STARe system under nitrogen atmosphere (50 mL min⁻¹). Calibration of the device was done using indium and zinc standards. Samples of around 8 mg were sealed in 40 μL hermetic aluminium pans. The analysis of PODC was carried out with a heating scan at a rate of 10 °C min⁻¹ from -60 to 250 °C. Experiments were done in duplicate. The degree of crystallinity of PLA 4042D was determined by a heating scan performed at 10 °C min⁻¹ from 25 to 200 °C, considering an enthalpy of fusion of 93.1 J g⁻¹ for a 100% crystalline PLA homopolymer¹⁴ using the following equation:

$$\chi_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_{m0} (1 - W_{\text{PODC}})} \times 100 \quad (2)$$

where χ_c is the degree of crystallinity of PLA, ΔH_m is the measured heat of fusion, ΔH_c is the heat of cold crystallization, ΔH_{m0} is the enthalpy of fusion of 100% crystalline PLA homopolymer having infinite crystal thickness and W_{PODC} is the averaged weight fraction of PODC obtained from solvent extraction and TGA measurements. Experiments were performed in duplicate.

T_g of neat and formulated films (PLA 4060D and PLA 4042D) was investigated using temperature-modulated DSC (MDSC; Q100, TA Instruments). Instrument calibration was done with sapphire standards for calibration of the heat capacity, and indium and zinc standards for temperature and heat flow calibration. Analyses were carried out under nitrogen flow (50 mL min⁻¹). Samples of around 4 mg were put into hermetic aluminium pans (TZero, TA Instruments). Heating scans were performed under sinusoidal temperature modulation in 'heat only' mode at a heating rate of 2 °C min⁻¹, a period of 60 s and a modulation of 0.318 °C from 0 to 85 °C. T_g was taken from the reversing signal at the midpoint of the heat capacity change. Experiments were carried out in triplicate.

Tensile tests

Tensile properties were investigated at 23 °C, relative humidity (RH) regulated at 50 ± 10% and crosshead speed of 25 mm min⁻¹, using a universal tensile machine (Instron model 4301) equipped

with a load cell of 100 ± 0.1 N for films and 1000 ± 1 N for sheets. Dog-bone shaped samples (ISO 527-2, type 5A) were directly cut from the materials. Prior to tensile testing, the samples were conditioned at 23 °C and 50 ± 10% RH for at least 72 h. Each mechanical testing value is an average of at least eight measurements.

Oxygen permeability

Oxygen transmission rate was measured with a Mocon Ox-Tran model 2/21 apparatus at 23 °C and 0% RH. Oxygen permeability was calculated by multiplying the oxygen transmission rate by the film thickness. Analyses were done in triplicate.

Biodegradation

A biodegradation study of film samples was done according to the EN 14855-1 standard (test under composting conditions). According to the norm the maximum testing duration was six months. The requirements to draw conclusions on biodegradability of a sample are: (i) achieving a mineralization percentage of cellulose of at least 70% after 45 days for validation of the test set-up and (ii) achieving a degree of mineralization of the sample material of at least 90% of the mineralization degree of the reference material (cellulose) once a plateau value is reached. Microcrystalline cellulose (44% carbon content), purchased from Aldrich (France), was used as reference material. Biodegradation was carried out at 58 °C. The testing series consisted of film samples, cellulose reference, and a blank assay without carbon source. All assays were inoculated with a mature compost (pH = 7.2 ± 0.3%, C/N = 13.7 ± 0.5% and organic carbon content = 26.9 ± 0.2%) supplied by Compomar Company (France). Purified air (without CO₂) was bubbled in each reaction vessel, and air output flow rate was determined with an Aalborg AIR 0-10 L/MIN mass flowmeter. Quantification of carbon mineralization was done based on the respirometry principle. The quantity of carbon dioxide generated during fermentation was measured with a Vaisala IR GMP343 sensor calibrated from 200 ppm to 2%. A weight ratio sample/compost of 1/20 was used for the reference material and the formulated PLA films. Experiments were done in duplicate.

Migration of PODC in food simulants

Quantification of the PODC migration from a cast extruded PLA 4060D/PODC film into food simulants was conducted according to the EN 1186 standard and Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food. Sunflower oil, ethanol (50%) and acetic acid (3%), which are simulants of fatty foods, acid foods and milk and dairy products, respectively, were used. Film was cut into 1 dm² pieces and placed in contact with food simulants for 10 days at 5 or 40 °C using a migration cell with a ratio of 1 L of simulant per 6 dm² of film. Analyses were done in duplicate.

After the contact time, samples conditioned in sunflower oil were wiped to remove oil droplets and stored in a conditioned chamber at 23 ± 2 °C and 50 ± 5% RH for 16 h. For analysis of sunflower oil sorbed in the films, samples were extracted using a Soxhlet apparatus for 7 h with 240 mL of pentane plus 10 mL of methyl 7-phenylheptanoate at 0.5 g L⁻¹ in pentane as internal standard. The extract was then reduced to 10 mL with a rotary evaporator (Buchi Rotavapor® R-3000) and dried using a heating plate. The dried extract was dissolved in 10 mL of heptane. Saponification of triglycerides was carried out by addition of 10 mL of KOH at 11 g L⁻¹. For analysis by gas chromatography, methylation of free fatty acids was done under reflux for 2 min upon addition of

5 mL of BF_3 . The solution was dried using sodium sulfate and decanted. The organic phase was analysed by gas chromatography using a PerkinElmer Clarus 500 apparatus equipped with an SEG Analytical Science BPX70 column (130 m, 0.32 mm, 0.25 μm) and a flame ionization detector set at 250 °C. The oven temperature was programmed to increase from 165 to 177 °C at 2 °C min^{-1} then from 177 to 200 °C at 30 °C min^{-1} . Each sample was injected in split mode and the injector port was heated to 250 °C.

For samples tested in aqueous simulants, i.e. acetic acid (3%) and ethanol (50%), the simulants were evaporated to dryness using a heating plate and then an oven set at 107 °C for 1 h. Dried residues were conditioned at 23 ± 2 °C and $50 \pm 5\%$ RH for 16 h. The migration was determined by weighting. Experiments were done in triplicate.

Sensorial testing

Changes in the flavour and taste of packaged foods were assessed using the Robinson test according to Analytical Methods of the Office International du Cacao et du Chocolate (OICC), Analytical methods page 12 – E/1964a. Transfer of packaging odours to cacao and chocolate products. Samples were placed close to pieces of chocolate at 23 °C and 50% RH in a glass recipient for 48 h in a dark room. Then a panel of 10 trained judges tasted standards and chocolates conditioned with the PLA samples. Flavour and taste changes were evaluated on a scale from 0 to 4. A comparison between neat PLA and formulated film was done after performing a Grubbs statistical test, then averaging the marks. In fact, to characterize a packaging, calculations were based on the difference between marks attributed to a 'chocolate reference' and a 'chocolate sample'. The maximum statistical difference (D) authorized was 1, meaning that, if the average mark was lower than D , no modification of the flavour nor the taste was observed.

RESULTS AND DISCUSSION

Processability of PLA/PODC blends

The twin-screw extrusions of both neat PLA 4060D and neat PLA 4042D were realized at 180 °C with a screw rotation speed of 250 rpm. The residence time was measured using coloured pellets to be about 6 min. This temperature was high enough to plasticize/melt PLA pellets without exceeding the maximum admissible torque of the device, determined from the amount of the electric charge (A) provided to the motor.

When 10 wt% PODC was introduced in the twin-screw extruder at its mid-length (ninth zone of 15), an important lowering of the torque by a factor of 2, i.e. from about 14 to 7 A, was observed. Temperatures of the ninth to fifteenth zones were then set decreasing from 170 to 140 °C along the extrusion flow, raising the melt viscosity of the blend to get drawable strands. Using these conditions, the torque increased (electric charge ≈ 12 A), with a significantly lower deviation than that observed when processing neat PLA. The residence time was measured at about 5 min, which is a significantly shorter than that for neat PLA. Actually, PODC acted, for both PLA types, as a processing aid stabilizing the extrusion flow and lowering the extrusion temperature.

Single-screw cast extrusion of neat PLA 4060D and PLA 4060D/PODC films showed similar behaviour as observed during the melt-blending step. Using the conditions of PLA 4060D extrusion, the PLA/PODC blend was not filmable because of its melt strength being too low. When maintaining the same screw rotation speed, the temperature profile of the extruder and the

temperature of the flat die had to be lowered to get a semi-solid sheet able to be cast with chill rolls. The obtained output film rate flow of PLA/PODC mixture was about 3.1 kg h^{-1} , which is higher than for neat PLA (2.4 kg h^{-1}).

Blown film of neat PLA 4060D was impossible to obtain because of the too high a temperature needed (*ca* 180 °C) to extrude the PLA. In fact, at this temperature the melt strength of PLA is insufficient to yield a weak semi-solid tube. In contrast, by using PODC as a processing aid capable of lowering the required extrusion temperature, a blown film of PLA/PODC mixture was obtained. The blown film output of PLA/PODC mixture was about 3.0 kg h^{-1} , which is similar to the output of the cast extrusion process.

Molecular weights of neat PLA pellets, processed PLA and PLA/PODC blends are given in Table 1. A reduction of both number-average (M_n) and weight-average molecular weight (M_w) with an increase in the dispersity (I) is observed after processing. Despite the vigorous drying of PLA pellets, the polymer most probably suffered thermo-hydrolysis, being the main degradation mechanism of PLA.¹⁵ Introduction of PODC brings about additional reduction in chain length. One reason might be additional water brought into the melt, as water is contained in PODC (0.16 wt%; supporting information S1). Drying of the PODC might be one possibility to further improve the polymer-processing step. Furthermore, the acid groups of fatty acids might cause chain scission by transesterification, a process described for other additives containing reactive hydroxyl groups.^{16,17}

The amount of PODC (Table 1) in the pellets and films was characterized using TGA. The amounts of PODC agreed with the results obtained using Soxhlet extraction. However, the PODC contents using both methods are lower than the expected value of 10 wt% of PLA. TGA curves of neat PODC (supporting information S2) showed a weight loss starting around 140 °C with a maximal loss rate reached at 195 °C. Because the different sample processes require set-point temperatures greater than 140 °C, a part of PODC was most likely volatilized. Processing of PLA/PODC granules did decrease further the PODC content, but this was significant only for film blowing and after annealing for 24 h. In conclusion, the PODC content was nearly stable during plastic processing.

Thermal and mechanical properties of amorphous PLA/PODC blends

Table 2 summarizes the thermal properties of the films measured using MDSC. This methodology was chosen for analysis of T_g to discriminate the PLA glass transition from the melting of fatty acids contained in PODC. Unsaturated fatty acid molecules such as linoleic acid ($T_{\text{melt}}^{\circ} = -14$ and -7 °C)¹⁸ or oleic acid ($T_{\text{melt}}^{\circ} = 13$ °C)¹⁸ are liquid at room temperature, while saturated ones such as palmitic acid ($T_{\text{melt}}^{\circ} = 63$ °C)¹⁸ are crystallized. Blending of PLA with about 8 wt% PODC decreased T_g only by 14 °C, which is caused by the low miscibility of both compounds.¹²

Tensile properties of the films are also given in Table 2 and sample curves can be found in the supporting information (S3 and S4). The addition of PODC to PLA increased considerably the elongation at break of PLA without much decreasing the apparent Young's modulus. Stress at yield and elongation at yield were nearly halved. Stress whitening was observed. The poor miscibility of PODC in PLA led to the inclusion of a dispersed phase in the glassy matrix. Because PODC is a mixture of fatty acids with different chain lengths and therefore different melting points, two types of inclusions were present at room temperature: crystallites composed of fatty acids with high melting point (mainly

Table 1. PODC content and molecular weights of formulations

| Sample | PODC content (wt%) | | Molecular weight (SEC) | | |
|--|---------------------------|--------------------------|------------------------------|------------------------------|-----------|
| | Soxhlet extraction method | Thermogravimetric method | M_w (g mol ⁻¹) | M_n (g mol ⁻¹) | I |
| | | | | | |
| PLA 4060D (neat pellets) | – | – | 242 800 ± 2 100 | 108 700 ± 2 200 | 2.2 ± 0.1 |
| PLA 4060D (twin-screw extruded pellets) | – | – | 221 000 ± 3 600 | 90 200 ± 1 100 | 2.5 ± 0.1 |
| PLA 4060D (cast extruded film) | – | – | 209 600 ± 4 200 | 83 600 ± 1 800 | 2.5 ± 0.1 |
| PLA 4060D/PODC (twin-screw pellets) | 8.4 ± 0.5 | 9.0 ± 0.2 | 194 300 ± 3 700 | 84 100 ± 3 000 | 2.3 ± 0.1 |
| PLA 4060D/PODC (cast extruded film) | 8.1 ± 0.3 | 8.7 ± 0.1 | 164 100 ± 4 800 | 77 400 ± 3 600 | 2.1 ± 0.2 |
| PLA 4060D/PODC (blown extruded film) | 7.7 ± 0.6 | 8.4 ± 0.2 | 152 600 ± 4 200 | 73 200 ± 2 900 | 2.1 ± 0.1 |
| PLA 4042D (neat pellets) | – | – | 198 300 ± 2 200 | 111 900 ± 3 200 | 1.8 ± 0.1 |
| PLA 4042D (twin-screw pellets) | – | – | 182 300 ± 2 900 | 92 100 ± 900 | 2.0 ± 0.1 |
| PLA 4042D (thermo-moulded sheet) | – | – | 173 300 ± 3 000 | 83 700 ± 4 100 | 2.1 ± 0.1 |
| PLA 4042D (thermo-moulded sheet + annealed 24 h at 90 °C) | – | – | 160 100 ± 1 900 | 70 600 ± 4 400 | 2.3 ± 0.2 |
| PLA 4042D/PODC (twin-screw pellets) | 8.3 ± 0.4 | 8.1 ± 0.3 | 156 600 ± 4 300 | 87 400 ± 4 000 | 1.8 ± 0.1 |
| PLA 4042D/PODC (thermo-moulded sheet) | 7.6 ± 0.3 | 7.9 ± 0.1 | 144 100 ± 2 000 | 83 400 ± 2 400 | 1.7 ± 0.1 |
| PLA 4042D/PODC (thermo-moulded sheet + annealed 24 h at 90 °C) | 6.1 ± 0.4 | 6.4 ± 0.3 | 121 000 ± 4 100 | 66 600 ± 1 900 | 1.8 ± 0.1 |

Table 2. Physical properties of PLA 4060D and PLA 4042D films

| | | Glass transition (MDSC) | | Tensile properties | | | | | Barrier properties O ₂ permeability (× 10 ¹⁸ m ³ m m ⁻² s ⁻¹ Pa ⁻¹) |
|--------------------------------------|----------|-------------------------|------------|-------------------------|---|-----------------------|-------------------------|-----------------------|---|
| | | χ_c (%) | T_g (°C) | Elongation at break (%) | App. Young's modulus ^a (MPa) | Stress at yield (MPa) | Elongation at yield (%) | Stress at break (MPa) | |
| | | | | | | | | | |
| PLA 4060D (cast extruded film) | t_0 | 0 ^b | 57.7 ± 0.1 | 6 ± 1 | 1520 ± 85 | 56 ± 3 | 4.3 ± 0.2 | 55 ± 3 | 3.26 ± 0.05 |
| | 6 months | 0 | 56.0 ± 0.3 | 5 ± 2 | 1670 ± 90 | 64 ± 5 | 3.9 ± 0.1 | 62 ± 2 | 3.02 ± 0.09 |
| PLA 4060D/PODC (cast extruded film) | t_0 | 0 | 43.1 ± 0.6 | 135 ± 25 | 1330 ± 50 | 29 ± 2 | 2.3 ± 0.1 | 22 ± 2 | 3.31 ± 0.08 |
| | 6 months | 0 | 48.6 ± 0.3 | 90 ± 25 | 1420 ± 55 | 35 ± 3 | 2.3 ± 0.2 | 24 ± 1 | 3.20 ± 0.11 |
| PLA 4060D/PODC (blown extruded film) | t_0 | 0 | 44.0 ± 0.4 | 100 ± 15 | 1260 ± 70 | 24 ± 1 | 2.5 ± 0.1 | 22 ± 2 | 3.17 ± 0.07 |
| | 6 months | 0 | 47.4 ± 0.2 | 65 ± 20 | 1340 ± 35 | 27 ± 2 | 2.2 ± 0.2 | 25 ± 1 | 2.96 ± 0.08 |
| PLA 4042D | Quenched | <2 | 56.9 ± 0.3 | 6 ± 1 | 1550 ± 85 | 57 ± 4 | 4.8 ± 0.1 | 55 ± 2 | n.d. |
| | Annealed | 35 ± 1 | 60.2 ± 0.3 | 5 ± 2 | 1710 ± 70 | – | – | 70 ± 6 | n.d. |
| 4042D/PODC | Quenched | 20 ± 2 | 46.1 ± 0.4 | 120 ± 45 | 1200 ± 115 | 20 ± 2 | 1.7 ± 0.1 | 19 ± 2 | n.d. |
| | Annealed | 48 ± 2 | 39.8 ± 0.3 | 55 ± 10 | 1195 ± 95 | 21 ± 1 | 1.8 ± 0.2 | 21 ± 1 | n.d. |

^a Apparent Young's modulus measured without extensiometer.

^b Non-crystallizing PLA type.

palmitic acid) and liquid inclusions composed of fatty acids with low melting point (mainly oleic acid) (see supporting information S1). Each inclusion of PODC could therefore act as a stress concentration point, promoting the appearance of a large number of small crazes by debonding at the crystallite–polymer interface. Furthermore, the stress concentration in liquid inclusions could promote cavitation.¹² Both mechanisms cause toughness of glassy materials, because they allow dissipation of mechanical energy during stretching.¹⁹ The miscible part of PODC, which was responsible for the small T_g depression, had most likely a supplementary compatibilizing effect with the surrounding polymer matrix helping to ease polymer deformation. In conclusion, the obtained mechanical properties are of high interest for food packaging

applications of PLA films and containers, as they combine stiffness, T_g higher than room temperature and important ductility.

Oxygen barrier properties of amorphous PLA/PODC blends

Oxygen barrier is an important property of food packaging. Therefore the PLA/PODC blends were tested and results are presented in Table 2. The measured oxygen permeability of the neat films was consistent with literature values ranging from 1.2×10^{-18} to 4.3×10^{-18} m³ m m⁻² s⁻¹ Pa⁻¹.^{20–23} The value is in the higher permeability range likely because of the high D-lactide content in PLA, which induces higher irregularity in the chain packing. Interestingly, despite a decrease in T_g of the PLA/PODC blends, the oxygen

permeability was maintained. In contrast to conventional plasticizers of PLA, which are largely soluble in the matrix but lead therefore to an important decrease of the oxygen barrier properties,^{16,24} PODC present as inclusions of insoluble particles does not change the barrier properties compared to neat PLA. PODC is therefore a suitable additive for food applications where the oxygen barrier properties of PLA are satisfactory.

Stability of amorphous PLA/PODC blends at ambient conditions

The stability of the PLA/PODC blends at ambient conditions ($25 \pm 5^\circ\text{C}$) was tested after storage of the films for six months. T_g values and mechanical properties of aged blends are given in Table 2. Typical stress–strain curves are provided in the supporting information (S4). The film surfaces did not become greasy or sticky with time. The heat flow curves showed an increase of the enthalpic relaxation peak and T_g shifted to higher values in blends (Table 2). Both phenomena can be related to physical aging. Increased aging rates of plasticized PLA leading to higher T_g values were recently investigated.²⁵ Oxygen permeability (Table 2) has been used in previous studies as a structure probe for densification phenomena during physical aging.^{26–28} In the present case, no change is observed, even for neat PLA. The aging behaviour of the present PODC additive with low solubility is thus very different from that of miscible plasticizers where barrier properties increased with aging.^{26–28} Again, the overall high T_g of the PLA films including PODC might be responsible for this favourable behaviour. Embrittlement of samples was observed, though (Table 2). Even if no densification was shown by oxygen permeability, mobility of polymers is reduced during physical aging, but here to a lesser degree compared to commonly employed petrochemical plasticizers of PLA.^{26,27,29}

Effect of crystallization of PLA/PODC blends on thermal and mechanical properties

Most PLA grades are semi-crystalline. In the case of food packaging, crystallization of the polymer is favourable for most applications. In particular, crystallization of PLA enhances its structural stability at temperatures higher than T_g . Therefore we investigated crystallization of PLA/PODC blends for thermo-moulded sheets using DSC analysis (Table 2). The fabrication of a sheet by thermo-compression and quenching of PLA 4042D yields an almost amorphous sample. Neat PLA crystallized to a final degree of crystallinity of 35% after annealing at 90°C for 24 h. The PLA 4042D/PODC sheets, which were obtained by thermo-compression and quenching in water, presented in contrast a degree of crystallinity of 20%. Subsequent annealing at 90°C for 24 h increased further the degree of crystallinity of PLA 4042D/PODC to 48%. Both samples, PLA 4042D and PLA 4042D/PODC, showed a small exotherm before the melting peak in the thermograms, which is caused by the phase transition of the crystallites from α form to δ (former α') form.³⁰ The crystallization of PLA in δ (former α') form at 90°C is coherent with the known behaviour of the polymer. In conclusion, PLA seemed to be able to crystallize more quickly when blended with PODC. Furthermore, the crystallization of PLA 4042D/PODC afforded a decrease of T_g . This effect was already observed in the case of PLA/poly(ethylene glycol) blends and is likely due to an enrichment in plasticizer of the amorphous phase at the expense of the crystalline one.³¹ Ruellan *et al.*¹² studied PLA/PODC blends at different concentrations and showed that, at 15 wt% of PODC, T_g of PLA was 35°C .

The mechanical properties of the semi-crystalline samples are presented in Table 2 and stress–strain curves of the samples can be found in the supporting information (S4). While the amorphous PLA 4042D failed just after yielding, showing some plasticity, the crystallized one broke with a brittle fracture. Not surprisingly, the semi-crystalline sample had higher rigidity. The non-annealed blend of PLA 4042D/PODC showed an elongation at break close to that of the fully amorphous sample despite a degree of crystallinity of about 20%. A low degree of crystallinity is advantageous for development of crazes in semi-crystalline polymers³² and the presumed mechanism for increasing PLA ductility by PODC is the more efficient craze nucleation.¹² It seems that a degree of crystallinity of 20% did not alter this mechanism. In contrast, stress at yield was slightly lower compared to amorphous PLA 4060D films containing the same amount of PODC, presumably due to the enrichment in PODC of the amorphous phase over the crystallization. Annealing of PLA 4042D/PODC brought about halved elongation at break compared to the non-annealed reference. The apparent Young's modulus remained the same, though. Probably additional enrichment in PODC of the amorphous phase around crystallites could lead to early fracture, as proposed by Kulinski and Piorkowska.³¹ In conclusion, even if reduced, the ductility of the semi-crystalline material remained importantly higher than that of neat PLA, which makes PODC a suitable additive for semi-crystalline PLA.

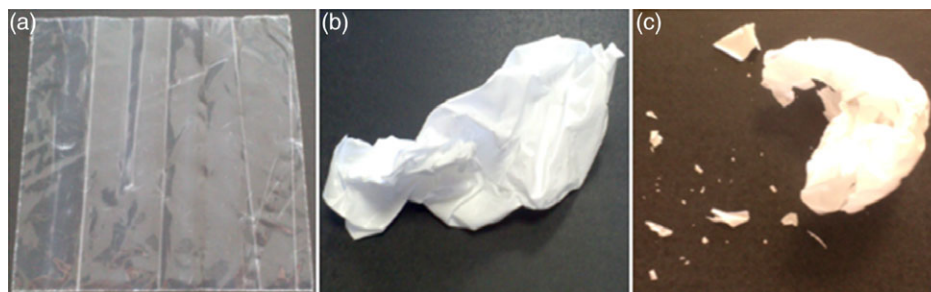
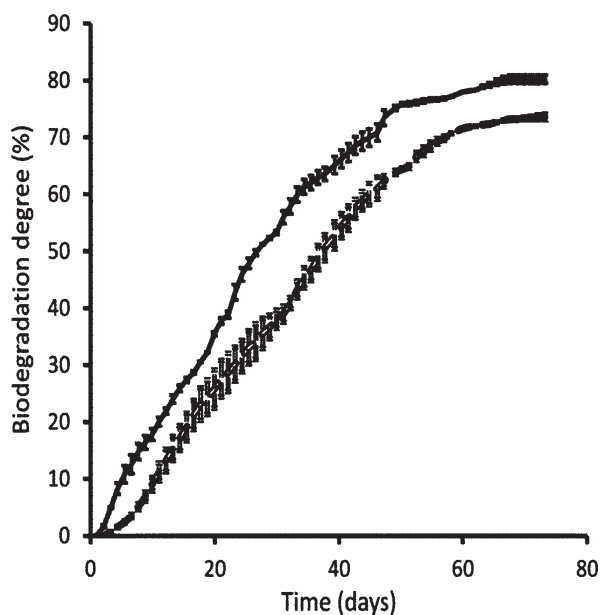
Compliance of PLA/PODC film with requirements of food contact material regulations

Qualification of PODC as an additive for food packaging was evaluated with the help of normed overall migration tests after European regulation and sensorial evaluation. The food simulants were sunflower oil mimicking fatty foods, ethanol–water (50/50) mimicking dairy products and acetic acid mimicking acidic aqueous foods and drinks. Testing at 5°C simulates refrigerated storage conditions, testing at 40°C ambient storage conditions. Results are presented in Table 3. The criteria for compliance with the EU regulation are (i) that the overall migration is below 10 mg leached out from 1 dm^2 of packaging film (and 60 mg kg^{-1}) and (ii) that the physical aspect of the material is not altered by the test conditions. The overall migration of additives from the PLA/PODC blend into the food simulants complied with the regulation in all cases, except for acidic foods and drinks at ambient conditions (Table 3). Whiteness of the films occurred with ethanol and acetic acid simulants at 40°C , as shown in Fig. 1. Because of the change in physical appearance due to interaction of PLA with ethanol–water at 40°C , the PLA/PODC samples failed the compliance for dairy foods stored at ambient temperature. Consequently, when using ethanol–water as a food simulant the blends can be approved for all types of simulated foods at refrigerated storage conditions, but only for fatty foods at ambient storage conditions.

The change in flavour or taste of foodstuff occasioned by the packaging material was assessed using the Robinson test. Differences were noted on a scale between 0 and 4, i.e. from no taste difference to strong taste difference. Neat PLA 4060D film received an average mark of 0, whereas PLA 4060D/PODC cast film got an average mark of 0.25 ± 0.79 , which is not statistically different from the reference sample. No deterioration of the sensorial properties due to PLA and PLA/PODC blends was observed, which, in consequence, makes the films suitable for food packaging.

Table 3. Results of overall migration tests in food simulants

| Temperature (°C) | Vegetable oil | | Ethanol (50% v/v) | | Acetic acid (3% v/v) | |
|------------------|--|----------------------------|--|----------------------------|--|------------------------|
| | Overall migration (mg dm ⁻²) | Physical appearance change | Overall migration (mg dm ⁻²) | Physical appearance change | Overall migration (mg dm ⁻²) | Physical aspect change |
| 5 | <1 | No | <1 | No | <1 | No |
| 40 | <1 | No | <1 | Yes | 18.4 | Yes |

**Figure 1.** Physical aspect changes of films: (a) PLA 4060D/PODC reference film; (b) PLA 4060D/PODC film after 10 days at 40 °C in ethanol (50% v/v); (c) PLA/PODC film after 10 days at 40 °C in acetic acid (3% v/v).**Figure 2.** Biodegradation curves of PLA 4060D/PODC cast extruded film (dashed curve) and cellulose reference film (solid curve).

Biodegradation

The influence of PODC addition on film biodegradability was assessed according to the EN 14855 standard. The biodegradation curves are shown in Fig. 2. Biodegradation of 90% of the carbon content of amorphous PLA 4060D/PODC blend compared to the reference material, cellulose, was obtained after 60 days. The film therefore complies with the requirements of biodegradability.

CONCLUSIONS

PODC, a natural and biodegradable by-product of oil refining, which is available at low price and in sufficient amount, was used as shipped and successfully improved the elongation at break of

amorphous PLA as well as semi-crystalline PLA, while retaining its interesting stiffness and glassy state. Processing aid abilities were pointed out, reducing the required heating temperatures and enabling the film blowing extrusion process of PLA. An increase in the maximum degree of crystallinity after annealing compared to neat PLA was noted. Oxygen permeability of formulated films remained close to that of neat PLA, allowing for preserving applications where PLA is already suitable for packaging. Aging behaviour of films after six months stored at ambient conditions showed an ordinary embrittlement process with a slower degradation of mechanical properties as observed with usual plasticizers. Biodegradation of the amorphous blends was fully achieved and compliance with requirements of the food contact materials regulation was obtained for all types of simulated foods at refrigerated storage conditions and fatty food at ambient storage conditions. Also, preservation of the PLA biodegradability when blended with PODC would be of interest because fatty food packages are often soiled with fat, prohibiting recyclability. For example, cheese packaging could therefore constitute an appropriate application.

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SUPPORTING INFORMATION

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

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