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Preparation and characterization of blends made of poly(L-lactic acid) and β-cyclodextrin: Improvement of the blend properties by using a masterbatch

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ABSTRACT

β-Cyclodextrin (β-CD), an enzymatically modified starch with a hydrophilic exterior and a hydrophobic cavity, can form inclusion complexes with a variety of hydrophobic molecules. In this study, β-CDs were mixed with poly(L-lactic acid) (PLA) and then extruded, pelletized, and cast into sheets to create biodegradable and bio-based materials with the capacity to carry hydrophobic molecules to enable new applications for polymers in the food and pharmaceutical packaging area. The effects of different β-CD contents (0, 15, or 30%), and that of using a masterbatch (MB) (pellets containing 30% β-CD content) on the morphology and the physical properties of the PLA/β-CD blends were investigated. Thermal stability, tensile strength, modulus of elasticity, elongation at break, and oxygen and water-barrier capacity of the PLA decreased with higher β-CD contents and revealed that β-CDs and PLA are incompatible. Similarly, the crystalline content and color change increased with higher β-CD contents. The addition of β-CDs in the form of a masterbatch notably reduced these effects and increased the compatibility of the PLA and the β-CDs.

1. Introduction

Public concern about the environment has stimulated interest in biodegradable polymers as alternatives to conventional polymers (Ke & Sun, 2000). Poly(lactic acid) (PLA) is one of the more widely studied biodegradable polymers, because many of its properties are equivalent or superior to those of some petroleum-based plastics, which makes this polymer suitable for a variety of applications (Rasal, Janorkar, & Hirt, 2010).

PLA is a linear aliphatic thermoplastic polyester derived from lactic acid and it is mainly synthesized from the commercial fermentation of sugar feedstock (Lunt, 1998) which means it is a compostable polymer at specific conditions (Kijchavengkul & Auras, 2008). PLA has a transparent and glossy finish (Dorgan, Braun, Wegner, & Knauss, 2006: Chapher 7). PLA in its semicrystalline form is used in applications where high mechanical strength and toughness are required (Byrne et al., 2009). The CO_2, O_2, and N_2 permeability coefficients of PLA are lower than those for poly(styrene) (PS), but higher than those for poly(ethylene terephthalate) (PET) (Auras, Harte, & Selke, 2004). PLA is suitable for a wide range of processing technologies including injection and blow molding, thermoforming, cast film and sheet, extrusion blow film, foaming, and others (Lim, Auras, & Rubino, 2008). The toxicity of PLA is low, which makes it an adequate material for food packaging applications (Conn et al., 1995). All these properties make PLA attractive as a petroleum plastic substitute. However, PLA is more expensive than commonly used petroleum-based plastics (Lim et al., 2008). PLA has a relatively low glass transition temperature and any further reduction thereof limits the application of the polymer further (Kulinski & Piorkowska, 2005). Its impact strength and elongation at break are lower than those of widely used polymers such as high density poly(ethylene) and poly(propylene) (PP) (Dorgan et al., 2006: Chapter 7). Based on some of these properties, PLA offers vast potential for the development of biodegradable packaging systems that carry active compounds for food and pharmaceutical applications. While some aspects of the potential for active packaging have been explored (Jin & Zhang, 2008), further research and development is needed.

Cyclodextrins (CDs) are cyclic oligosaccharides composed of β-(1,4) linked glucopyranose subunits produced by enzymatic degradation of starch by bacteria. They have a cage-like supramolecular structure that allows them to interact with molecules, ions, and radicals (Del Valle, 2004). CDs are used to synthesize copolymers with PLA for drug delivery or for improving the miscibility of PLA with others (Adeli, Zarnegar, & Kabiri, 2008; Södergård & Stolt, 2002). CDs also enable the controlled release of different hydrophobic molecules like antimicrobials as shown by several investigators (Almenar, Auras, Harte, & Rubino, 2007; Almenar, Auras, Rubino, & Harte, 2007; Almenar, Auras, Wharton,

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Table 1
Sample codes for neat PLA and PLA/β-CDs blends (produced with or without masterbatch (MB)).

Sample code	PLA (wt%)	β-CDs (wt%)	PLA-β-CD30% (wt%)	β-CD content (wt%)[a]
PLA	100	0	0	0
PLA-β-CD15%	85	15	0	15
PLA-β-CD30%	70	30	0	30
PLA-β-CD15%-MB	50	0	50	15

[a] Nominal values of active ingredient.

Rubino, & Harte, 2007) By blending CDs with PLA, membranes with the capacity to carry hydrophobic molecules can be developed to enable new applications for biopolymers in the food and pharmaceutical packaging area. Despite the possible development of these functional biopolymers, information on blending this modified starch with PLA is scarce. In contrast, PLA/starch blends have been widely studied since blending starch with PLA is a promising approach (Rafler, Lang, Jobmann, & Bechthold, 2001): starch is abundant and cheap, and PLA has good mechanical properties and can reduce the sensitivity of starch to moisture (Ke & Sun, 2001; Yu, Dean, & Li, 2006; Yu, Petinakis, Dean, & Liu, 2010). In addition, the resulting blend is biodegradable and is derived from renewable sources. However, hydrophobic PLA and hydrophilic starch are thermodynamically immiscible because of the hydroxyl and carboxyl end groups in the PLA and the numerous hydroxyl groups in the starch (Zhang & Sun, 2005). Starch remains in a separate conglomerate form in a PLA matrix (De Graaf & Janssen, 2001). Due to this weak interfacial adhesion between phases, the mechanical strength of PLA/starch blends is low and the material is weak and brittle (Ke & Sun, 2000; Zhang & Sun, 2005). Numerous studies have been undertaken to improve the interfacial interactions of these blends through the use of compatibilizers and other additives (Ke and Sun, 2003; Zhang & Sun, 2004).

Masterbatch is another way to improve properties in a polymer blend and it has been broadly used with polymers like PP (Ahmed, Shamey, Christie, & Mather, 2006), poly(ethylene terephthalate) (Kim, Seo, Hong, & Kim, 1999), and others. Four commercial masterbatches have been blended with PLA and some properties of PLA such as clarity and impact resistance have been improved by the addition of the masterbatch. However, the four masterbatches had a slight negative effect on the tensile strength of PLA (Byrne et al., 2009). PLA and poly(butylenes adipate-co-butylene terephthalate) have been blended by using masterbatches as multicompatibilizer to enhance compatibility (Yuan, Liu, & Ren, 2009).

In this study, β-CDs were mixed with PLA in order to create a bio-based polymer with a capacity for carrying hydrophobic molecules. Different blends were created with the objective to achieve specific properties that make these blends fit for a number of packaging applications. Due to the expected weak interfacial adhesion between phases (PLA and modified starch), a masterbatch was tested in an attempt to improve the dispersion of the β-CDs into the PLA matrix and thus to enhance the compatibility and mechanical properties of the blend. The effects of the β-CD content (0, 15, or 30%) and the use of a masterbatch (MB) on the morphology and on the physical properties of the blends PLA-β-CDs were investigated.

2. Experimental

2.1. Materials

Poly(L-lactic acid) 4050D (PLA 4050D) resin (95% L-lactide, density = 1.24 g/cm^3) produced by NatureWorks LLC (Blair, NE) was kindly provided by Wilkinson Inc. (Calhoun, NE, US). β-Cyclodextrin (β-CD) (purity >99%, density = 0.5 g/cm^3, and Food grade) was purchased from Wacker Chemical Corporation (Adrian, MI, US).

2.2. Formulation and preparation of pellets

PLA 4050D resin and β-CDs were dried in a vacuum oven (1430 VMR International, Cornelius, OR, US) at 65 °C for 4 and 24 h, respectively. Quantities of PLA resin and β-CDs according to the calculated compositions (Table 1) were premixed and subsequently blended (Fig. 1, step 1). The premix was extruded using a pilot scale extruder

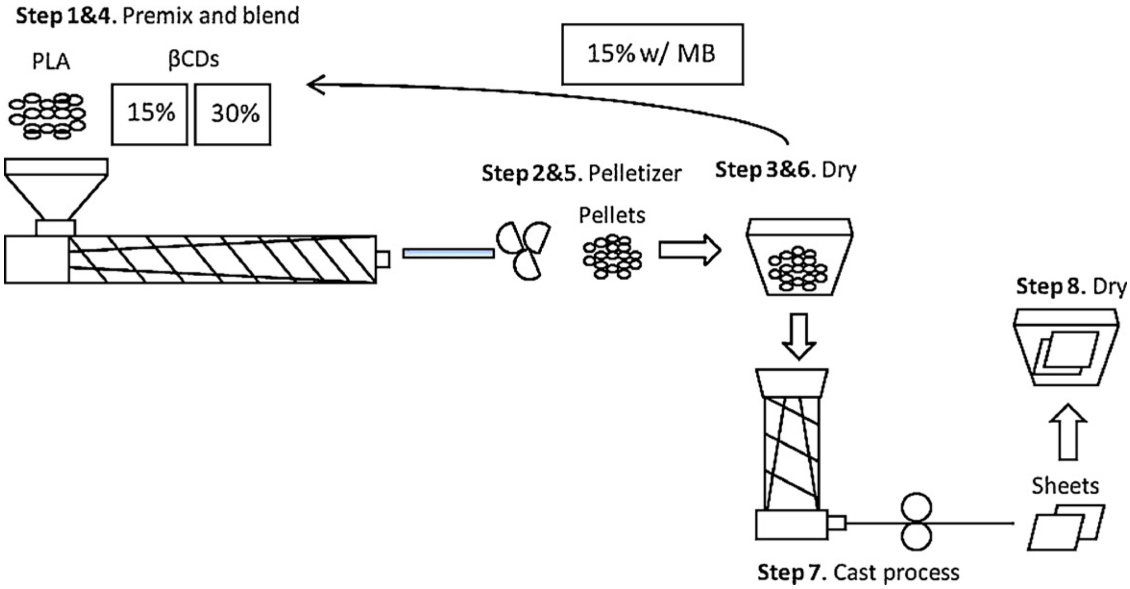

Fig. 1. Steps used in the preparation of the different types of sheets: PLA (steps 1–3, 7, and 8), PLA-β-CD (steps 1–3, 7, and 8), PLA-β-CD-MB (steps 1–8).

(Century extruders CX-30, Traverse city, MI, US) with 30 mm diameter twin screws with a L/D ratio of 42:1, and ten separate barrel zones temperature. This temperature profile was controlled with a water system and set from feeder to die to temperatures of 27, 81, 129, 144, 150, 161, 161, 160, 161, and 161 °C. The screw speed was 100 rpm and the level of torque was controlled at 70–75%. The blend was collected from the die and allowed to cool down prior to being granulated into pellets using a pelletizer (Scheer Bay Co. N. Euclid, Bay city, MI, US) ((Fig. 1, step 2). The pellets containing 0 (PLA), 15 (PLA-β-CD15%), and 30% (PLA-β-CD30%) CDs were stored until use in a desiccator at 23 °C (Fig. 1, step 3).

The masterbatch was prepared by mixing β-CD and PLA at a concentration ratio of 30/70. Quantities of PLA and MB pellets according to the calculated compositions (Table 1) were premixed and subsequently blended (Fig. 1, step 4) using the same equipment and processing as described above. The blend was collected from the die and allowed to cool down prior to being granulated into pellets using the same equipment as previously described (Fig. 1, step 5). The pellets containing 15% β-CDs (PLA-β-CD15%-MB) were stored until use in a desiccator at 23 °C (Fig. 1, step 6).

2.3. Preparation of sheets

All four different pellets (Table 1) were first dried in a vacuum oven prior to use to remove remaining moisture (Fig. 1, steps 3 and 6). The pellets were converted into sheets by cold cast process (Fig. 1, step 7). A single screw microextruder (Randcastle RCP-0625 Microextruder, Randcastle Extrusion System Inc., Cedar Grove, NJ, US) with a screw diameter of 15 mm and a length to diameter ratio (L/D ratio) of 24:1 was used. The screw speed of the extruder was 35 rpm. The temperature profile of the extruder was controlled by a water cooling system and set from the feeder zone to the die zone at 149, 160, 177, 177 and 177 °C. Chill rolls temperature was 52 °C. Ambient air was used to cool the sheets on top of the roll. All samples were stored in a desiccator at 23 °C to prevent moisture absorption (Fig. 1, step 8).

2.4. Mechanical characterization

Neat PLA and PLA/β-CD sheets were cut into specimens with a width of 1 in. and a length of 8 in. prior to use. The thickness of the specimens (0.17 mm) was determined by averaging the three readings taken at different points. The tensile properties: tensile strength, elongation at break, and modulus of elasticity were measured according to ASTM D882-02 (ASTM, 2002a), using an Instron Universal Testing Machine (Model 5565, Instron, Norwood, MA, US) with a crosshead speed of 0.5 in./min, and a gage length of 5 in. Tensile properties of neat PLA and PLA/β-CD blends were determined from an average of 10 samples.

2.5. Thermal and thermo-mechanical characterization

Thermal transitions of neat PLA and PLA/β-CD sheets were determined using a TA Instruments Q100V 9.8 Differential Scanning Calorimeter (TA Instruments, New Castle, DE, US). The temperature calibration of the equipment was performed in accordance with ASTM E967-03 (ASTM, 2003a) and the heat flow calibration was performed in accordance with ASTM E968-02 (ASTM, 2002b). Glass transition (T_g) and melting (T_m) temperatures were measured and calculated in accordance with ASTM D3418-03 (ASTM, 2003b). The degree of crystallinity ($\%X_c$) for neat PLA and PLA/β-CD sheets was calculated as follows (Ke & Sun, 2001):

$$\%X_c = \left(\frac{\Delta H_m + \Delta H_c}{93 \times X_{PLA}}\right) \times 100$$

where ΔH_m, ΔH_c, and X_{PLA} are the melting enthalpy, crystallization enthalpy, and PLA content, respectively. A value of 93 J/g for the melting enthalpy for 100% crystalline PLA was obtained from the literature (Fischer, Sterzel, & Wegner, 1973).

An amount between 7 and 9 g of PLA and PLA/β-CD sheets was used for each experiment. Samples were heated from 40 to 190 °C at a rate of 10 °C/min. The β-CD content was taken into consideration when determining $\%X_c$. Three replications of each type of sheet were tested.

Mass loss or gain due to the decomposition of the neat PLA and PLA/β-CD sheets was measured using a thermogravimetric analyzer (Hi Res TGA 2950, TA Instruments, New Castle, DE, US) under a nitrogen flow of 70 in.^{3}/min. The samples were scanned with a constant heating rate of 10 °C/min from 40 to 600 °C.

Dynamic mechanical analysis was used to characterize and to compare the viscoelastic nature of neat PLA and PLA/β-CD sheets. Storage modulus (E'), loss modulus (E''), and damping coefficient (tan delta) of all materials were measured as a function of temperature in accordance to ASTM D4065-06 (ASTM, 2006) by using a TA Instruments Model Q800 dynamic mechanical analyzer equipped with tension clamps and operating at a heating rate of 3 °C/min (from −20 to 120°C), and a frequency of 1.0 Hz. All specimens were 40 mm long, 5 mm wide, and 0.17 mm thick. Three samples for each type of material were tested.

2.6. Optical characterization

The color of the neat PLA and of the PLA/β-CD sheets was measured using a colorimeter (LabScan XE, HunterLab, Reston, VA, US) with a 17-mm-diameter measuring area. The CIELAB color system was used to characterize the color. The different sheets were square-shaped (60 mm × 60 mm) and then placed on the measuring area where CIE L^*, a^*, and b^* values were measured. The variable L^* represents the lightness of the color of a sample, and ranges from 0 (black) to 100 (white). The variables a^* and b^* define the degree of greenness, redness, blueness, or yellowness, and ranged from $-a^*$ (greenness) to $+a^*$ (redness), and $-b^*$ (blueness) to $+b^*$ (yellowness).

2.7. Morphological characterization

Scanning electron microscopy (SEM) was used to assess the PLA/β-CD interphase. PLA and PLA/β-CD pellets were fractured into small pieces of 2–3 mm and then stored until use in a desiccator at 23 °C. Individual pieces were placed horizontally or vertically on the sticky patch of the SEM sample holder, coated with 3 nm of gold and then images acquired using a scanning electron microscope (JSM-model 6400 SEM, JEOL, Peabody, MA, US) with an accelerating voltage of 12 kV and a working distance of 25 mm at 500× magnification. For each piece, a surface of about 100 μm × 100 μm was visualized.

2.8. Barrier characterization

Water vapor transmission rates (WVTR) of neat PLA and PLA/β-CD sheets were measured in accordance to ASTM F1249-05 (ASTM, 2005a) using a Permatran W Model 3/33 Water Permeability Analyzer (MOCON, Minneapolis, MN, US). Three to five sheets of each type were tested at 23 and 37.8 °C, and 100% RH. Oxygen transmission rates (OTR) of the sheets were measured in accordance to ASTM D3985-05 (ASTM, 2005b) using an 8001 Oxygen Permeation Analyzer (Mocon, Minneapolis, MN, US). Three to five sheets of each type were tested at 23 °C and 0% RH. All samples were masked with an adhesive type aluminum foil (McMaster-Carr, Aurora, Ohio, US), leaving an uncovered test area of 3.14 cm^2.

Table 2
Tensile strength, modulus of elasticity and elongation at break of the neat PLA and the PLA/β-CDs blends.

Sample code	Tensile strength (MPa)	Elongation at break (%)	Modulus of elasticity (GPa)
MD			
PLA	37.9 ± 0.9a	3.5 ± 0.4a	2.4 ± 0.0a
PLA-β-CD15%	11.6 ± 1.3b	1.6 ± 0.1b	0.9 ± 0.1b
PLA-β-CD15%-MB	19.7 ± 2.3c	1.9 ± 0.1b	1.4 ± 0.1c
PLA-β-CD30%	11.3 ± 1.3b	2.1 ± 0.5b	0.5 ± 0.2b
TD			
PLA	29.2 ± 1.8a	1.7 ± 0.3a	2.3 ± 0.0a
PLA-β-CD15%	6.6 ± 0.8bc	1.1 ± 0.1b	0.8 ± 0.1b
PLA-β-CD15%-MB	10.5 ± 1.5b	1.3 ± 0.2b	1.3 ± 0.1c
PLA-β-CD30%	3.8 ± 1.2c	1.1 ± 0.0b	0.7 ± 0.2b

a–d indicate significant differences between samples.

2.9. Statistical methods

All statistical analyses were performed using a univariate analysis of variance (ANOVA). Means were separated using the Tukey honestly significant difference (HSD) test ($p < 0.05$) in the analytical software SPSS version 15 (SPSS Inc., Chicago, IL, USA). Comparisons were made between the neat PLA and its blends and between blends as well. The data were analyzed and graphically plotted using Sigma-plot software version 10 (Systat Software Inc., Richmond, CA).

3. Results and discussion

3.1. Mechanical characterization

The tensile strength, modulus of elasticity, and elongation at break of neat PLA and PLA/β-CD blends were measured in the machine direction (MD) and in the transverse direction (TD) and the results are listed in Table 2. In general, all mechanical properties of the PLA changed significantly with the addition of the β-CDs. When the β-CDs were directly blended with the PLA (PLA-β-CD15% and PLA-β-CD30%), the tensile strength, elongation at break, and modulus of elasticity of the PLA decreased by about a factor of three, two, and two, respectively. This can be attributed to the β-CDs acting as fillers in the PLA continuous matrix and due to the poor interfacial interaction between the hydrophilic β-CD and hydrophobic PLA the continuous matrix became discontinuous. These perturbations of the otherwise continuous matrix resulted in changes of the mechanical properties. A similar incompatibility has been reported for blends of PLA and starch (Wang, Yu, Chang, and Ma, 2008). A reduction of the strength and of the elongation at break in the PLA/starch blends have been observed regardless of starch type and composition (Ke & Sun, 2000; Ke, Sun, and Seib (2003)). It has also been reported that the reduction of the tensile strength and of the elongation of the PLA/starch blends are related to the nucleating effect of the starch on the PLA matrix (Garlotta, Doane, Shogren, Lawton, & Willett, 2003). This could also be applicable to β-CDs since those play a role as a nucleating agent for PLA (Almenar et al., 2009).

With increasing starch content in the PLA/starch blends, the PLA matrix becomes more discontinuous resulting in decrease of strength and elongation (Ke & Sun, 2000, 2003b). Thus, the tensile strength and elongation at break of these and other bio-based blends have been reported to depend on its composition. In contrast to these results, strength and elongation at break in the PLA/β-CD blends did not depend on the β-CD content (15% vs. 30%). The tensile strength of the PLA/β-CD blends PLA-β-CD15% and PLA-β-CD30% was 11.6 ± 1.3 MPa vs. 11.3 ± 1.3 MPa, and 6.6 ± 0.8 MPa vs. 3.8 ± 1.2 MPa, for MD and CD, respectively. No effect of the CD content on the elongation at break of the PLA/β-CD blends was observed. All samples ranged around a value of 2% and 1% for MD and TD, respectively. The same trend was observed for the modulus of elasticity of the blends.

The mechanical properties of the blends improved with the use of the masterbatch to incorporate the β-CDs. This indicated better mixing between PLA and β-CDs. The tensile strength of the blends increased by the use of the masterbatch. PLA-β-CD15%-MB showed approximately twice the tensile strength of the blends PLA-β-CD15% and PLA-β-CD30%. The modulus of elasticity of the blends was also improved with the use of the masterbatch. In this case, PLA-β-CD15%-MB showed 2-3 times the modulus of elasticity of the blends PLA-β-CD15% and PLA-β-CD30%. However, no effect of the masterbatch on the elongation at break of the blends was observed. These results indicate that the blends were less breakable and more flexible in the presence of the masterbatch.

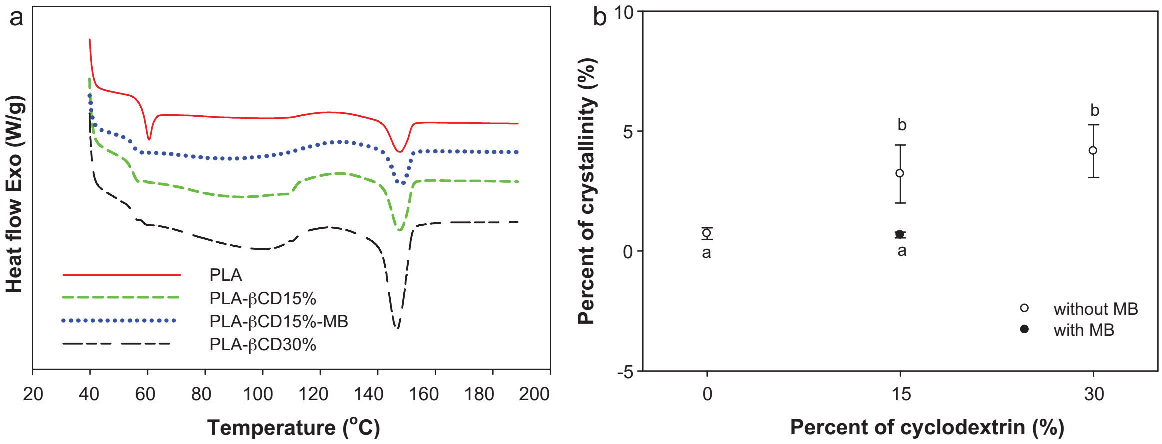

Fig. 2. DSC thermograms (1st cycle) (a) and percent of crystallinity (%) (b) of the neat PLA and the PLA/β-CD blends (a and b indicate significant differences between samples).

Table 3
Glass transition temperatures and melting temperatures of the neat PLA, β-CDs, and the PLA/β-CDs blends.

Sample code	T_g (°C)	T_m (°C)
PLA	57.0 ± 0.9a	148.2 ± 0.4a
PLA-β-CD15%	53.9 ± 0.4b	147.5 ± 0.3ab
PLA-β-CD15%-MB	54.3 ± 0.5b	147.9 ± 0.2ab
PLA-β-CD30%	54.2 ± 0.5b	147.1 ± 0.6c
β-CDs	–	145.4 ± 1.2c

a–c indicate significant differences between samples.

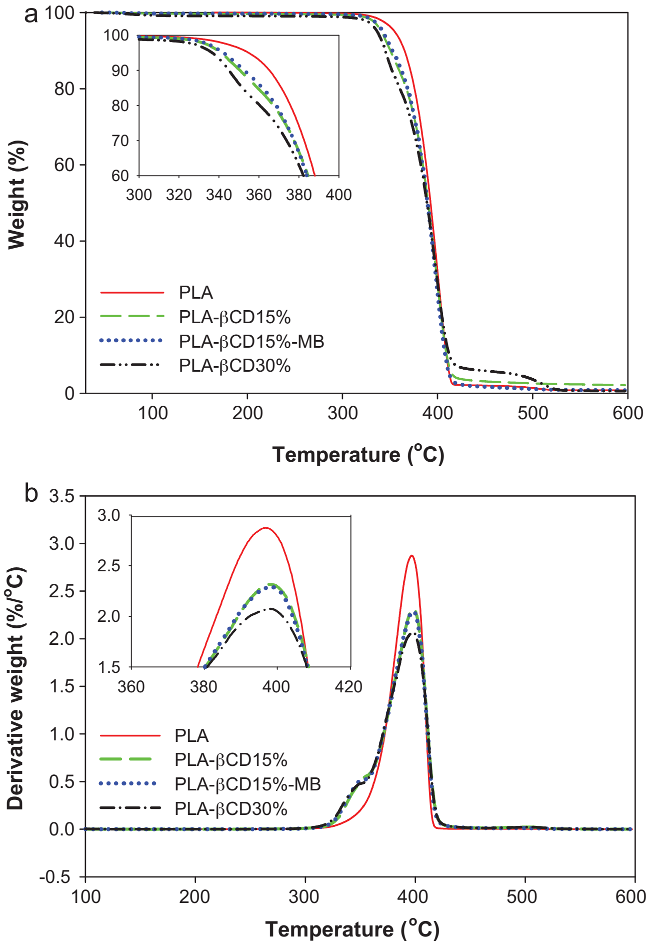

Fig. 3. Weight change (%) as a function of the temperature (°C) (a) and derivative weight (%/°C) as a function of the change of temperature (°C) (b) of the neat PLA and the PLA/β-CD blends.

3.2. *Thermal and thermo-mechanical characterization*

Table 3 summarizes some of the DSC results for the neat PLA and for the PLA/β-CD blends. The neat PLA exhibited a T_g of 57 °C and a T_m of 148 °C. The addition of β-CDs slightly decreased both of these thermal transitions in the PLA. The T_g of all the PLA/β-CD blends was about 54 °C and all T_m were about 147 °C. Similarly, Ke and Sun (2000) did not observe a significant difference in T_g among polymer blends of PLA and corn or wheat starches at various ratios (Ke & Sun, 2000). The distribution of the β-CDs among the polymer chains increased chain separation and mobility as shown by the decreased T_g of the PLA. Fig. 2(a) shows in detail how crystallinity and melting peaks were modified with the addition of β-CDs. As the amounts of β-CDs increased, the melting peak became broader and deeper and the crystallization peak became larger than those of the neat PLA. The broader melting peak was possibly caused by a wide range of size of the crystals formed by the interaction between the PLA and the β-CDs. The latter had a T_m of 145 °C (Table 3). These broader melting peaks in the PLA/β-CD blends may lead to higher hot tacks under a broader range of T_m, especially at lower ones. The larger crystallization peak was caused by the nucleating capacity of the β-CDs in the PLA matrix (Almenar et al., 2009). The fraction of crystallinity of the neat PLA and of the blends PLA/β-CDs is presented in Fig. 2(b). In the calculation of the crystallinity of the blends only PLA was considered since PLA was the main load-bearing phase. The crystallinity of the PLA/β-CD blends was low but higher than that of the neat PLA. The slight increase was correlated to the amount of β-CDs (15 and 30%). The higher amount of β-CDs, the higher the crystallinity as shown by the average value trend. This agrees with Almenar et al. (2009) who reported that the crystallinity of PLA increased with the increase of the β-CD content. However, it has been reported that the crystallinity of blends with starch contents of <20% is the same as that of extruded pure PLA, and that the crystallinity decreases slightly as the starch content increases to 40% (Ke & Sun, 2000). The crystalline contents of PLA-β-CD15%-MB and neat PLA did not differ. The reduction of the crystalline content of the PLA in the PLA-β-CD15%-MB blend compared to that of the PLA/β-CD15% blend was due to the use of the MB. Lower crystalline contents have been related to higher impact resistance and ductility (Sarasua, Lopez-Arraiza, Balerdi, & Maiza, 2005). A reduction in crystallinity of the PLA with the addition of commercial masterbatches has been reported (Byrne et al., 2009).

An endothermic peak at 63 °C associated with the T_g of neat PLA and its blends is also shown in Fig. 2(a). This peak is an aging peak (Ke & Sun, 2000) and resulted from an increase in the excess enthalpy of relaxation during processing (Cai, Dave, Gross, & McCarthy, 1996). The use of the masterbatch did not affect the thermal properties of the blends. The same T_g and T_m were observed for PLA-β-CD15%-MB and for PLA-β-CD15% (Fig. 2(a) and Table 3). Similarly, Byrne et al. (2009) who evaluated four commertial masterbatches in order to improve the impact strength, flexibility, and clarity of PLA reported no effect of the masterbatch on the T_g and on the T_m of the PLA.

TGA thermograms of the neat PLA and of the PLA/β-CD blends are presented in Fig. 3. The degradation of the neat PLA markedly started at around 366 °C and ended at 411 °C (Fig. 3(a)).The PLA/β-CD blends showed a lower thermal stability than that of the neat PLA and this was a β-CD content dependent. The higher the β-CD content the lower the thermal stability. This effect can be attributed to the lower thermal stability of the β-CDs. A degradation of around 8% vs. 0.2% was observed for β-CDs and neat PLA, respectively, when heating the materials from 0 °C to 150 °C (data not shown). No effect of the masterbatch on the thermal stability of the blends was observed. Fig. 3(a) shows the rates of decomposition for the neat PLA and for the PLA/β-CD blends. The rates of decomposition for PLA/βCD blends were faster than for the neat PLA. PLA-β-CD30% showed the fastest rate of decomposition. The derivative thermogravimetric curve shows the temperature at the maximum rate of weight loss, and this corresponds to the decomposition temperature (Wenget et al., 2008). PLA-β-CD15% and PLA-β-CD15%-MB showed similar rates of decomposition as observed in Fig. 3(b). The remaining water in the β-CDs was possibly the reason for a faster decomposition rate for the blends than for the plain PLA. It has been reported that the initial moisture content of the starch had a significant effect on the decomposition of PLA during processing of PLA/starch blends. The PLA hydrolyzes and degrades in the presence of water under the high levels of heat used during processing (Ke & Sun, 2001). The derivative thermogravimetric curves of the PLA/β-CD blends showed a shoulder which results from the degradation of the β-CDs. This was confirmed by performing the same study on β-CDs (data not shown) which resulted in the same bimodal peak. Further confirmation comes from a study of
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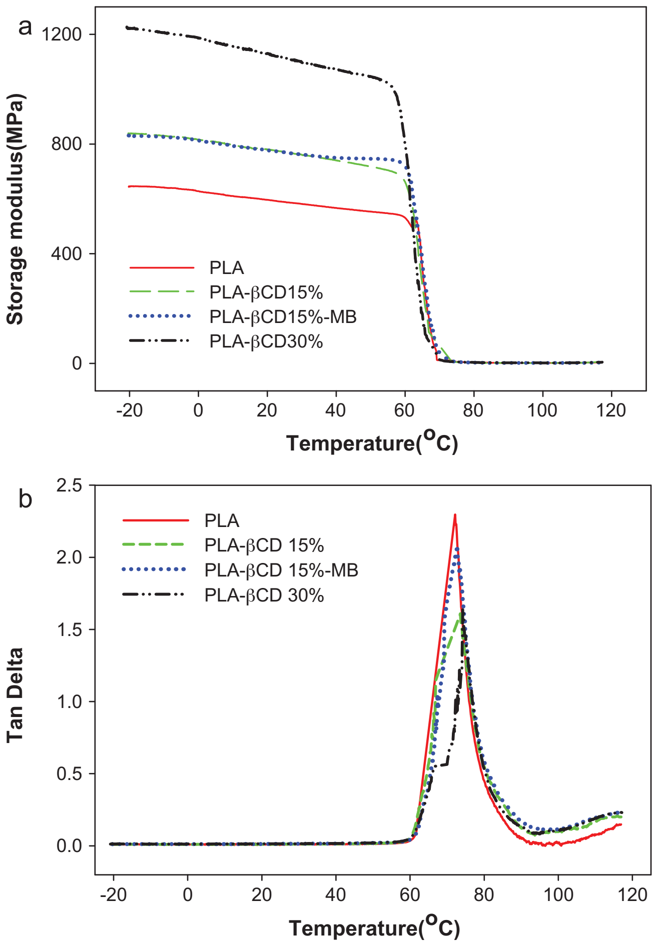

Fig. 4. Storage modulus changes (a) and Tan delta changes (b) of neat PLA and PLA/β-CD blends.

the derivative weight of poly(β-CD/2 benzoxazine IC) under nitrogen which showed a bimodal peak at about 300–350 °C (Su, Chen, & Chang, 2005).

Dynamic mechanical characterization was performed on the neat PLA and on its blends. E' and tan delta of all samples are presented as a function of temperature in Fig. 4. As shown in Fig. 4(a), the PLA blends showed higher E' than that of the plain PLA over the entire temperature range below the T_g. This confirms that the PLA matrix is restrained by the loading of β-CDs because of the incompatibility between components. Therefore, E' increased proportionally with the concentration of β-CDs. These results are in agreement with those reported by Almenar et al. (2009). No effect of the masterbatch on E' was observed. Therefore, the use of the masterbatch did not improve the applicability of the blends in applications that require rigorous processing conditions. E' dropped at 60–65 °C because of the increase in the segment mobility of the polymer chain at around the T_g.

The neat PLA showed the highest value of tan delta (Fig. 4(b)) and this decreased in the following order: PLA-β-CD15%-MB > -β-CD15% > -β-CD30%. It has been reported that the neat PLA shows a very sharp and intense peak because there is no restriction to the chain motion (Huda, Mohanty, Drzal, Schut, & Misra, 2005). The reduction of height of tan delta confirmed the hindrance of the chain mobility by the presence of β-CDs. Less reduction in height was observed in the blend containing the masterbatch. The masterbatch seems to improve the chain motion and therefore, the processability of the PLA/β-CD blends. The T_g of the blends obtained from the DMA curve was a little higher than that obtained from the DSC curve as previously reported for other polymers (Aitken et al., 1991).

3.3. Optical characterization

Fig. 5(a) shows the lightness of the neat PLA and of the PLA/β-CD blends. As observed, the blends presented a higher lightness than the neat PLA (92.53 ± 0.16 vs. 93.24 ± 0.15 and 93.34 ± 0.21, for PLA, PLA-β-CD15%, and PLA-β-CD30%). There are two reasons for this lightness increase. The first one is the natural white color of the β-CDs which became part of the polymer matrix during processing and, the second one is the higher crystallinity in the blends due to the nucleating agent capacity of the β-CDs. In general, the higher the crystalline content in a polymer, the higher its lightness. However, there were no significant differences between PLA-β-CD15%, and PLA-β-CD30% because the reduced mobility of the PLA molecules caused a similar crystallinity of the material in spite of the different amounts of nucleating agent. Similarly, extrudates of PLA/starch are opaque and of white color (Ke & Sun, 2001). Ke and Sun (2000) reported PLA/starch blends with 20% of starch as light gray and it turned into off-white as the starch contents increased to ≥40%. PLA-β-CD15%-MB showed less lightness compared with PLA-β-CD15%. This is in agreement with the reduction of the crystallinity resulting from the use of the masterbatch (Fig. 2(b)). Therefore, the use of the masterbatch improved the transparency of the new material.

Fig. 5(b) shows the color variables a^* and b^* for the neat PLA and of the PLA/β-CD blends. All samples exhibited high b^* value due to the natural yellow color of the PLA (Auras et al., 2004). Both b^* and a^* increased as β-CD content increased. Therefore, the blends became redder and more yellowish and with a total color more saturated. Of the blends, PLA-β-CD15%-MB showed the lowest redness, close to that of the neat PLA, while at the same time PLA-β-CD15%-MB showed the same yellowness as PLA-β-CD30%. This was due to the presence of β-CDs in the polymer matrix. Byrne et al. (2009) also reported an increase of the yellowness index of PLA with the use of the commercial masterbatches Biomax strong, and PLA dcS515-N (Byrne et al., 2009).

3.4. Morphological characterization

Scanning electron micrographs of the surface of fractured neat PLA and PLA/β-CD blends were taken to better understand the interaction between PLA and β-CDs. All samples were prepared in the same way, and all micrographs were taken under the same conditions. The results are shown in Fig. 6. Panel (a) shows the continuous phase of the neat PLA, while panels (b)–(d) show the micrographs for PLA with different β-CD contents and how this continuous phase became discontinuous with the addition of β-CDs. The mix of PLA and β-CDs produced a two-phase system. This claim was based on:

(1) The higher the amount of β-CDs in the blend the larger the β-CD conglomerates that are formed. An increased size of the β-CDs conglomerate was observed in the blend with the highest β-CD content (30%) (panel (d)). It seems that larger β-CD conglomerates (approximately 15 μm width) were formed by interaction between smaller ones during processing and that higher amounts of β-CDs led to the formation of larger conglomerates (Fig. 6, black arrows). This is in agreement with previous studies done with CDs that report the ability of CDs to form supramolecular complexes by linking covalently or non covalently specifically to other CDs (Del Valle, 2004), and that the size of the CD macromolecules is primarily determined by the concentration of CD (Rao & Geckeler, 2011).

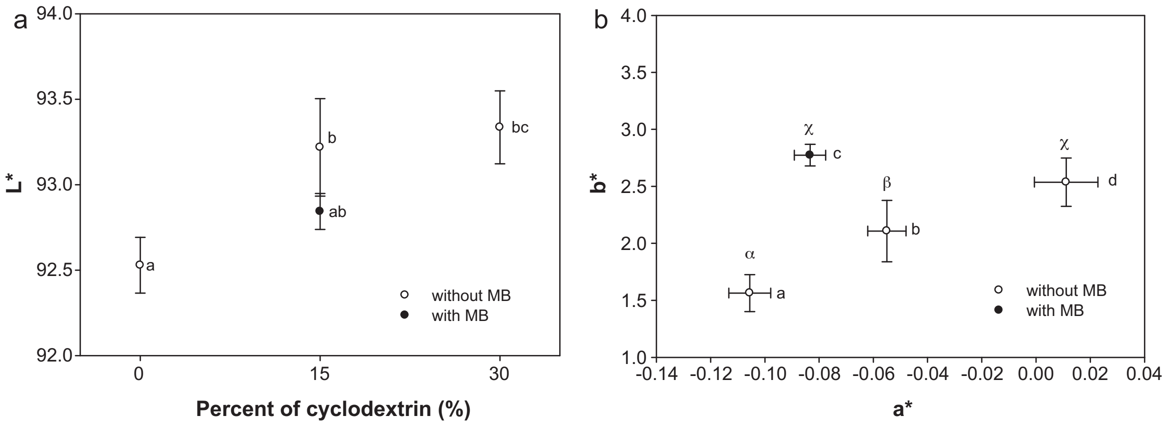

Fig. 5. L^*, a^*, and b^* color values of neat PLA and PLA/β-CD blends (a–d and α–χ indicate significant differences between samples).

(2) The presence of gaps between the PLA and the β-CDs (Fig. 6, white arrows). The higher the amount of β-CDs, the larger the gaps were. This illustrates the poor adhesion between the phases PLA and the β-CDs. These results are supported by similar ones published for PLA/starch blends. Some gaps between PLA and starch in PLA/starch blends were observed which indicated likely poor adhesion between the two phases (Ke & Sun, 2000). Visual comparison of the PLA/starch micrographs (Ke & Sun, 2000) with those of PLA/β-CDs for the same content of filler shows that the miscibility between PLA and β-CDs was higher than that of PLA and starch. In addition, microscopic observations revealed non-uniformly dispersed holes in TPS/PLA blends which indicated a separation of phases between thermoplastic starch (TPS) and PLA (Martin & Avérous, 2001). However, this poor adhesion can be improved by interfacial modification as reported by Huneault and Li (2007). Similar modifications may help to reduce the presence of gaps between the PLA and the β-CDs and therefore should be evaluated in the future.

The micrograph of PLA-β-CD15%-MB (panel (c)) shows a better mixing between PLA and β-CDs, that is, an improved dispersion of the CDs into the PLA matrix. The use of the masterbatch resulted in a larger number of β-CD conglomerates with reduced size and more uniformly distributed (Fig. 6, black and white arrows). Also, the gaps between the PLA and the β-CDs seem to be reduced in number and size. The micrograph of PLA-β-CD15%-MB (panel (c)) shows improved interfacial adhesion compared to PLA-β-CD15% (panel (b)) in most cases. Therefore, the use of the masterbatch should improve the compatibility between the two phases due

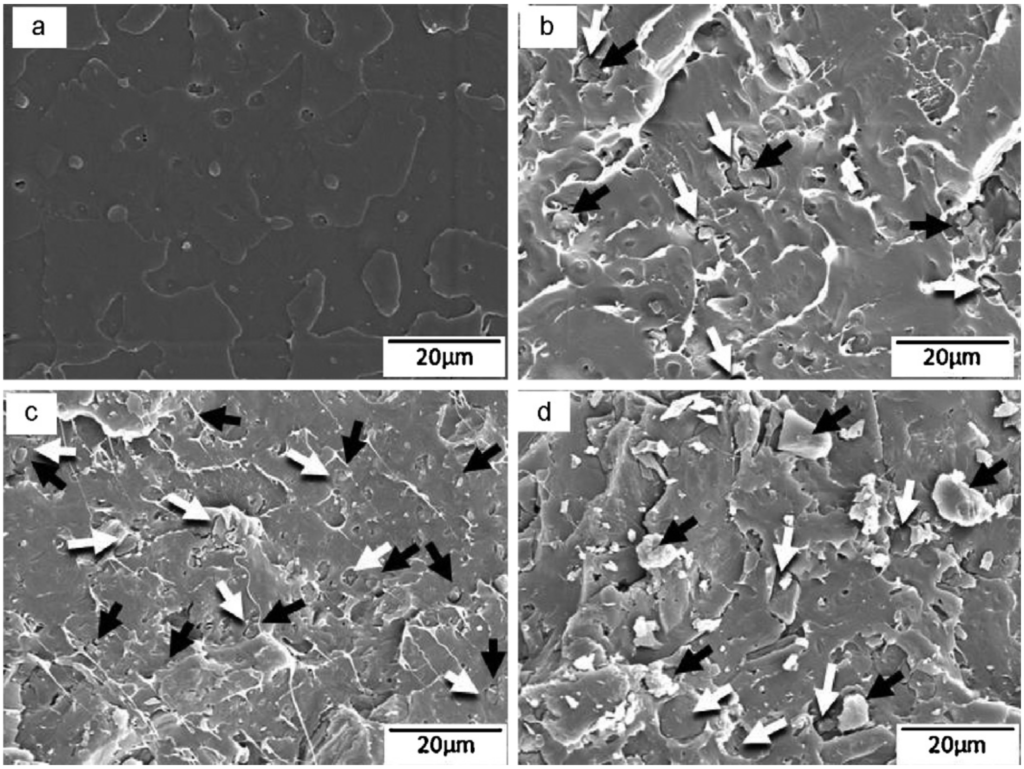

Fig. 6. Scanning electron micrographs of impact fracture surfaces of neat PLA and PLA/β-CDs pellets. Panel (a) shows neat PLA while panels (b)–(d) show PLA/β-CDs blends: PLA-β-CD15%, PLA-β-CD15%-MB, PLA-β-CD30%, respectively (white arrows point to the gaps at the interphase between PLA and CDs and black arrows point to the CD conglomerates).

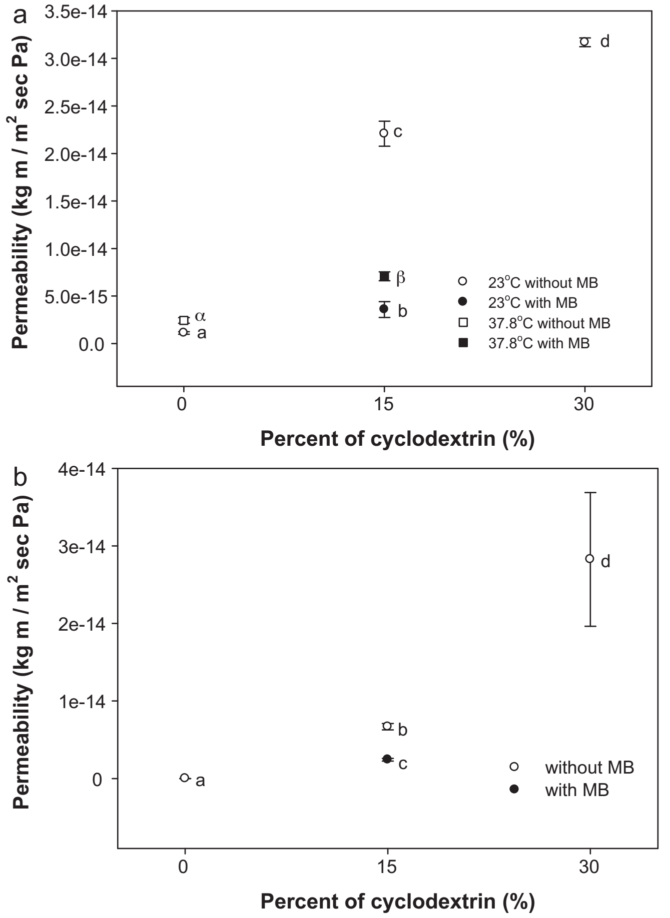

Fig. 7. Water permeability coefficient (23 °C and 37.8 °C, and 100% RH) (a) and oxygen permeability coefficient (23 °C and 0% RH) (b) of the neat PLA and of the PLA/β-CDs blends (not data for PLA-β-CD15%, PLA-β-CD30% at 37.8 °C) (a–d and α, β indicate statistical difference among samples).

to the reduction of the conglomerate size and of the number of cavities.

3.5. Barrier characterization

Fig. 7 shows the water vapor permeability coefficients of neat PLA and of the PLA/β-CD blends. The permeability of neat PLA was $1.11 \times 10^{-15} \pm 1.34 \times 10^{-16}$ kg m/m^2 s Pa and $2.43 \times 10^{-15} \pm 3.00 \times 10^{-16}$ kg m/m^2 s Pa, at 23 °C and at 37.8 °C, respectively. Higher permeability values for water vapor have been reported in the literature (2.0×10^{-14} kg m/m^2 s Pa at 20 °C and 90% RH) (Auras et al., 2004). This might be due to differences in thickness, processing history and other parameters. The permeability of the blends increased over that of the neat PLA with the increase of the β-CD content. The immiscibility of phases in the blends allowed more water molecules to penetrate. Some of the water molecules were possibly absorbed by the polymer matrix since part of them was removed in the drying process before the processing of the material. Similarly, it has been reported that water can penetrate the PLA/starch blends through the voids between phases and that some water was absorbed by the starch (<20%) (Ke & Sun, 2000). The permeability of the PLA-β-CD30% blends at 37.8 °C was so high that it could not be measured in the described equipment. The use of the masterbatch improved the barrier properties of the blends. The PLA-β-CD15%-MB blend had a water vapor permeability of $3.58 \times 10^{-15} \pm 8.34 \times 10^{-16}$ kg m/m^2 s Pa and $7.07 \times 10^{-15} \pm 4.64 \times 10^{-16}$ kg m/m^2 s Pa at 23 °C, and at 37.8 °C. Both values were lower than $2.21 \times 10^{-14} \pm 1.31 \times 10^{-15}$, the value obtained for PLA-β-CD15%.

The oxygen permeability coefficients of neat PLA and its blends are presented in Fig. 7. The permeability of the neat PLA was $8.71 \times 10^{-18} \pm 1.17 \times 10^{-18}$ kg m/m^2 s Pa at 23 °C and this value was in agreement with the value of 6.0×10^{-18} kg m/m^2 s Pa reported in the literature for PLA films exposed to the same temperature (Auras et al., 2004). For higher temperature (25 °C), oxygen permeability of PLA films has been reported as 3.3×10^{-17} kg m/m^2 s Pa (Lehermeier, Dorgan, & Way, 2001). The values for the PLA/β-CD blends were over several orders of magnitude larger than the neat PLA, and this difference was more pronounced for the higher β-CD content ($6.69 \times 10^{-15} \pm 4.10 \times 10^{-16}$ and $2.83 \times 10^{-14} \pm 8.62 \times 10^{-15}$ kg m/m^2 s, for PLA-β-CD15% and PLA-β-CD30%, respectively). The increased permeability was possibly caused by the discontinuity between the β-CDs and the PLA. The voids between phases allowed the oxygen molecules to diffuse faster through the matrix. The use of the masterbatch improved the barrier properties of the blends due to the reduction of discontinuities in the polymer matrix. PLA-β-CD15%-MB showed a lower permeability than PLA-β-CD15% ($2.43 \times 10^{-15} \pm 1.64 \times 10^{-16}$ kg m/m^2 s Pa vs. the data above).

4. Conclusions

In this study, a bio-based polymer with the capacity to carry hydrophobic molecules has been developed and characterized. Testing of mechanical, thermal, thermo-mechanical, barrier, optical, and morphological properties revealed that β-CDs and PLA are incompatible. The higher the β-CD content, the higher the incompatibility due to the increase in size of the β-CD conglomerates, and the poor adhesion between phases. The use of a masterbatch (PLA containing high β-CD content) is an effective way to improve the compatibility between PLA and β-CDs, and the properties of PLA/β-CD blends.

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References

Adeli, M., Zarnegar, Z., & Kabiri, R. (2008). Amphiphilic star copolymers containing cyclodextrin core and their application as nanocarrier. *European Polymer Journal*, *44*(7), 1921–1930.

Ahmed, S. I., Shamey, R., Christie, R. M., & Mather, R. R. (2006). Comparison of the performance of selected powder and masterbatch pigments on mechanical properties of mass coloured polypropylene filaments. *Coloration Technology*, *122*(5), 282–288.

Aitken, D., Burkinshaw, S. M., Cox, R., Catherall, J., Litchfield, R. E., Price, D. M., et al. (1991). Determination of the T_g of wet acrylic fibers using DMA. *Journal of Applied Polymer Science: Applied Polymer Symposium*, *47*, 263–269.

Almenar, E., Auras, R., Harte, B., & Rubino, M. (2007). Micro-encapsulation of volatile compounds into cyclodextrins: A new technology to reduce post harvest losses. US 2007/0207981 A1, United States.

Almenar, E., Auras, R., Harte, B., & Rubino, M. (2009). Beta-cyclodextrins as nucleating agents for poly(lactic acid). US 2009/0060860 A1, United States.

Almenar, E., Auras, R., Rubino, M., & Harte, B. (2007). A new technique to prevent main post harvest diseases in berries during storage: Inclusion complexes β-CD-hexanal. *International Journal of Food Microbiology*, *118*(2), 164–172.

Almenar, E., Auras, R., Wharton, P., Rubino, M., & Harte, B. (2007). Release of acetaldehyde from β-CD inhibits postharvest decay fungi *in vitro*. *Journal of Agricultural and Food Chemistry*, *55*(17), 7205–7212.

ASTM International. (2003). *Standard test for transition temperatures and enthalpies of fusion and crystallization of polymers by differential scanning calorimetry*. D3418-03: American National Standards Institute.

ASTM International. (2002). *Standard practice for heat flow calibration of differential scanning calorimeters*. E968-02: American National Standard Institute.

ASTM International. (2003). *Standard practice for temperature calibration of differential scanning calorimeters and differential thermal analysers*. E967-03: American National Standard Institute.

ASTM International. (2006). *Standard practices for plastics: Dynamic mechanical practices: Determination and report of procedures*. D4065-06: American National Standard Institute.

ASTM International. (2005). *Standard test method for oxygen gas transmission rate through plastic film and sheeting using a coulometric sensor*. D3985-05: American National Standard Institute.

ASTM International. (2002). *Standard test method for tensile properties of thin plastic sheeting*. D882-02: American National Standard Institute.

ASTM International. (2005). *Standard test method for water vapor transmission rate through plastic film and sheeting using a modulated infrared sensor*. F1249-05: American National Standard Institute.

Auras, R., Harte, B., & Selke, S. (2004). An overview of polylactides as packaging materials. *Macromolecular Bioscience*, *4*(9), 835–864.

Byrne, F., Ward, P., Kennedy, J., Imaz, N., Hughes, D., & Dowling, D. (2009). A study of the effect of masterbatch addition on the mechanical, thermal, optical and surface properties of poly(lactic acid). *Journal of Polymers and the Environment*, *17*(1), 28–33.

Cai, H, Dave, V., Gross, R. A., & McCarthy, S. P. (1996). Effects of physical aging,crystallinity, and orinetation on the enzymatic degradation of poly(lactic acid). *Journal of Polymer Science Part B: Polymer Physics*, *34*(16), 2701–2708.

Conn, R. E., Kolstad, J. J., Borzelleca, J. F., Dixler, D. S., Filer, L. J., Jr., Ladu, B. N., Jr., et al. (1995). Safety assessment of polylactide (PLA) for use as a food-contact polymer. *Food and Chemical Toxicology*, *33*(*4*), 273–283.

De Graaf, R. A., & Janssen, L. P. B. M. (2001). Properties and manufacturing of new starch plastics. *Polymer Engineering & Science*, *41*(3), 584–594.

Del Valle, E. M. M. (2004). Cyclodextrins and their uses: A review. *Process Biochemistry*, *39*(*9*), 1033–1046.

Dorgan, J. R., Braun, B., Wegner, J. R., & Knauss, D. M. (2006). *Degradable polymers and materials*. Washington, DC: American Chemical Society.

Fischer, E. W., Sterzel, H. J., & Wegner, G. (1973). Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Colloid & Polymer Science*, *251*(11), 980–990.

Garlotta, D., Doane, W., Shogren, R., Lawton, J., & Willett, J. L. (2003). Mechanical and thermal properties of starch-filled poly(D,L-lactic acid)/poly(hydroxy ester ether) biodegradable blends. *Journal of Applied Polymer Science*, *88*(7), 1775–1786.

Huda, M. S., Mohanty, A. K., Drzal, L. T., Schut, E., & Misra, M. (2005). 'Green' composites from recycled cellulose and poly(lactic acid): Physico-mechanical and morphological properties evaluation. *Journal of Materials Science*, *40*(16), 4221–4229.

Huneault, M. A., & Li, H. (2007). Morphology and properties of compatibilized polylactide/thermoplastic starch blaends. *Polymer*, *48*, 270–280.

Jin, T., & Zhang, H. (2008). Biodegradable polylactic acid polymer with nisin for use in antimicrobial food packaging. *Journal of Food Science*, *73*(3), M127–M134.

Ke, T., & Sun, X. (2000). Physical properties of PLA and starch composites with various blending ratios. *Cereal Chemistry*, *77*(6), 761–768.

Ke, T., & Sun, X. (2001). Effects of moisture content and heat treatment on physical properties of starch and poly(lactic acid) blends. *Journal of Applied Polymer Science*, *81*(12), 3069–3082.

Ke, T., & Sun, X. (2003). Starch, poly(lactic acid), and poly(vinyl alcohol) blends. *Journal of Polymers and the Environment*, *11*(1), 7–14.

Ke, T., Sun, X., & Seib, P. (2003). Mechanical properties of starch/poly (lactic acid) blend as affected by physical aging. *Journal of Applied Polymer Science*, *89*(13), 3639–3646.

Kijchavengkul, T., & Auras, R. (2008). Perspective compostability of polymers. *Polymer International*, *57*, 793–804.

Kim, D. J., Seo, K. H., Hong, K. H., & Kim, S. Y. (1999). Effects of dispersing agents on dispersity and mechanical properties of carbon black PET. *Polymer Engineering & Science*, *39*(3), 500–507.

Kulinski, Z., & Piorkowska, E. (2005). Crystallization, structure and properties of plasticized poly(L-lactide). *Polymer*, *46*(23), 10290–10300.

Lehermeier, H. J, Dorgan, J. R., & Way, J. D. (2001). Gas permeation properties of poly(lactic acid). *Journal of Membrane Science*, *190*(2), 243–251.

Lim, L. T., Auras, R., & Rubino, M. (2008). Processing technologies for poly(lactic acid). *Progress in Polymer Science*, *33*(8), 820–852.

Lunt, J. (1998). Large-scale production, properties and commercial applications of polylactic acid polymers. *Polymer Degradation and Stability*, *59*, 145–152.

Martin, O., & Avérous, L. (2001). Poly(lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymer*, *42*(14), 6209–6219.

Rafler, G., Lang, J., Jobmann, M., & Bechthold, I. (2001). Biodegradable polymers. 9. Technologically relevant aspects of kinetics and mechanisms of ring-opening polymerization of L, L-dilactide. *Macromolecular Materials and Engineering*, *286*(12), 761–768.

Rao, J. P., & Geckeler, K. E. (2011). Cyclodextrin supramacromolecules: Unexpected formation in aqueous phase under ambient conditions. *Macromolecular Rapid Communications*, *32*, 426–430.

Rasal, R. M., Janorkar, A. V., & Hirt, D. E. (2010). Poly(lactic acid) modifications. *Progress in Polymer Science*, *35*(3), 338–356.

Sarasua, J. R., Lopez-Arraiza, A., Balerdi, P., & Maiza, I. (2005). Crystallinity and mechanical properties of optically pure polylactides and their blends. *Polymer Engineering & Science*, *45*(5), 745–753.

Södergård, A., & Stolt, M. (2002). Properties of lactic acid based polymers amd their correlation with composition. *Progress in Polymer Science*, *27*(6), 1123–1163.

Su, Y. C., Chen, W. C., & Chang, F. C. (2005). Preparation and characterization of polyseudorotaxanes based on adamantane-modified polybenzoxazines and β-cyclodextrin. *Polymer*, *46*(5), 1617–1623.

Wang, N., Yu, J., Chang, P. R., & Ma, X. (2008). Influence of fromamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydrate Polymers*, *71*(1), 109–118.

Yu, L., Dean, K., & Li, L. (2006). Polymer blends and composites from renewable resources. *Progress in Polymer Science*, *31*(6), 576–602.

Yu, L., Petinakis, E., Dean, K., & Liu, H. (2010). Poly (lactic acid)/starch blends. In R. Auras, L. T. Lim, S. E. M. Selke, & H. Tsuji (Eds.), *Poly(lactic acid): Synthesis, structure, properties, processing and applications* (pp. 217–226). New Jersey: Wiley Series in Polymers and Technology.

Yuan, H., Liu, Z., & Ren, J. (2009). Preparation, characterization, and foming behavior of poly(lactic acid)/poly(butylene adipate-co-butylene terephtalate) blend. *Polymer Engineering & Science*, *49*(5), 1004–1012.

Zhang, J. F., & Sun, X. (2004). Mechanical and thermal properties of poly(lactic acid)/starch blends with dioctyl maleate. *Journal of Applied Polymer Science*, *94*(4), 1697–1704.

Zhang, J., & Sun, X. (2005). Poly (lactic acid)-based bioplastics. In R. Smith (Ed.), *Biodegradable polymers for industrial applications*. Boca Raton: CRC Press LLC.