Incorporating Amylopectin in Poly(lactic acid) by Melt Blending Using Poly(ethylene-*co*-vinyl alcohol) as a Thermoplastic Carrier. II. Physical Properties

M. D. Sanchez-Garcia,[1] D. Nordqvist,[2] M. Hedenqvist,[2] J. M. Lagaron[1]

[1]*Novel Materials and Nanotechnology Group, IATA-CSIC, Apdo Correos 73, Burjassot 46100, Spain*
[2]*Royal Institute of Technology, Department of Fibre and Polymer Technology, Stockholm SE-100 44, Sweden*

ABSTRACT: This study adds to a previous morphological work (paper I) with further characterization of the developed poly(lactic acid) (PLA) blends containing amylopectin, which made use of an ethylene-vinyl alcohol copolymer (EVOH) as a melt-compoundable carrier for the polysaccharide in the biopolyester. The effect of using glycerol as compatibilizer was also characterized. Water and oxygen transport parameters, mechanical properties, and comparative biodegradability tests were evaluated for the blends. From the results, the barrier properties to oxygen were only seen to improve at 0%RH and mostly for the PLA-EVOH blends, which furthermore showed a positive deviation from the rule of mixtures. At high relative humidity, the blends showed somewhat poorer barrier performance due to the comparatively higher improvement in barrier of the neat PLA at 80% RH. Interestingly, room temperature biodegradability testing suggested that low additions of the blending elements seemed to facilitate the biodegradability of the biopolyester. Despite the fact that properties were not so dramatically improved, incorporating renewable resources within PLA seems as a potentially viable route to reduce PLA supply dependency, retain good optical properties and to overcome some drawbacks associated to the use of this biopolyester. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3708–3716, 2011

Key words: polylactic acid; renewable resources; packaging; bioplastis; amylopeptine

INTRODUCTION

Poly (lactic acid) (PLA) is today one of the most important renewable/biodegradable plastic materials. Hence, this linear aliphatic thermoplastic polyester is receiving a lot of attention from researchers all over the world as an alternative material for packaging applications. Besides being renewable and biodegradable, its transparency, mechanical properties, and processability make PLA an attractive and interesting material from an application point of view.[1,2] A problem with PLA is, as with many other environmentally friendly materials, the fact that the biopolymer and processing costs are too high compared to its petroleum-based polymers. The properties of this biodegradable polymer are still considered to be insufficient for some applications and demand continuous efforts to exceed production capacity. Therefore, several studies have been carried out where PLA has been mixed with other biodegradable and nonbiodegradable materials.[3–6] By choosing a less expensive, biodegradable polymer as blending material for PLA the production costs and inaccessibility could be potentially lowered at the same time as the "eco" factor is retained.

Several materials can be considered as a blending component for PLA. The low price, good availability, and performance along with its biobased origin make starch an attractive and promising candidate for renewable applications. Starch consists of a mixture of amylose ($\sim$ 30%) and amylopectin ($\sim$ 70%), both based on chains of 1,4-linked α-D-glucose.[7] Amylose is linear, whereas amylopectin (AP) is highly branched and forms transparent films, a very attractive feature when it comes to the packaging area.[8] Martin and Averous[9] previously studied melt-blended PLA/starch systems. The results showed a relatively low level of compatibility between the two systems, reported after observation of two glass transition temperatures (T_g). Also their SEM studies indicated a low degree of compatibility and the use of adequate compatibilizers was suggested as the right way forward.

Ethylene-vinyl alcohol (EVOH) copolymers are a family of semicrystalline materials with excellent barrier properties to gases and hydrocarbons (in drier conditions), and with outstanding chemical resistance.[10] These materials have been increasingly implemented in many pipe and packaging applications where stringent criteria in terms of chemical resistance and gas, water, aroma, and hydrocarbon

Correspondence to: J. M. Lagaron (lagaron@iata.csic.es).

permeation are to be met. In particular, the copolymers with low contents of ethylene (below 38 mol % ethylene) have outstanding barrier properties under dry conditions compared to most other polymeric materials. Despite the low gas permeation, EVOH copolymers generally show a high hydrophilic character that can be tuned by composition. The hydrophilicity results in high water uptake in high relative humidity environments. The EVOH end properties can be designed for different applications by controlling the EVOH composition ratio. Even when the EVOH family comprises no sustainable polymers, some grades of the homopolymer PVOH are water soluble and are classified as biodegradable. Moreover, EVOH grades with high vinyl contents (i.e., higher that 71 mol % of vinyl alcohol) are highly hygroscopic and can biodegrade under certain conditions.[11,12] The similarities to biopolymers exhibited by EVOH in properties have also led to studies and trials where blends with biodegradable materials have been produced.[13,14] By using this material the biodegradation time could be shortened, prices lowered and at the same time hopefully the properties kept at an acceptable level.

Despite above, limited work on pure blends of PLA and EVOH has been performed, even if the topic has been under investigation for some years.[15] Lee at al.[16] used reactive blending to induce a reaction between the two components, and the material obtained was compared with EVOH/PLA simple blends. The mechanical properties were far better when a reactive blending component was used, also the morphology studies indicated that this route resulted in better compatibility. Orts et al.[17] recently studied blends of EVOH and thermoplastic starch with water/glycerol as a plasticizer. They found that the most important factor altering the mechanical properties and the change in morphology was the relative humidity (RH) at which the samples were stored since this affects the degree of crystallinity in the materials. The crystallinity of amylopectin films has been studied before and showed that the level of humidity at film forming can affect the crystallization process.[18,19] The produced films in this study were, therefore, handled in the same way and stored at the same RH before testing.

In this study, the feasibility of using EVOH-29 (containing 29 mol % of ethylene in the copolymer) to implement AP into PLA via melt compounding is presented. In this first study, the blend morphology was investigated using optical microscopy, scanning electron microscopy, and Raman imaging spectroscopy, and the thermal properties were measured by differential scanning calorimetry. Despite the fact that EVOH and amylopectin are both highly polar, their blends were immiscible. Still, the blends exhibited an excellent phase dispersion on a micron level,

which was enhanced further by the addition of glycerol. A good phase dispersion was finally observed by incorporation of the latter blends in the PLA matrix, suggesting that the proposed blending route can be successfully applied for these systems. Finally, the DSC data showed that the melting point of EVOH dropped in the EVOH/amylopectin blends, but the properties of the PLA phase was still relatively unaffected as a result of blending with the above components.[20]

In this second study of the materials, the barrier properties against oxygen and water as well as the mechanical properties are investigated. Furthermore, room temperature simple comparative biodegradability tests between the different systems are presented.

MATERIALS AND METHODS

Materials

A semicrystalline extrusion grade of poly(lactid acid) (PLA) (Natureworks) with a D-isomer content of approximately 2% was used in this study. It had a weight-average molecular weight (M_w) of 150,000 g/mol and a molecular weight (M_n) of ca. 130,000 g/mol. Soarnol® standard grades (EVOH2903) of EVOH copolymer with 29 mol % ethylene was supplied by Nippon Synthetic Chemical Industry (Nippon Goshei, Osaka, Japan). Amylopectin (AP) (α-1,4-glucan with α-1,6-cross-linking; one terminal group per 25 glucose units) from maize [CAS: 9037-22-3] was purchased from Sigma-Aldrich (Sweden), and glycerol was purchased from Panreac Quimica S.A. (Spain).

Preparation of blends

To get the highest degree of dispersion, several different routes were investigated. These are described more thoroughly in part I of this study.[20] The preparation process selected in the end was a direct melt-mixing step. Different concentrations of EVOH/AP with and without glycerol were first melt-mixed in a Brabender Plastograph mixer (16 cm³) for 4 min at 195°C. The mixing temperature was chosen low enough to avoid excessive thermal exposure to the AP but high enough to melt EVOH. The AP was added in a water solution as that resulted in better films than simply adding AP in its granular form. Subsequent to the mixing, the batches were left at room temperature to cool-down. After drying the resulting EVOH/AP blends, in a second melt-blending step, were mixed with PLA. The sample codes used throughout the paper are 45/45/10 and refer to the content (in wt %) of EVOH/AP/glycerol, respectively. The samples containing PLA were

coded throughout the paper as follows: PLAx% (45/ 45/10), where x% corresponds to the content of the EVOH/AP/glycerol blend in the polymer matrix. Mixing times were finally selected to 5 min at 40 RPM followed by 1 min at 60 RPM at 190°C. The batches were allowed to cool-down to room temperature after removal and were after this pressed into films using a hot-plate hydraulic press (190°C and 2 MPa for 4 min). By averaging four independent measurements for each sample using a Mitutoyo micrometer, the thicknesses of the films were determined to be between 80 and 110 μm. Figure 1 shows typical optical pictures of PLA and of PLA-blend films containing 5 wt % of EVOH, of (EVOH29/AP) and of (EVOH29/AP/Gly). From these pictures, it can be seen that all samples remain transparent at 100 μm thickness. The biocomposites exhibit good optical properties and clarity, even with the addition of EVOH, amylopectin or with the addition of glycerol. The samples after pressing were conditioned at 54% RH and tested within 2 weeks of preparation.

Gravimetric measurements

Direct permeability to water was determined from the slope of weight loss versus time experiments at 24°C and 40% RH. The films were sandwiched between the aluminum top (open O-ring) and bottom (deposit for the permeant) parts of aluminum permeability cells. A Viton rubber O-ring was placed between the film and the bottom part of the cell to enhance sealability. Then the bottom part of the cell was filled with the permeant and the pinhole was secured with a rubber O-ring and a screw. Finally, the cell was placed in the desired environment and the solvent weight loss through a film area of 0.001 m^2 was monitored and plotted as a function of time. The samples were preconditioned at the desired testing conditions for 24 h, and to estimate permeability we used only the linear part of the weight loss data to ensure sample steady state conditions. Cells with aluminum films (with thickness of $\sim$ 100 μm) were used as control samples to estimate solvent loss through the sealing. The permeability sensitivity of the permeation cells was determined to be of $\sim$ 0.01 $\times$ 10^{-13} kg m/s m^2 Pa based on the weight loss measurements of the aluminum cells. Cells clamping polymer films but with no solvent were used as blank samples to monitor water uptake. Solvent permeation rates were estimated from the steady-state permeation slopes. Water vapor weight loss was calculated as the total cell loss minus the loss through the sealing and plus the water weight gain. The tests were done in duplicate and one-way analysis of the variance (ANOVA) was performed using XLSTAT-Pro (Win) 7.5.3 (Addinsoft, NY) software package.

Comparisons between samples were evaluated using the Tukey test.

Water uptake

The water uptake was estimated during the sorption experiments at 24°C and 100% RH by means of weight gain using an analytical balance Voyager® V11140. Thus, at saturation conditions, no changes in successive weight uptake were observed during the measurements of the specimens.

Oxygen transmission rate

The oxygen permeability coefficient (P) was derived from oxygen transmission rate (OTR) measurements recorded using an Oxtran 100 equipment (Modern Control, Minneapolis, MN). The temperature was kept at 24°C, while experiments were performed at two different relative humidities, 0% RH and 80% RH. The reason for the latter is that such conditions are closer to real applications. 80% relative humidity was generated by a built-in gas bubbler and was checked with a hygrometer placed at the exit of the detector. Experiments were done in duplicate. Diffusion and solubility coefficients were also estimated at 0% and at 80% RH. The samples were purged with nitrogen for a minimum of 20 h, prior to exposure to a 100% oxygen flow of 10 mL/min, and a 5 cm^2 sample area was measured by using an in-house developed mask. The Diffusion (D) coefficient was estimated from fitting the OTR-time curve to the first six sum terms of the following solution of the Fick's second law:[21,22]

$$\text{OTR}(t) = \frac{Pp}{l}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{D\pi^2 n^2 t}{l^2}\right)\right] \quad (1)$$

In eq. (1), p is the oxygen partial pressure and l is the film thickness.

The solubility coefficient was calculated by solving for S in the following equation[20]:

$$P = D \times S \quad (2)$$

Mechanical properties

Tensile tests were carried out at 24°C and 50% RH on an Instron 4400 Universal Tester. Dumb-bell shaped specimens with initial gauge length of 25 mm and 5 mm in width were die-stamped from the sheets in the machine direction according to ASTM D638. The thickness of all specimens was approximately 100 μm. A fixed crosshead rate of 10 mm/min was utilized in all cases, and results were taken as the average of four tests. The samples were preconditioned at 54% RH before testing and were assayed within 2 weeks after preparation of the films.
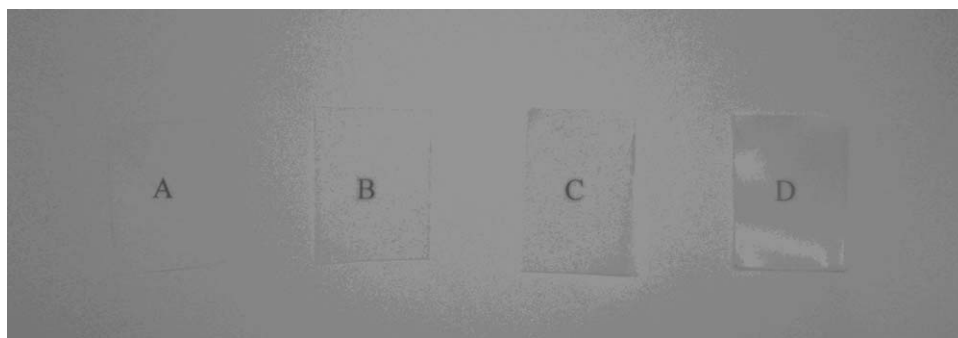
Figure 1 Typical photographs of 100 μm thickness cast films of (A) PLA, (B) PLA + 5 wt % EVOH, (C) PLA + 5 wt % (EVOH/AP), (D) PLA + 5 wt % (EVOH/AP/Gly).

Biodegradability

Biodegradability may be tested by various methods. For simplicity in experimental setup, we chose a comparative method. Polycaprolactone (PCL), known to be readily biodegradable, was chosen as a reference material.[23] Biodegradability of the films was tested in a composting plant, filled with fresh compost, and "fed" regularly with apple slices. The temperature of the compost was around 25°C at all times, while the relative humidity was around 60–70%. The samples were sandwiched between wire nets, placed in the composting plant and covered with the fresh compost. Photographs were taken regularly during a period of 60 days to monitor the biopolymer degradation.

RESULTS AND DISCUSSION

Mass transport properties

Table I summarizes measured direct permeability of water and water uptake for the PLA film and their blends together with permeability values reported in the literature for EVOH29.[24]

EVOH films have, as expected, poorer water barrier than PLA films, hence the addition of EVOH29 to PLA leads to higher water permeability when compared to pure PLA. Thus, the blends of PLA with an EVOH29 content of 1, 5, and 10 wt % have a water permeability increase of 17, 13, and 10%, respectively, compared to the unfilled material. The statistical analysis indicates that the variations on permeability between the different EVOH sample contents are not significant. The water uptake was also seen to increase and was found to be for these samples of 1.1, 1.4, and 1.4%, respectively, whereas was of 0.85% for the pure PLA.

In a similar fashion, the addition of amylopectin to these blends led to a further increase in water permeability. Blends of PLA with 1, 5, and 10 wt % (EVOH29 + 50%AP) content exhibited a water permeability increase of 19, 19, and 26%, respectively, compared to the unfilled material. This is not surprising since the water uptake of amylopectin is also much higher than that of PLA.[25] Amylopectin is a hydrophilic material, which also leads to slightly higher water uptake when present in the blend. The water uptake for the different amylopectin blends was found to be 0.8, 1.1, and 2.2%, respectively.

Glycerol is a very hydrophilic material and, therefore, the addition of it to the different blends leads to additional increases in the water permeability. PLA-blends with 1, 5, and 10 wt % (EVOH29 + 50% AP + 10% glycerol) content showed water permeability increases of 52, 50, and 58%, respectively, compared to the unfilled material. The water uptake increases further until 1.1, 2.2, and 3.2%, respectively, in these blends. This is expected and a normal behavior due to the hydrophilic character of glycerol.[26]

Table II shows the measured oxygen permeability and also oxygen diffusion and solubility coefficients for the films. Table II also gathers permeability values reported in the literature for PLA.[24,27] The oxygen permeability coefficients reported from different authors for pure PLA, measured at dry and wet conditions, provide similar values as those measured in our laboratory and suggest that %RH has a minor effect on the permeability for the biopolymer. In this context, Auras et al.[1] also reported a reduction in the oxygen permeability coefficient for the pure PLA with increasing water activity (at a constant temperature).

From Table II, it is observed that EVOH29 is at 0% RH and at 80% RH a much better barrier than PLA. Therefore, the rationale behind the current blending work was that the addition of EVOH29 to the PLA should result in enhanced oxygen permeability compared to the unfilled PLA, and that this enhancement should be greater at 0% RH, due to the better permeability of the EVOH29 at low humidity.

The results measured at 0% RH and 24°C indicate that blends of PLA with EVOH29 have a lower average oxygen permeability compared to the unfilled material. This decrease is higher, particularly for the

TABLE I
Water Permeability and Water Uptake for PLA Films and Their Blends

Sample	P water (kg m/s m^2 Pa)	Water uptake 100% RH (%)
PLA	[a]$1.18 \pm 0\ e^{-14}$	Literature value[33] 0.85
PLA + 1% EVOH29	[b]$1.38 \pm 0.04\ e^{-14}$	1.05
PLA + 5% EVOH29	[b]$1.33 \pm 0.03\ e^{-14}$	1.42
PLA + 10% EVOH29	[b]$1.30 \pm 0.10\ e^{-14}$	1.43
PLA + 1% (E29 + 50% AP)	[c]$1.40 \pm 0.04\ e^{-14}$	0.81
PLA + 5% (E29 + 50% AP)	[c]$1.40 \pm 0.03\ e^{-14}$	1.06
PLA + 10% (E29 + 50% AP)	[c]$1.49 \pm 0.04\ e^{-14}$	2.22
PLA + 1% (E29 + 50% AP + 10%Gly)	[d]$1.79 \pm 0.03\ e^{-14}$	1.14
PLA + 5% (E29 + 50% AP + 10% Gly)	[d]$1.71 \pm 0.009\ e^{-14}$	2.15
PLA + 10% (E29 + 50% AP + 10% Gly)	[d]$1.87 \pm 0.05\ e^{-14}$	3.19
PLA + 5% (E29 + 65% AP + 10% Gly)	[d]$1.79 \pm 0.03\ e^{-14}$	2.82
EVOH29		9.33
Literature value[24] EVOH29	$1.70\ e^{-14}$	
EVOH29 + 50% AP		19.01
EVOH29 + 65% AP		28.04
Literature value[25] amylopectin	$1.15\ e^{-14}$	21[28]

The a, b, c, and d letters correspond to the ANOVA statistical analysis and Tukey test of the data that indicate that with a 95% level of confidence the values are significantly different.

10 wt % loading, than expected by the simple rule of mixtures as seen in Figure 2. The rule of mixtures predicts a permeability drop of 10% for 10 wt % loading, but the experimental value shows a decrease of ca. 26%. A reduction in the oxygen diffusion coefficient of ca. 38% can also be seen and as a result a corresponding increase in oxygen solubility of around 20%. Curiously, the previous work indicated that the crystallinity of the PLA phase, but also the T_g, decreased to a small extent by blending with EVOH.[20] Hence, the increase of the oxygen solubility may be attributed to the different phase structures in the blend suggested by the crystallinity alterations reported in the previous work.[20]

Unfortunately, at 80% RH the oxygen permeability provided no apparent improvement with the addition of EVOH. The oxygen diffusion coefficient and the oxygen solubility coefficient measured at 80% RH showed no improvement compared to the pure PLA. The reason for this behavior must then be attributed to the interaction of the blends with water, which seems to be detrimental for the blends. Table II shows that while pure PLA reduces somewhat permeability with increasing humidity, the blends reduce to a much lesser extent and in some cases remain unmodified.

The addition of amylopectin to these blends results in a slight decrease in the oxygen permeability measured at 0% RH. However, in the case of the

TABLE II
Oxygen Permeability and Standard Deviation, Oxygen Diffusion Coefficient at 80% RH and 0% RH, and at 24°C for These Blends

|	P oxygen 80% RH, 24°C (m^3 m/s m^2 Pa)	P oxygen 0% RH, 24°C (m^3 m/s m^2 Pa)	D oxygen 80% RH, 24°C (m^2/s)	D oxygen 0% RH, 24°C (m^2/s)	S oxygen 80% RH, 24°C (g/g Pa)	S oxygen 0% RH, 24°C (g/g Pa)
PLA	$1.64 \pm 0.27\ e^{-18}$	$2.26 \pm 0.01\ e^{-18}$	$1.97\ e^{-12}$	$1.53\ e^{-12}$	$9.28\ e^{-7}$	$14.80\ e^{-7}$
Literature value[24] PLA	$2.21\ e^{-18}$	$2.25\ e^{-18}$				
Literature value[27] PLA	$1.75\ e^{-18}$					
PLA + 1% EVOH29	$2.03 \pm 0.46\ e^{-18}$	$2.21 \pm 0.02\ e^{-18}$	$1.82\ e^{-12}$	$1.72\ e^{-12}$	$9.34\ e^{-7}$	$12.88\ e^{-7}$
PLA + 5% EVOH29	$1.81 \pm 0.15\ e^{-18}$		$2.08\ e^{-12}$		$8.20\ e^{-7}$	
PLA + 10% EVOH29	$1.72 \pm 0.07\ e^{-18}$	$1.67 \pm 0.08\ e^{-18}$	$1.83\ e^{-12}$	$0.95\ e^{-12}$	$9.12\ e^{-7}$	$17.64\ e^{-7}$
PLA + 1% (E29 + 50% AP)	$2.42 \pm 0.36\ e^{-18}$		$1.85\ e^{-12}$		$11.70\ e^{-7}$	
PLA + 5% (E29 + 50%AP)	$2.18 \pm 0.17\ e^{-18}$	$2.24 \pm 0.05\ e^{-18}$	$2.31\ e^{-12}$	$1.54\ e^{-12}$	$8.65\ e^{-7}$	$14.50\ e^{-7}$
PLA + 10% (E29 + 50%AP)	$2.19 \pm 0.10\ e^{-18}$		$1.94\ e^{-12}$		$10.91\ e^{-7}$	
PLA + 1% (E29 + 50% AP + 10% Gly)	$2.12 \pm 0.06\ e^{-18}$		$1.68\ e^{-12}$		$12.32\ e^{-7}$	
PLA + 5% (E29 + 50% AP + 10% Gly)	$1.69 \pm 0.19\ e^{-18}$		$1.97\ e^{-12}$		$7.89\ e^{-7}$	
PLA + 10% (E29 + 50% AP + 10% Gly)	$2.13 \pm 0.17\ e^{-18}$		$1.80\ e^{-12}$		$11.13\ e^{-7}$	
PLA + 5% (E29 + 65% AP + 10%Gly)	$1.99\ e^{-18}$		$2.18\ e^{-12}$		$9.10\ e^{-7}$	
Literature value EVOH29, 20°C	$0.0023\ e^{-18}$	$0.00084\ e^{-18}$				
Literature value[28] amylopectin 50% RH, 20°C	$0.004\ e^{-18}$					
Literature value[28] amylopectin + 10% Gly 50% RH, 20°C	$0.006\ e^{-18}$					
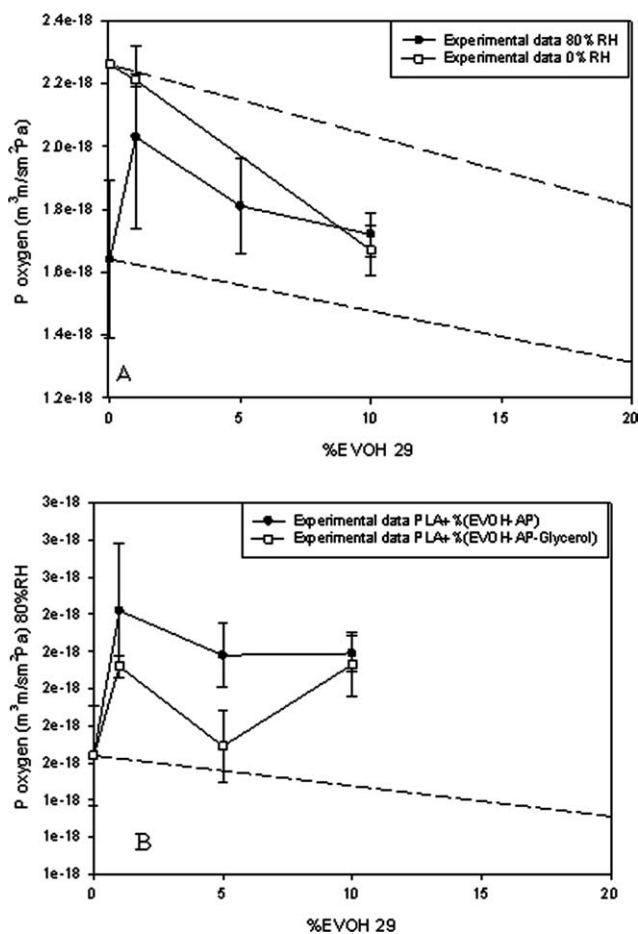
Figure 2 (A) Oxygen permeability as a function of the content of EVOH29 in PLA and (B) oxygen permeability as a function of the content of EVOH/amylopectin, with or without glycerol, in PLA. The dashed lines correspond to the application of the simple rule of mixtures.

measurements in moist conditions, the oxygen permeability measured at 80% RH increases and remains almost unmodified compared to the permeability at 0% RH case, while for pure PLA the permeability decreases at high humidity. Blends of PLA with 1, 5, and 10 wt % (EVOH29 + 50% AP) show an increase in oxygen permeability of, respectively, 47, 32, and 34%, compared to the unfilled material measured at 80% RH and 24°C. From the results, the oxygen diffusion coefficient tends to decrease slightly, however the oxygen solubility coefficient increases.[20] As it can be seen in the previous study of the thermal properties, data on the PLA blends showed that crystallization was reduced to some extent when EVOH and amylopectin was added, so this could be affecting the solubility and the role of humidity in the blends.

Blends of PLA with 1 and 10 wt % (EVOH29 + 50% AP + 10 Gly) filler content have an oxygen permeability increase of 29 and 30%, respectively, again compared to the unfilled material measured at 80% RH and 24°C. However, the oxygen diffusion coefficient decreases. The reason for the increase in the

oxygen permeability is in fact attributed to an increased solubility.[20] Nevertheless, the sample of PLA with 5 wt % (45/45/10) content has the lowest oxygen permeability increase, i.e., only 3%. Hence, the better barrier performance may be attributed to the presence of a fine dispersion of the EVOH phase in the blend, which establishes a positive interaction with the PLA as suggested from the previous work. The results indicate, in conclusion, that this amylopectin based blend has the best morphology (as shown by Nordqivst et al. in the former study[20]) and least impact in oxygen barrier properties.

Mechanical properties

Table III summarizes the mechanical properties of the PLA films and of their blends. With the addition of EVOH29 the Young's Modulus decreases slightly. With the addition of AP and glycerol to the blend this change is also very small suggesting that stiffness is rather unchanged in the polymer since the three polymers have relatively similar E modulus, being smallest for amylopectin.

Also the tensile strength of the films does not significantly change with the addition of EVOH29. The strength was not affected greatly by the addition of AP at lower levels. However, for the sample containing 10% (EVOH/AP) or when glycerol was present the strength decreased. The reason for this is that AP is naturally weaker than PLA and EVOH, and to the plasticizing effect of glycerol. From Table III, it can be seen that pure amylopectin has lower tensile strength, so as expected with the addition of AP the tensile strength of the blends decreases.

Finally, the elongation at break decreases slightly with the addition of EVOH, but with the addition of

TABLE III
Young's Modulus, Stress at Break, and Elongation at Break for the Different Samples

Sample	E (GPa)	Strength (MPa)	E_b (%)
PLA	2.01 ± 0.04	54.16 ± 5.22	9.20 ± 0.09
PLA + 1% EVOH29	1.97 ± 0.13	57.05 ± 5.00	8.84 ± 5.46
PLA + 5% EVOH29	1.83 ± 0.17	51.15 ± 2.20	8.10 ± 2.85
PLA + 1% (E29 + 50% AP)	1.98 ± 0.09	53.91 ± 4.71	6.59 ± 1.17
PLA + 5% (E29 + 50% AP)	2.01 ± 0.03	52.19 ± 1.80	4.37 ± 0.84
PLA + 5% (E29 + 50% AP + 10% Gly)	1.81 ± 0.06	45.25 ± 7.25	4.66 ± 1.28
PLA + 10% (E29 + 50% AP)	2.00 ± 0.02	49.52 ± 1.75	3.59 ± 0.30
Literature value[29] EVOH29, dried films conditions	2.398		46.16
Amylopectin[a]	1.93 ± 0.07	40.0 ± 1.3	2.3 ± 0.3

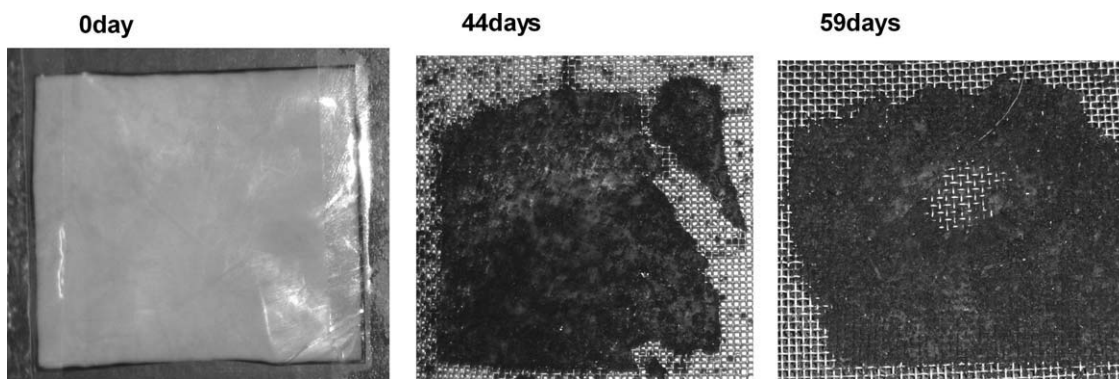[a] Unpublished data by Nordqvist et al.

Figure 3 Degradation of PCL films – reference material for biodegradability.

amylopectin the elongation at break decreases considerably. This result is not surprising since amylopectin as a very brittle material and hence is expected to translate this effect into the blend. Another result that might seem surprising is that when glycerol is added this does not increase the strain at break. At low glycerol content the plasticizing effect is not noticeable, something that has been shown for the AP system earlier.[26,30]

Biodegradability

A significant drawback of using PLA as a biodegradable material is the slow rate of degradation when compared to other biodegradable materials. The biodegradation of PLA in a composting environment has two steps. In the first step, the high-molecular-weight PLA chains hydrolyze into low-molecular-weight oligomers. This step is catalyzed by temperature and moisture. The second step is the conversion of the oligomeric components into CO_2, water, and humus by

means of the action of microorganisms. Therefore, any factors that increase the hydrolysis tendency can promote the degradation of PLA. Other factors affecting the biodegradation of polymers are the molecular weight and the degree of crystallinity. Lower molecular weight PLA materials do show higher rates of enzymatic degradation due to the higher concentration of accessible chain-end groups. It is also known that the amorphous phase is easier to biodegrade compared to the crystalline phase.[31–32]

Figure 3 shows the degradation patterns of a polycaprolactone (PCL) film. PCL is often used as reference material in biodegradability tests, and accordingly the PCL films degraded within 60 days.

Figure 4 shows the time dependence of the biodegradation study for the pure PLA. In this case, the PLA samples did not degrade within 60 days as did the PCL. After 90 days the PLA films had still not degraded. This further confirmed that PLA presents very slow rate of degradation compared to polycaprolactone.[32]
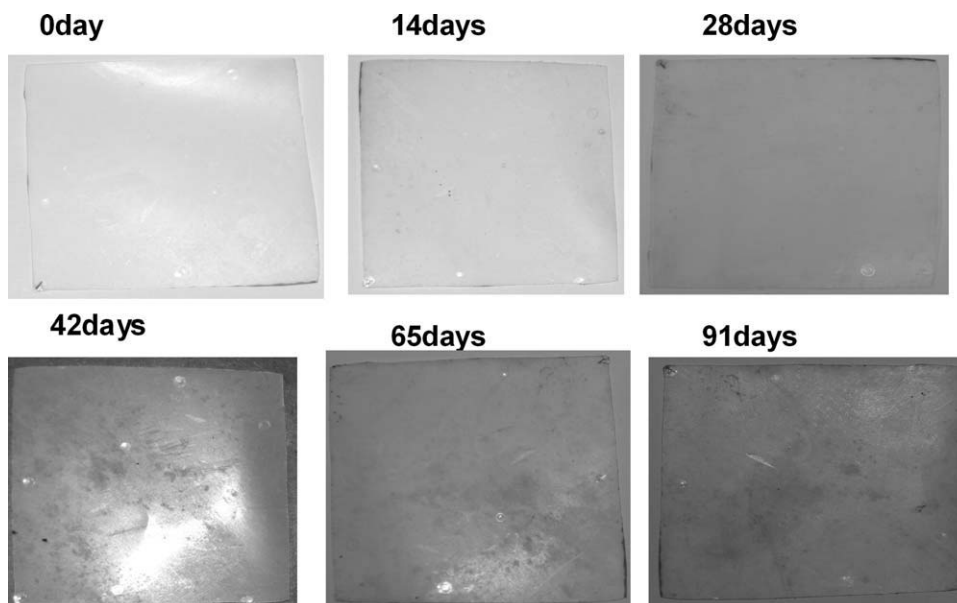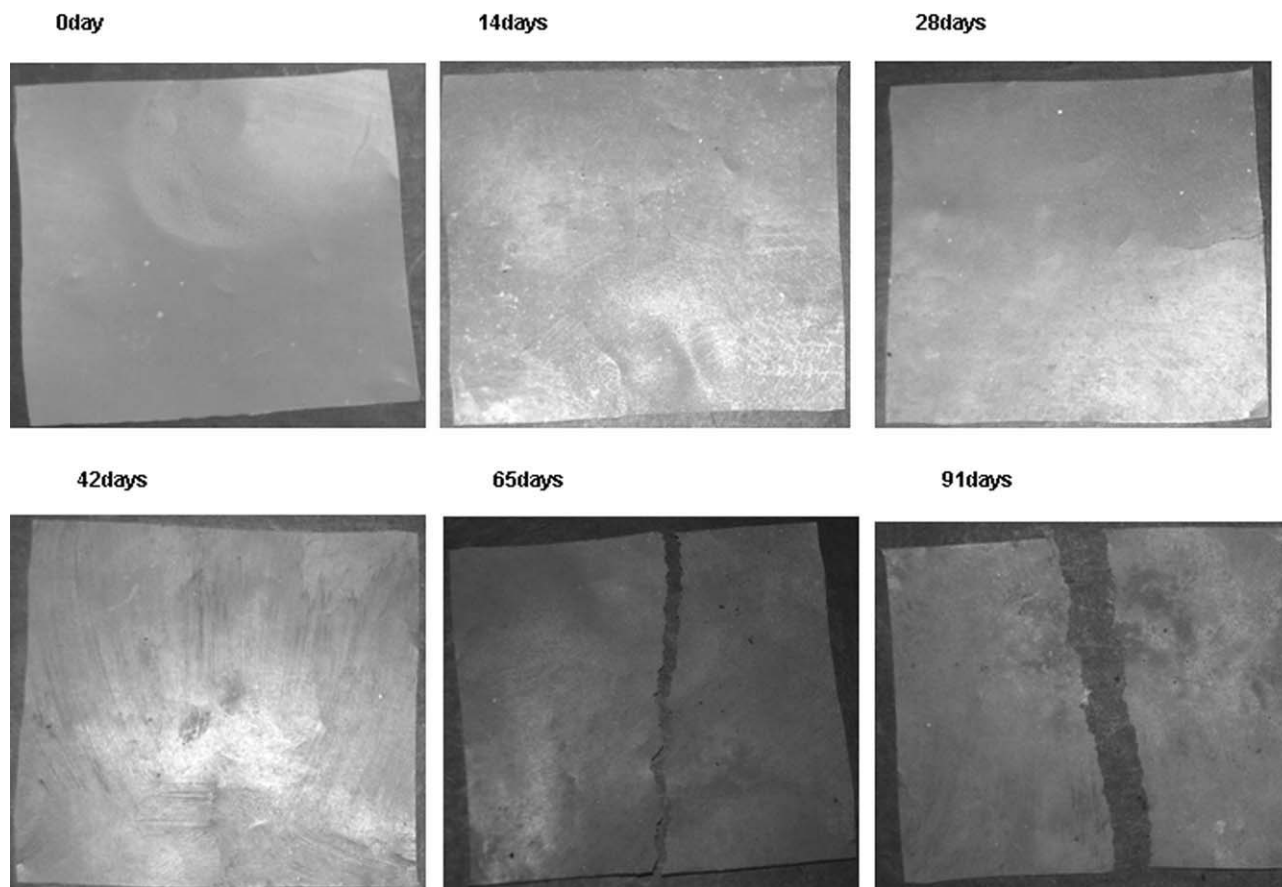

Figure 4 Degradation of pure PLA films.

Figure 5 Degradation of pure PLA + 5% (E-29 + 65% AP + 10% gly).

Curiously, Figure 5 shows that the films of PLA with low contents of EVOH and amylopectin and with added glycerol became extremely fragile and developed biofilm layer during the composting period suggesting that the biodegradability of PLA in the blends containing EVOH, amylopectin, and glycerol seemed to be enhanced. Similar results were found for the blend without glycerol (results not shown). The biodegradability of PLA has elsewhere also been found to increase considerably with the addition of a cellulosic component.[33]

In summary, the biodegradability tests indicated that while the blends did not biodegrade in the time of the evaluation, they showed better availability to do so in comparison with the neat PLA. The more favorable tendency towards biodegradability could be related to the addition of the biodegradable amylopectin component and perhaps also to the somewhat lower crystallinity of the blends.[20]

CONCLUSIONS

In this study, amylopectin was melt blended with PLA by using a thermoplastic EVOH carrier with and without glycerol as plasticizer/compatibilizer. The rationale behind using EVOH as carrier is double, on the one hand, EVOH is a highly polar polymer with very high gas barrier properties and potentially good interaction with the starch component; and on the other hand, the EVOH material can be melt-compounded and, therefore, could serve as a vehicle to incorporate amylopectin into PLA by melt blending. From the results, barrier properties to oxygen were only seen to improve at 0% RH. At 80% RH the blend of PLA with 5 wt % of (45/45/10) content showed the lowest oxygen permeability increase, due to the presence of glycerol promoting the best blend morphology, as shown by the previous work (Paper I). Despite the fact that properties were not dramatically improved, incorporating renewable resources within PLA seems to be a potentially viable route to obtain new cost-effective biocomposites with good optical properties and clarity, and also with enhanced biodegradability properties.

References

1. Auras, R.; Harte, B.; Selke, S. Macromol Biosci 2004, 4, 835.
2. Fang, Q.; Hanna, M. A. Ind Crops Prod 1999, 10, 47.
3. Sarazin, P.; Li, G.; Orts, W.;Fauis, B. O. Polymer 2008, 49, 599.
4. Nijenhuis, A. J.; Colstec, E.; Czejpma, D. W.; Penning, A. J.. Polymer 1996, 37, 5849.

5. Wang, L.; Ma, W.; Gzors, R. A.; Mc Carthy, S. P.. Polym Degrad Stab 1998, 59, 161.
6. Ma, X. F.; Yu, J. G. Carbohyd Polym 2004, 57, 197.
7. Ritzl, A.; Regev, O.; Yerushalmi-Rozen, R. Acta Polym 1998, 49, 566.
8. Rindlav-Westling, A.; Stading, M.; Gatenholm, P. Biomacromolecules 2002, 3, 84–91.
9. Martin, O.; Averous, L. Polymer 2001, 42, 6209.
10. Lagaron, J. M.; Powell, A. K.; Bonner, G. Polym Test 2001, 20, 569.
11. Tomita, K.; Kojoh, K.; Suzuki, A. J Ferment Bioeng 1997, 84, 400.
12. Mejia, A. I.; Lopez, B. L.; Sierra, L. Mater Res Innovations 2001, 4, 148.
13. Stenhouse, P. J.; Ratto, J. A.; Schneider, N. S. J Appl Polym Sci 1997, 64, 2613.
14. Jiang, T.; et al. Eur Polym J 2005, 41, 459.
15. Jacobsen, S.; Fritz, H. G. Polym Eng Sci 1996, 36, 2799.
16. Lee, C. M.; Kim, E. S.; Yoon, J. S. J Appl Polym Sci 2005, 98, 886.
17. Orts, W. J.; et al. Polym Adv Technol 2007, 18, 629.
18. Myllarinen, P.; et al. Carbohydr Polym 2002, 48, 41.
19. Rindlav-Westling, A.; et al. Carbohydr Polym 1998, 36, 217.
20. Nordqvist, D.; Dolores Sanchez, M.; Hedenqvist, M. S.; Lagaron, J. M. J Appl Polym Sci Febrero 2010, 15, 1315.
21. Crank, J. Mathematics of Diffusion, 2nd ed.; Oxford Science Publications: Oxford, 1975.
22. Hiltner, A.; Liu, R. Y. F.; Hu, Y. S.; Baer, E. J Polym Sci Part B: Polym Phys 2005, 43, 1047.
23. Yang, H. S.; Yoon, J. S.; Kim, M. N. Polym Degrad Stab 2005, 87, 131.
24. Cava, D.; Gimenez, E.; Gavara, R.; Lagaron, J. M. J Plast Films Sheeting 2006, 22, 265.
25. Rindlav-Westling, A.; Stadingb, M.; Anne-Marie, H.; Paul, G. Carbohydr Polym 1998, 36, 217.
26. Myllärinen, P.; Partanen, R.; Seppälä, J.; Forsell, P. Carbohydr Polym 2002, 50, 355.
27. Petersen, K.; Nielsen, P. V.; Olsen, M. B. Starch 2001, 53, 356.
28. Forsell, P.; et al. Carbohydr Polym 2002, 47, 125.
29. Russo, P.; Acierno, D.; Di Maio, L.; Demma, G. Eur Polym J 1999, 35, 1261.
30. Nordqvist, et al. J Biobased Mater Bioenergy 2009, 3, 1.
31. Guralp, O.; Sebnem, K. J Appl Sci 2009, 114, 2481.
32. Ray, S. S.; Okamoto, M. Macromol Rapid Commun 2003, 24, 815.
33. Levit, M. R.; Farrel, R. E.; Gross, R. A.; McCarthy, S. P. ANTEC '96: Plastics - Racing Into the Future 1996, 42, 1387.