

Incorporating Amylopectin in Poly(lactic Acid) by Melt Blending Using Poly(ethylene-*co*-vinyl Alcohol) as a Thermoplastic Carrier. (I) Morphological Characterization

D. Nordqvist,¹ Maria D. Sanchez-García,² Mikael S. Hedenqvist,¹ Jose M. Lagaron²

¹Department of Fiber and Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

²Novel Materials and Nanotechnology Lab, Institute of Agrochemistry and Food Technology (IATA), CSIC, Burjassot, Valencia, Spain

Received 18 November 2008; accepted 11 February 2009

DOI 10.1002/app.31290

Published online 7 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this study, the possibility of using a biodegradable grade of thermoplastic poly(ethylene-*co*-vinyl alcohol) with high (71 mol %) vinyl alcohol (EVOH-29), as a carrier to incorporate the renewable and biodegradable component amylopectin (AP) into poly(lactic acid) (PLA) through melt blending, was investigated. The effect of using a plasticizer/compatibilizer (glycerol) in the blend systems was also investigated. In a first step, the EVOH/AP blends were produced and thereafter, in a second step, these were mixed with PLA. 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 AP 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 Differential scanning calorimetry (DSC) data showed that the melting point of EVOH dropped in the EVOH/AP blends, but the properties of the PLA phase was still relatively unaffected as a result of blending with the above components. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1315–1324, 2010

Key words: polymer blends; biopolymers; EVOH copolymers; amylopectine; PLA; packaging applications; biomedical applications; morphology; raman imaging

INTRODUCTION

Poly(lactic acid) (PLA) is a biodegradable linear aliphatic thermoplastic polyester that has received significant attention among researchers as an alternative material for packaging applications. Today, PLA is one of the most important biodegradable/renewable plastic materials on the market; to a great extent due to its interesting mechanical, optical, and processing properties, and, of course, to its renewability and biodegradability aspects.^{1,2} In attempt to improve desired properties or lower the processing costs both blends and composites have been produced. Several studies have been carried out on PLA blends, both with non-biodegradable and biodegradable materials.^{3–6} By blending PLA with other, less expensive, biodegradable polymers, the “green” factor can be retained at the same time as properties are improved and cost lowered. A possi-

ble candidate is starch, due to its biobased origin, low price, good availability, and high performance. Starch consists of a mixture of amylose (~30%) and amylopectin (AP) (70%), both based on chains of 1,4-linked α -D-glucose.⁷ Amylose is linear whereas AP is highly branched and forms transparent films, a very attractive feature when it comes to the packaging industry.⁸ Martin and Averous⁹ previously studied melt-blended PLA/starch systems. The observation of two glass transition temperatures (T_g), and a two-phase morphology, indicated a low compatibility between the two polymers. The use of adequate compatibilizers was, therefore, suggested.

Poly(ethylene-*co*-vinyl alcohol) (EVOH) polymers are a family of semicrystalline random co-polymers with excellent barrier properties to gases and hydrocarbons, and with outstanding chemical resistance.¹⁰ EVOH copolymers are commonly produced via a saponification reaction of a parent ethylene-*co*-vinyl acetate copolymer, whereby the acetoxo group is converted into a secondary alcohol. These materials have been, increasingly, implemented in many pipe and packaging applications where high demands on chemical resistance and gas, aroma, and hydrocarbon

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

permeation have to be met. In particular, copolymers with low contents of ethylene (below 38 mol % ethylene) have outstanding barrier properties under dry conditions compared with other polymeric materials. In spite of the low gas permeation, EVOH copolymers generally show a high hydrophilic character that can be tuned by composition. A higher vinyl alcohol content gives a more water sensitive polymer. The EVOH properties can be designed for different applications by controlling the ethylene/vinyl alcohol ratio. Even though the EVOH family is not made from renewable resources, some grades of the poly(vinyl alcohol) homopolymer (PVOH) are water soluble and classified as biodegradable. Moreover, EVOH grades with high vinyl alcohol content (i.e., higher than 71 mol %) 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} This highly transparent and excellent barrier material is thought to improve some properties for PLA and serve as an adequate melt blending carrier for highly polar polymers, e.g., many proteins and polysaccharides, which otherwise are not so readily melt blendable with PLA.

In spite of the above, only limited work on pure blends of PLA and EVOH have been performed.¹⁵ Lee et al.¹⁶ used reactive blending to induce a reaction between the two components in blends with different concentrations, 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. Recently, Orts et al.¹⁷ 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 because this affected the degree of crystallinity of the materials. Also in the case of AP films, the RH affects the crystallization process and the degree of crystallinity.^{18,19} Therefore, the films produced in this study were stored at the same RH before testing.

The present study reports on the feasibility of using EVOH-29 (containing 29 mol % of ethylene in the copolymer) to implement AP into PLA via melt compounding. Also the different properties of these binary and ternary systems are investigated. This first article discusses the morphology obtained using several different microscopy techniques and Raman imaging spectroscopy as well as thermal property data of the blends. In a subsequent study, the mechanical, oxygen, and moisture transport properties as well as biodegradability tests will be presented and discussed.

EXPERIMENTAL

Materials

An extrusion grade of semicrystalline (PLA) manufactured by Natureworks (with a D-isomer content of approximately 2%) was used in this study. The material was disclosed to have a molecular weight (M_n) of ca. 130,000 g/mol and a weight-average molecular weight (M_w) of 150,000 g/mol. Soarnol[®] standard grade (EVOH2903) of ethylene-vinyl alcohol copolymers with 29 mol % of ethylene in the composition was supplied by Nippon Synthetic Chemical Industry Co. (Nippon Goshei, Osaka, Japan). A very low ethylene-content EVOH grade was selected to promote both higher compatibility with the starch component and biodegradability. Even lower ethylene content EVOH grades exist, such as the one with 26 mol % ethylene (EVOH26); however, these have higher melting points and, therefore, require processing temperatures that may degrade the starch component. AP from maize [CAS: 9037-22-3] was purchased from Sigma-Aldrich (Sweden) and glycerol was obtained from Panreac Quimica S.A. (Spain).

Film preparation

Several different routes were investigated to find the best dispersion. In the first trials, the intention was to disperse AP in EVOH using a solution (isopropanol/water), which could be melt mixed with PLA in a following step, this because AP, in contrast to EVOH, is not a thermoplastic polymer. The route involving solvent casting of EVOH/AP films, followed by grinding and melt mixing with PLA, resulted in poor dispersion and was abandoned at an early stage. Consequently, the study was focused on using a direct melt-mixing step. EVOH/AP at different relative concentrations, with and without glycerol, were first melt mixed in a Brabender Plastograph mixer (16 cm³) during 4 min at 195°C. The mixing temperature was just above the melting point of EVOH but low enough to avoid excessive thermal exposure for AP. Higher mixing temperatures led to browning of the mixture and degradation that was later observed as tiny dark spots in the PLA matrix after subsequent blending. On the other hand, lower temperatures did not melt the EVOH phase sufficiently. Trials in which AP was added to the molten EVOH, either as granules or in a water solution, were performed. From the preliminary dispersion results, the latter procedure yielded the best films and was, therefore, selected throughout this study. After mixing, the batches were allowed to cool-down at room temperature and after drying the resulting EVOH/AP blends were mixed with PLA in a second melt-blending step. The sample codes

used throughout the article are 45/45/10 and refer to the content (in wt %) of EVOH/AP/glycerol, respectively. The samples containing PLA were coded throughout the article as follows: PLAx% (45/45/10), where $x\%$ corresponds to the content of the EVOH/AP/glycerol blend in the PLA matrix. Mixing was finally performed during 5 min at 40 rpm followed by 1 min at 60 rpm (190°C). After removal, the batches were allowed to cool-down at room temperature, and subsequently compression molded into films using a hot-plate hydraulic press (190°C and 2 MPa for 4 min). The thicknesses of the films were between 80 and 110 μm as measured with a Mitutoyo micrometer by averaging four measurements on each sample.

Optical light polarized microscopy

Polarized light microscopy (PLM) examinations were carried out using an ECLIPSE E800-Nikon with a capture camera DXM1200F-Nikon. A minimum of four different pictures were taken from the examined samples.

Scanning electron microscopy

A Hitachi S-4100 Scanning Electron Microscope (SEM) was used to take SEM pictures on cryofractured samples. Prior to SEM examination, the cryofractured specimens were mounted on bevel sample holders and sputtered with Au/Pd under vacuum. An accelerating voltage of 10 kV was used.

Differential scanning calorimetry

DSC of EVOH, PLA and their blends were performed on a Perkin-Elmer DSC 7 thermal analysis system on typically 4 mg of dry material at a heating rate of 10°C/min from 40°C to 200°C, followed by a cooling step (at 10°C/min) back to 50°C, where it was kept isothermally for 5 min. The second heating started at 50°C and ended at 210°C, using a 10°C/min heating rate. N_2 was used as the purge gas. Before evaluation, the thermograms were subtracted with similar thermograms using an empty pan. The DSC parameters presented in the article were evaluated from the cooling and the second heating runs. The DSC equipment was calibrated using indium as standard and the results presented were based on the average of two measurements.

Raman spectroscopy

Raman images were taken with a Jasco NRS-3100 Confocal Micro-Raman spectrophotometer (Jasco, Easton, MD) using a short working distance 100 \times objective, which under high confocal conditions pro-

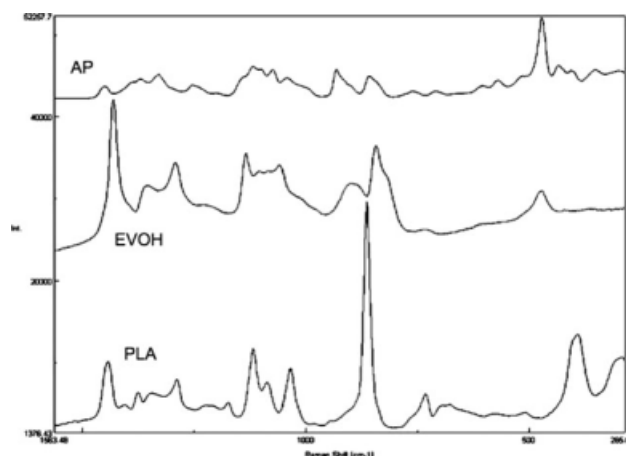


Figure 1 Raman spectra of the three components used. Higher intensity Raman bands can here be seen at $\sim 865\text{ cm}^{-1}$ for PLA, $\sim 472\text{ cm}^{-1}$ for AP, and $\sim 1443\text{ cm}^{-1}$ for EVOH.

vides, according to the manufacturer, a lateral resolution of ca. 1 to 2 μm and a depth resolution of 2 to 3 μm . An NIR excitation laser source, tuned at 785 nm to avoid excessive fluorescence in the Raman signal, was used. Raman imaging was carried out in the point by point mode by rationing the area of typical Raman bands (Fig. 1—Raman spectra of the three components used) of the compounds, i.e. $\sim 865\text{ cm}^{-1}$ for PLA, $\sim 472\text{ cm}^{-1}$ for AP, and $\sim 1443\text{ cm}^{-1}$ for EVOH, arising from the different phases of the composites, and were constructed by taken 15 \times 15 spectra equally spaced across the selected sample area.

RESULTS AND DISCUSSION

The first objective of this work was to generate blends of EVOH/AP with the highest possible content of AP to keep the final blends as “renewable” as possible. After trying several different relative mass concentrations of EVOH and AP, the 35/65 and 50/50 blends were found to have the “most promising” morphologies. A visually good blending was also observed at higher AP contents, but only when glycerol was present (31.5/58.5/10). Complementary information about the blends was obtained by analyzing fracture surfaces using SEM [Fig. 2(a–e)]. From this figure, some level of porosity or voids were seen when starch was present in the blend, with or without glycerol. Weak cohesion between the different blend constituents could explain the observed voiding (which could be thought as arising from detached phase separated particles and not as porosity). However, a clear pattern of phase separation is not unambiguously discerned.¹³ The glycerol containing samples can be differentiated because they give rise to surfaces that have smoother and

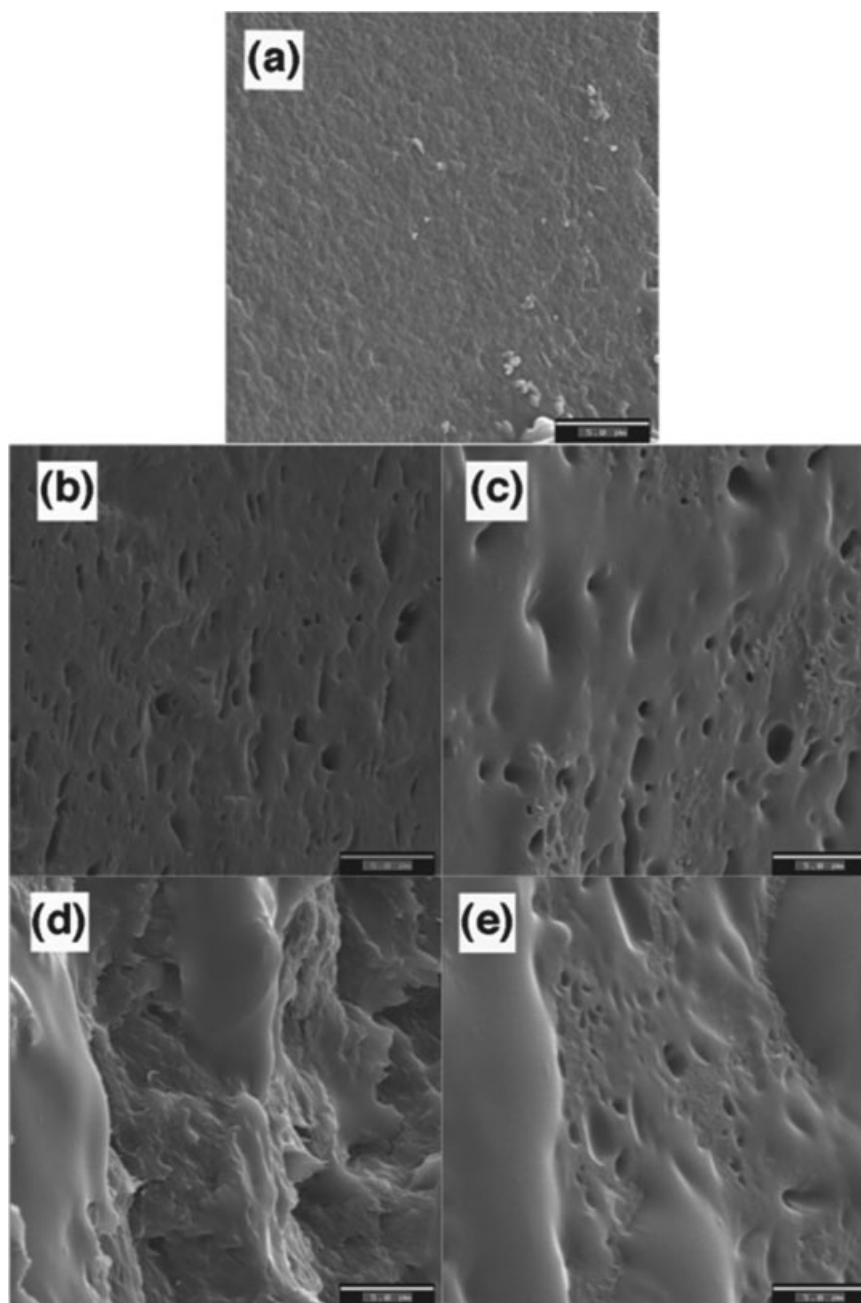


Figure 2 SEM micrographs showing fracture surfaces of (EVOH/AP/glycerol) films: a) (100/0/0), b) (50/50/0), c) (45/45/10), d), (35/65/0), and e) (31.5/58.5/10). The scale bars correspond to 5 μm .

more cohesive areas, hence indicating glycerol richer parts. The samples containing higher amounts of AP (without glycerol) show a considerably rougher fracture surface indicating a lower affinity between the two phases. However, when glycerol is also added to the AP-rich samples, the fracture surface becomes more homogenous suggesting that the glycerol can help the blending of the two polymers by promoting stronger phase adhesion and/or by reducing the EVOH polymer melting point and, therefore, reducing the blend viscosity at the mixing temperature (vide infra). This behavior has also been reported for

PLA/starch blends elsewhere.³ Furthermore, studies on the rheological properties of extruded starch/EVOH blends have shown similar results.²⁰

Raman imaging (Fig. 3) provides unique chemical images with spatial resolutions down to the micron level. In Figure 3, the Raman image of (50/50/0) is shown. From the analysis of individual spectra at contrasting points in the image, it was observed that there were areas in the sample where one component was more dominant. Complete phase separation was not observed at the present spatial resolution level, suggesting a good intermix between the

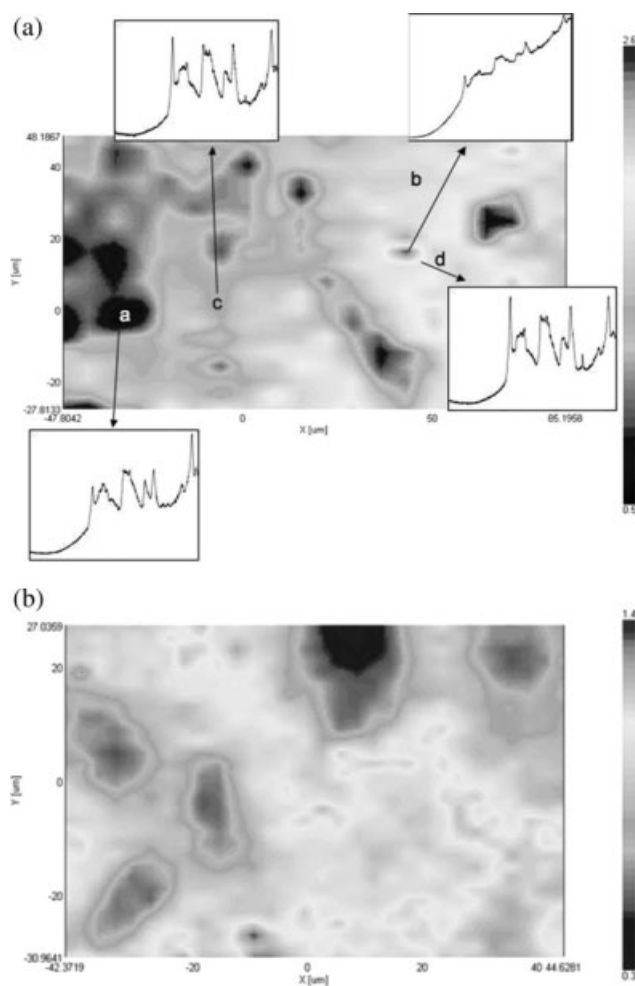


Figure 3 Raman imaging picture of EVOH/AP (50/50) at 100 \times magnification. The image displays the band intensity ratio E-29 (1443 cm^{-1})/AP (472 cm^{-1}). The intensity ratio scale runs from 0.5 to 2.6 and the size of the picture is ca. $75 \times 132\ \mu\text{m}$. Raman imaging map of EVOH/AP/glycerol (45/45/10) at 100 \times magnification. The image displays the band intensity ratio E-29 ($1,443\text{ cm}^{-1}$)/AP (472 cm^{-1}). The intensity ratio scale runs from 0.3 to 1.4 and the size of the picture is ca. $75 \times 132\ \mu\text{m}$.

two components. Some extreme band ratio points in the image, that might indicate phases filled with one component, were in fact often areas of high fluorescence (spectrum at point b in Fig. 3a). Still the more narrow intensity spectrum in Figure 3(b) as compared to Figure 3(a) suggested that a more homogeneous mixing occurred in the presence of glycerol. The reason for this might be that the glycerol increases the distances between the AP molecules and makes them more flexible and hence improve the miscibility between the components. It is well known that EVOH is strongly self associated and does not mix well with other polymers whether of polar or non-polar character.²¹ Despite this, the present blends showed a morphology indicative of a well-dispersed multi-component system. To con-

clude, the Raman technique was very useful in determining the phase morphology beyond the ambiguous phase structure provided by the SEM observations. Thus, the combination of SEM and Raman chemical imaging gives a more complete understanding of the phase morphology in the blends. In this case, the techniques yielded information on the beneficial effects of glycerol on providing a more homogeneous distribution of the blend components/polymers; a result that has also been shown elsewhere for starch/EVOH systems.²²

In a second mixing step, the EVOH/AP blends were mixed with PLA at contents of 1, 5, and 10%, and compression molded into films. The films containing EVOH/AP, with or without glycerol, retain transparency and when compared with the unfilled material they were not discernible to the naked eye. Figure 4 shows the optical microscopy pictures of these blends. No significant difference could be observed between the morphologies of the pure EVOH samples and those of the blends containing AP (not shown here). In the EVOH/AP/glycerol, glycerol could be easily discerned as well dispersed droplets throughout the matrix (Fig. 4). Apart from glycerol, no other differences in the constituent concentrations could be differentiated in Figure 4 between the various samples.

SEM observations did, however, reveal the presence of a fine and well-dispersed EVOH phase within the PLA matrix in all samples (Fig. 5). The pictures indicate some positive interactions at the interphase, albeit adhesion is not deemed to be very strong because some particle pull-outs leaving voids are clearly observed. Pull-outs were not as obvious in the samples with lower contents of EVOH/AP but they could still, to some extent, be observed. For the blend with 10% EVOH, the phase separation was more evident. When AP was introduced into the formulation of the segregated phase, the material became more homogenous than with neat EVOH. In this case, the interface between PLA and EVOH were not as distinct; indicating that a higher interface adhesion was obtained for the three-component systems. Also, one should note that as the AP was introduced, the EVOH content was lowered. It is probable that, by tuning/adjusting the process parameters and the quantity of AP in the blend formulation, the interfacial adhesion can, perhaps, be improved even further.²³

Raman imaging was also finally used to assess the chemical composition of the discrete phase in the PLA matrix. Figure 6 presents images (obtained from plotting the band ratio of EVOH/PLA as explained in the experimental part) of samples containing 5 wt % of EVOH, EVOH/AP (50/50), and EVOH/AP/glycerol (45/45/10). From the images, a micron level phase dispersion was observed for the

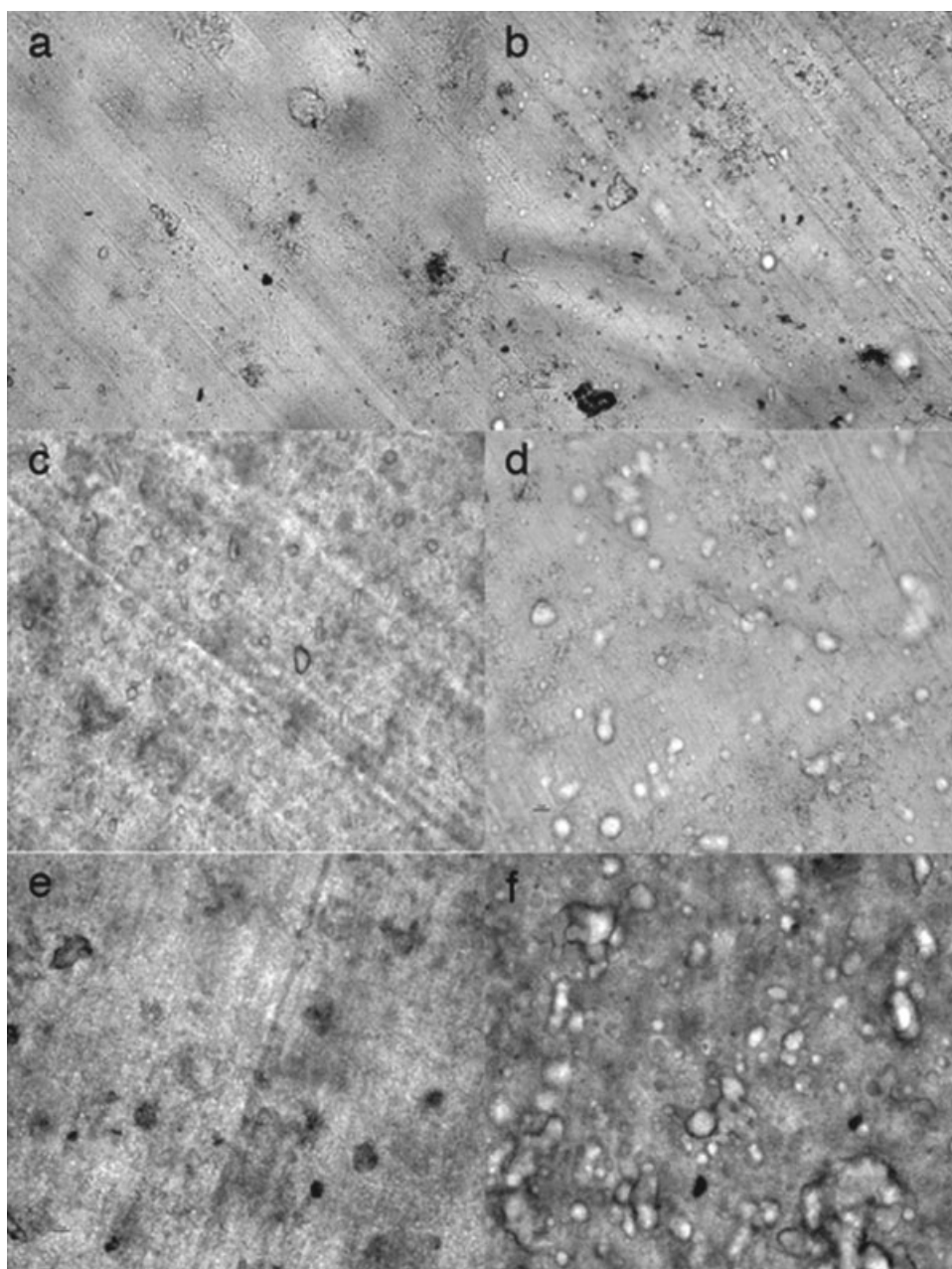


Figure 4 Optical microscopy pictures of a) PLA1% (100/0/0), b) PLA1% (45/45/10), c) PLA5% (100/0/0), d) PLA5% (45/45/10), e) PLA10% (100/0/0), f) PLA10% (45/45/10). The glycerol rich regions can easily be seen on the pictures to the right. Scale bars are 10 μm in the pictures.

added element with little variations across the image in the ratio of the two band intensities at contrasting regions. As the SEM experiments suggested, a fine dispersion of the discrete phase was observed. A slightly better distribution of the minor phase in the PLA matrix was seen for the two latter systems, particularly for the AP, as the spectra of the contrasting phases was more even. This might suggest that the presence of AP and also of glycerol slightly increased the dispersion of the discrete phase although the recorded variations between the three systems were small.

Thermal properties of the blends

Tables I to III summarize the melting enthalpy and temperature of EVOH based and PLA/EVOH based blends. The values for the melting enthalpy (ΔH) have all been normalized to the PLA or EVOH contents in the blends. The first observation in EVOH and its blends (Table I) was that the melting temperature (T_m) was not significantly affected by the addition of AP. However, when glycerol was also present, the T_m clearly dropped by ca. 10°C, illustrating the “solvent”-induced melting point depression.²⁴

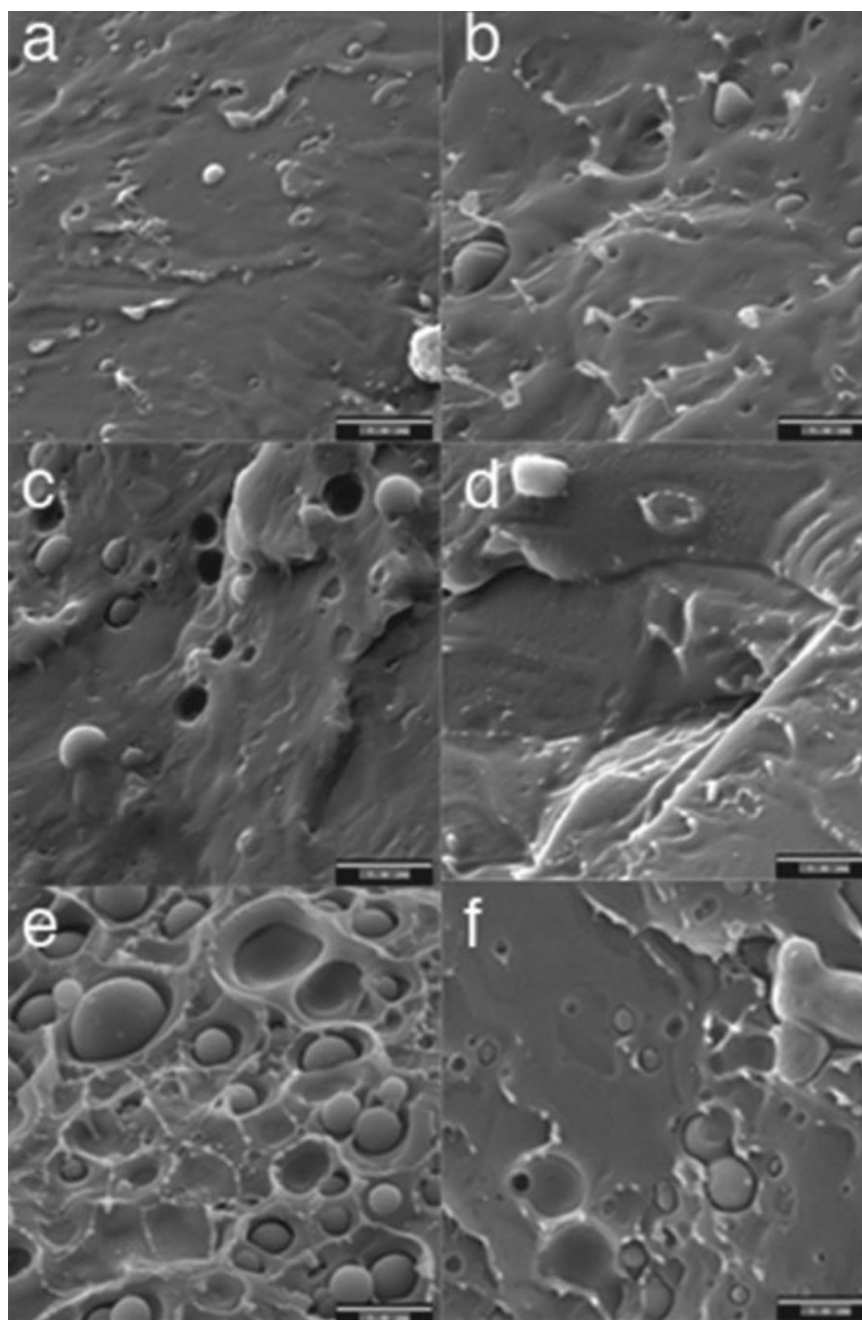


Figure 5 SEM pictures of fracture surfaces of the following films; a) PLA1% (100/0/0), b) PLA1% (50/50/0), c) PLA5% (100/0/0), d) PLA5% (50/50/0), e) PLA10% (100/0/0), f) PLA10% (50/50/0). The scale bars correspond to 5 μm .

Previous reports show that an increase in moisture level in starch-based materials decreases the melting point.^{17,25} Furthermore, in these studies ΔH_m and ΔH_c appeared to decrease somewhat when starch was introduced in the blend, this reduction was also observed in the presence of glycerol; the lower melting enthalpy is related to a decrease in crystallinity.²¹ Interestingly, the crystallization temperature of EVOH was not significantly affected by the presence of AP, albeit it may seem slightly reduced suggest-

ing some sort of phase interaction. On the other hand, the presence of glycerol clearly reduced the crystallization temperature demonstrating its strong interacting effect with EVOH. Orts et al.¹⁷ studied starch/EVOH blends and found a very similar T_c (153.4°C) for the same composition (45/45/10). The DSC data was in accordance with the morphology data, which suggested that phase separation between the blended components was clear, particularly from the Raman images, but that the presence

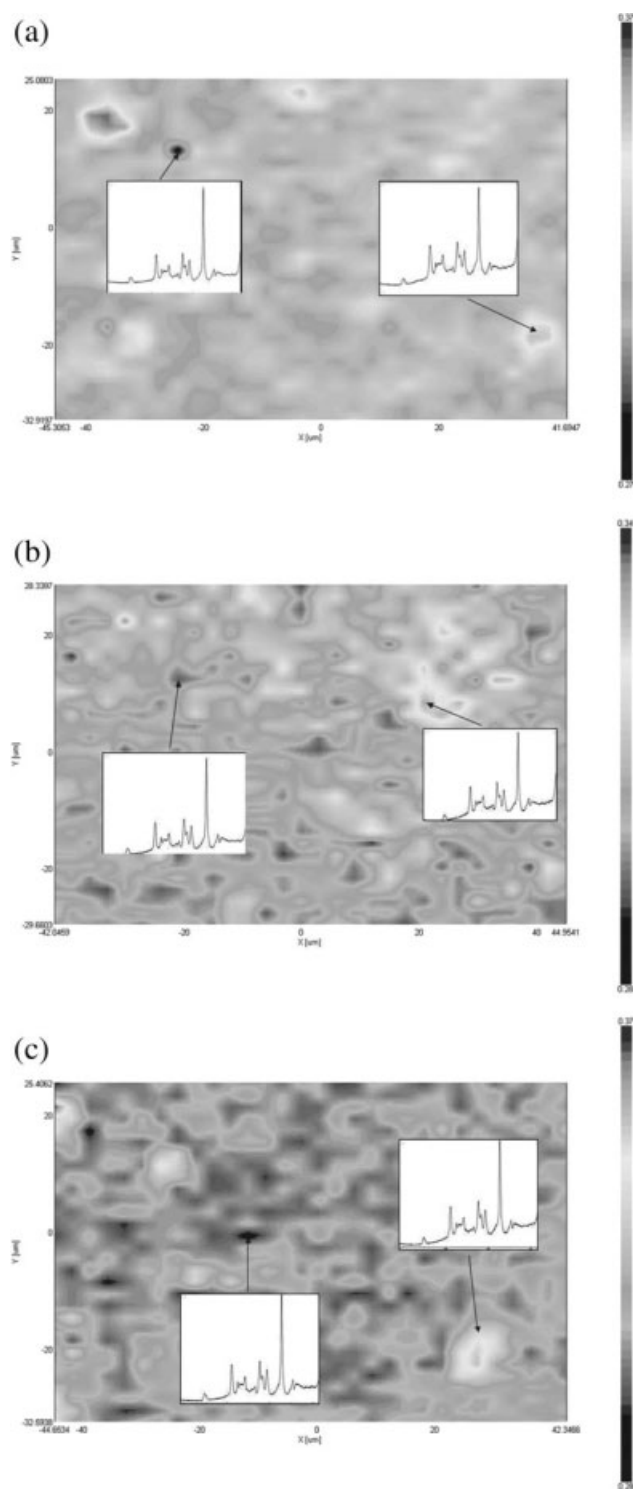


Figure 6 Raman imaging map of PLA5% (100/0/0) at 100 \times magnification. Peak height E-29 (1443 cm^{-1})/PLA (865 cm^{-1}). Scale from 0.27 to 0.37 and the size of the picture is ca. 57 \times 86 μm . Raman imaging picture of PLA5% (50/50/0) at 100 \times magnification. Peak height E-29 (1443 cm^{-1})/PLA (865 cm^{-1}). Scale from 0.29 to 0.34 and the size of the picture is ca. 57 \times 87 μm . Raman imaging picture of PLA5% (45/45/10) at 100 \times magnification. Peak height E-29 (1443 cm^{-1})/PLA (865 cm^{-1}). Scale from 0.29 to 0.37 and the size of the picture is ca. 57 \times 86 μm .

of glycerol helped to enhance dispersion and interaction between the constituents. It is also interesting to note that the presence of glycerol (Table II) did not decrease the melting point of the EVOH in the PLA blends to the same levels as in the EVOH blends, perhaps, indicating that it goes into the PLA matrix during mixing.

Table II indicates that the melting point of EVOH in the PLA blends was about 5 degrees lower than in the neat component. This regardless of whether it had AP or glycerol in the formulation. Interestingly, this effect was not observed in the EVOH/AP blends and, therefore, it must be a result of the interaction between the EVOH and PLA. The crystallinity also seemed to be reduced in the blends, suggesting again interactions and crystal formation interference between the blend components. The reason why EVOH and AP were not seen to interact so strongly in the DSC data in Table I compared with PLA, could lie in the fact that the samples selected were very close to the phase inversion and blends can often behave differently in compositions close to 50/50.

Table III shows the thermal data corresponding to the PLA phase. From this, it can be observed that the PLA melting and crystallization points were not significantly altered, albeit they tended to decrease in the blends again suggesting interfacial interactions. The T_g of the PLA was also seen to decrease slightly and perhaps more in the blends with glycerol, although the differences were small. The melting enthalpy, calculated by subtracting the cold crystallization exothermal peak from the endothermal fusion peak, was also lower in the case of EVOH but was somewhat higher for the case of AP and glycerol as blending components, although the differences were again small. Perhaps, the latter components could affect the PLA crystallization process, which is relatively slow, and lead to a somewhat less crystalline material. All these observations supported the phase-separated structure depicted by the morphology study presented above but also indicated that some level of interaction at the interphase between the components took place. Also moisture probably had some effects. This factor has been studied for wheat starch/PLA blends containing methylenedi-phenyl diisocyanate by Wang et al.,²⁶ reporting a negative effect on the interfacial binding at moisture levels of 10–20%. However, Ke and Sun²⁷ reported that the thermal, including the crystallization, properties of PLA, in a PLA/cornstarch blend, were not affected by the moisture content. Another study concluded that the degree of mixing between PLA and glycerol plasticized starch was relatively poor.²⁸ The role of glycerol in the PLA blends was not so clearly discerned by the DSC data albeit the T_g of the PLA seemed to be lowest in its presence. Indicating that

TABLE I
DSC Melting and Crystallization Points and Melting and Crystallization Enthalpies for EVOH and Its Blends Corresponding to the EVOH Phase

Sample	T_m [°C] _{EVOH}	T_c [°C] _{EVOH}	ΔH_m [J/g] _{EVOH}	ΔH_c [J/g] _{EVOH}
100/0/0	190.0 ± 0.8	165.6 ± 0.6	63.6 ± 5.2	78.4 ± 5.7
50/50/0	189.7 ± 0.6	163.5 ± 0.1	46.2 ± 2.3	55.5 ± 6.2
35/65	191.2 ± 0.3	164.3 ± 0.2	56.5 ± 1.2	48.7 ± 0.8
45/45/10	179.7 ± 0.7	154.5 ± 0.1	52.7 ± 2.8	65.9 ± 0.1
31.5/58.5/10	180.2 ± 0.2	153.1 ± 0.2	53.1 ± 0.2	64.9 ± 5.4

The sample names refer to wt.% content of EVOH/AP/glycerol.

TABLE II
DSC Melting Point and Enthalpy for PLA Blends Corresponding to the EVOH Phase

Sample	T_m [°C] _{EVOH}	ΔH_m [J/g] _{EVOH}
EVOH29	190.0 ± 0.8	63.6 ± 5.2
PLA10% (100/0/0)	185.0 ± 0.7	34.4 ± 1.3
PLA10% (50/50/0)	184.1 ± 1.5	50.9 ± 1.8
PLA10% (45/45/10)	185.2 ± 1.7	31.6 ± 1.6

TABLE III
DSC Melting Point and Enthalpy for the PLA Blends Corresponding to the PLA Phase

Sample	T_m [°C] _{PLA}	T_c [°C] _{PLA}	ΔH_m [J/g] _{PLA}	T_g [°C] _{PLA}
PLA	150.2	119.5	15.7	61.9
PLA1% (100/0/0)	150.1 ± 1.1	119.0 ± 1.1	14.0 ± 3.1	60.5 ± 3.1
PLA5% (100/0/0)	149.2 ± 1.0	116.0 ± 1.1	12.1 ± 0.4	58.6 ± 0.4
PLA10% (100/0/0)	149.7 ± 1.2	117.7 ± 1.0	13.9 ± 0.1	58.0 ± 0.4
PLA1% (50/50/0)	148.8 ± 0.4	117.2 ± 2.1	15.4 ± 3.4	57.7 ± 0.4
PLA5% (50/50/0)	149.4 ± 0.5	118.5 ± 0.2	13.1 ± 0.3	58.1 ± 0.1
PLA10% (50/50/0)	148.5 ± 0	114.8 ± 0.1	18.2 ± 2.7	58.7 ± 0.4
PLA1% (45/45/10)	149.0 ± 0.1	116.5 ± 0.0	17.2 ± 2.5	57.6 ± 0.1
PLA5% (45/45/10)	148.3 ± 0.1	115.3 ± 0.1	15.2 ± 6.2	57.2 ± 0.8
PLA10% (45/45/10)	149.5 ± 1.3	118.5 ± 0.6	17.2 ± 1.2	56.8 ± 0.0

the molecular mobility might increase due to the presence of the plasticizer (glycerol).

The PLA blends showed that the crystallization was induced when EVOH was added (Table III). The melting endotherm shifted to lower temperatures as more EVOH (with or without AP and glycerol) was added. The same effect was previously observed when plasticizers were added to PLA.²⁹ The explanation here was more likely to be that there were less crystalline areas in the blends leading to a lower melting point.³⁰ Something that could be a consequence of that glycerol contributed to prevent re-agglomeration as the plasticizer remained between the AP polymer chains.³¹

CONCLUSIONS

In this study, AP was melt blended with PLA by using a thermoplastic EVOH carrier with and without glycerol as plasticizer/compatibilizer. The inclu-

sion of AP in PLA seeks to enhance the properties of the latter, mainly gas barrier and biodegradability characteristics. 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 AP into PLA by melt blending. SEM and Raman imaging spectroscopy were applied to show that AP and EVOH were indeed well mixed up to 50 wt % of AP, albeit not miscible. At higher AP contents (65 wt %), the addition of glycerol was needed to obtain a more homogeneous system. In a second step, this material was blended with PLA. The presence of AP, with or without glycerol, was found to lead to a somewhat better dispersion in the PLA blends, although the variations were very small. DSC data showed that EVOH and its blends were not essentially affected by the addition of AP. When glycerol was added the

T_m , however, dropped by ca. 10°C. Minor effects on the thermal blends of PLA were also noticed and the T_g decreased slightly with the addition of AP, with or without glycerol.

The authors would like to acknowledge the EU integrated project SUSTAINPACK, the Spanish MEC project MAT2006-10261-C03-01 and the project CONSOLIDER CSD2007-00063 for financial support. The Nippon Synthetic Chemical Industry Co. (Nippon Goshei, Osaka, Japan) is also acknowledged for supplying the EVOH grade. Finally, M.D.S.G. would like to thank the FPI program of the GV associated to the CYCIT project MAT2003-08480-C3 for the research grant.

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