Microstructural Behaviors of Matrices Based on Polylactic Acid and Polyhydroxyalkanoates

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ABSTRACT: Individual films of polyhydroxyalkanoates (PHA) and polylactic acid (PLA) and their blends were developed by solvent casting. PHA was obtained from activated sludges from a wastewater-treatment system at a laboratory scale. This work focused on analyzing the microstructural properties and thermal behaviors of individual films of PHA and PLA as well as those of their blends. The behaviors of the biodegradation processes of the individual films and blends were examined from a microstructural point of view. ATR-FTIR spectra indicated the existence of weak molecular interactions between the polymers. The formulation of blend films improved the crystallinity of PLA; additionally, it induced the polymer-recrystallization phenomenon, because crystallized PHA acted as a PLA-nucleating agent. This phenomenon explains the improvements in the films’ water-vapor-barrier properties. The blends exposed to a biodegradation process showed an intermediate behavior between PLA and PHA, leading to a consistent basis for designing systems tailored to a particular purpose.

KEYWORDS: biopolymers, polymer blends, infrared spectroscopy, crystallinity, modulated DSC, morphology

INTRODUCTION

Polyhydroxyalkanoate (PHA) is a family of biopolymers synthesized by microorganisms from various carbon sources; they are accumulated intracellularly under nutrient stress and act as carbon and energy reserves. PHAs can be produced by both pure and mixed microbial cultures. Mixed cultures have the advantage that they do not need sterile conditions and are better able to adapt to complex substrates, such as industrial wastes, than pure cultures. For this, wastes from the dairy industry, the sugar industry, forestry, and biodiesel production can be utilized. Cheese whey is a surplus material from the dairy industry that is mainly discharged to both soils and water bodies, causing serious environmental problems. PHA production from cheese whey could valorize this dairy subproduct and, at the same time, solve the waste-disposal problems.

A relevant characteristic of PHA is its versatility, because there are more than a hundred different monomers, including hydroxyvalerate and butyrate among others. The properties of the synthesized polymer are modified depending on the position of its functional groups and degrees of polymerization. This chemistry allows PHAs to be tailored to provide similar properties to traditional thermoplastics, such as polyethylene (PE) and polypropylene (PP), while maintaining biodegradability.

Polylactic acid (PLA), a thermoplastic aliphatic polyester derived from lactic acid (2-hydroxy propionic acid), can be produced by condensation polymerization directly from its basic building block, lactic acid, which is derived from the fermentation of sugars from carbohydrates sources, such as corn starch, cassava root, chips and starch, and sugar cane. Polylactic acid is produced at the largest industrial scale of all biodegradable polymers, and it is considered the most promising candidate for replacing conventional plastics. It is being used in biomedical applications, for bottle production, filament production in 3D printing, and for compostable food-packaging production. It is also being evaluated as a material for tissue engineering. Mass production has reduced the cost of PLA production, making it an economically viable choice for the fabrication of containers, plastic bags, and fibers. Commercial-scale plants today produce hundreds of thousands of tons of PLA per year.

By controlling the molecular architecture, suppliers are able to tailor the polymer to specific applications. Consequently, new and improved grades of bioplastic resins are constantly being introduced to the market. NatureWorks LLC focuses on a multistep procedure involving the condensation reaction of aqueous lactic acid for the production of a low-molecular-weight PLA prepolymer. It is converted into a blend of lactide stereoisomers in order to produce a large spectrum of PLA grades. The films based on PLA have excellent optics and good machinability, barrier, and mechanical properties.

PLA and PHA polymers are polyesters and are used in consumer products by a wide industrial sector as a result of their biocompatibility and sustainability. They have thermal...
behaviors comparable to those of some conventional polymers, and this has generated much interest in exploring their physical and structural properties to identify potential applications. The combination of the two polymers allows the design of new materials with tailorable properties differing meaningfully from those of each component by adjusting the advantages of each polymer in order to obtain materials for different applications. In this sense, the formulation of blend systems is easier and faster than copolymerization methods. There are many studies focused on PLA modification, such as the addition of modifiers and copolymerization. The addition of a highly ordered stereochemical structure, such as that of PHA, could improve the film properties of PLA. In this sense, blending PLA with another biobased and biodegradable material, PHA, in order to obtain tailor-made materials constitutes a promising alternative.

This work focused on analyzing the microstructural properties and thermal behaviors of PHA and PLA individual films as well as those of their blends. Furthermore, the biodegradation processes of the individual films and PLA/PHA blends were examined from a microstructural point of view.

MATERIALS AND METHODS

Polyactic acid (PLA), grade 4043D in pellet form (98% l-lactide with a purity of 96% and a molar ratio of 95:5 HB) was obtained from Natureworks under the trademark Ingeo. As is well-known, the production of PLA involves fermentation by microorganisms to synthesize the chain of the polylactide polymer.

Polyhydroxalkanoate (PHA) was obtained from activated sludges with a purity of 96% and a molar relation of 95:5 HB enriched with PHA-accumulating bacteria. SBR enriched with PHA-accumulating bacteria.

Extraction and Quantification of PHA. Extraction and characterization of PHA from the batch-reactor biomass were performed following the method proposed by Venkateswar Reddy et al. A hydroxybutyrate–hydroxvalerate (HB–HV) copolymer with a purity of 96% and a molar relation of 95:5 HB–HV was obtained.

Film Preparation. The films were prepared by dissolving PHA and PLA in chloroform at 1 and 2% (w/w), respectively, under stirring for 3 h. PLA/PHA mixtures were prepared in the following proportions: 20/80, 40/60, 60/40, and 80/20 (w/w). They were stirred for 30 min at 60 °C.

Filmogenic solutions of PLA, PHA, and their blends were cast into plastic pots (400 cm³) were purchased from Natureworks under the trademark Ingeo. As is well-known, the production of PLA involves fermentation by microorganisms to synthesize the chain of the polylactide polymer.

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Filmogenic solutions of PLA, PHA, and their blends were cast into glass Petri dishes (9 cm diameter) that were left under a fume hood. Later, the samples were dried in a vacuum oven at 60 °C to ensure solvent removal from the matrices. When the solutions were cast, constant mass–molding-area ratios were maintained in order to ensure uniform thicknesses in the different samples, because the control solutions (PLA and PHA) had different concentrations.

Film thickness was measured by means of a coating-thickness gauge (Smart iTX accessory) placed on the diamond ATR crystal. The Cu Kα radiation (1.542 Å) was generated at 50 mA and 40 kV. Scattered radiation was detected in an angular range of 3° with a step size of 0.05°. The crystallinity degree (CD) was calculated following the procedure described in previous works.

ATR-FTIR Spectroscopy. The interactions between the system components were analyzed using the ATR-FTIR technique. Spectra of the samples were registered by using the Thermo Scientific Nicolet iS10 FT-IR Spectrometer in the wavenumber region of 400–4000 cm⁻¹, performing 64 scans at a 4 cm⁻¹ resolution. Spectra were placed onto the diamond ATR crystal (Smart iTX accessory), and the software Omnic 8 was used for the data-analysis process. To ensure the reproducibility of the results, the tests were performed in triplicate.

X-ray Diffraction. X-ray diffractograms of individual PVA and PLA films and their blends were evaluated by using an X’Pert Pro PW 3040/60 (Almelo) operated at room temperature. The Cu Kα radiation (1.542 Å) was generated at 30 mA and 40 kV. Scattered radiation was detected in an angular range of 3°–60° (2θ) at a step size of 0.02°. The crystallinity degree (CD) was calculated following the procedure described in previous works.

Structural Studies by SEM. The microstructures of the matrices were examined by using an FEI model Quanta 200 scanning electron microscope. Individual films and blend matrices were immersed in liquid nitrogen and fractured cryogenically. Samples were mounted onto metal stubs by using double-sided tape and observed at low pressure and an acceleration voltage of 12.5 kV, without any metal or carbon coating.

Biodegradation Test. A series of plastic pots (400 cm³) were used as soil containers, and the microflora present was used as a degrading medium. Square specimens of 3 × 3 cm with a thickness of approximately 25 μm on average were put into a plastic mesh to allow the access of moisture and microorganisms and the retrieval of degraded specimens. In order to guarantee aerobic degradation, the film samples were buried. The samples were conditioned at a relative humidity of 50% and a temperature of 20 °C. Containers were sprayed regularly with a defined and constant amount of water. Similar conditions were employed by Rivero et al. At specific time intervals, specimens were recovered from the soil and cleaned with a brush to avoid any possible damage of the structure.

In accordance with the described methodology in ASTM D5988–03, a ratio of 1 g of compost per 25 g of soil was used. Studies of the morphology of the degraded films were performed by means of SEM, MDSC, and ATR-FTIR analysis.

Statistical Analysis. For statistical analysis, version 10.0 of Systat software (Systat, Inc.) was used. Analysis of variance (ANOVA), linear regressions, and Fisher’s least-significant-difference test for mean comparison were performed. The significance level used was 0.05.
RESULTS AND DISCUSSION

Thermal Analysis. The thermograms obtained by means of MDSC from PLA, PHA, and their blends can be observed in Figure 1, where the stages of heating and cooling are shown. The temperatures of the thermal transitions and the enthalpy values (J g$^{-1}$) of the characteristic events during the heating and cooling stages obtained from MDSC curves are summarized in Table 1.

As it is possible to see in Figure 1a, the thermal analysis allowed us to observe a peak for each individual film, attributable to the melting of the crystalline domains corresponding to PLA and PHA at 147.7 and 172.7 °C, with the associated enthalpies of 20.1 and 86.6 J g$^{-1}$, respectively. The intensity of the melting peak is related to the number of crystals or crystalline populations (crystalline fraction) that exist in the material when the melting occurs. Using MDSC, Thellen et al. reported that crystal melting is produced at higher temperatures in samples of PHA containing lower percentages of valerate, because as the valerate content increases, the onset of crystal melting occurs at lower temperatures. In the present study, the PHA thermograms evidenced the presence of a peak with a shoulder, which could represent the melting of crystal lamellae, as was reported by Thellen et al. for extruded PHA.

On the other hand, PHA films exhibited a $T_g$ at −4.7 °C, whereas PLA showed a marked transition at 58.1 °C (Figure 1c). Glass-transition temperatures ranging from 2.7 to −4.4 °C for a PHA matrix obtained by casting were reported by da Silva et al.22

The thermograms of all the mixtures exhibited PLA-recrystallization peaks at 107 °C; this transition was more evident with higher PLA proportions in the mixture (Figure 1a). These results indicate that the incorporation of PHA contributes to the process of recrystallization of PLA in all the blend formulations. This effect was more marked in the 80/20 blend, a behavior that could be explained by bearing in mind that a low proportion of crystalline domains of PHA dispersed in a continuous matrix of PLA induced the phenomenon of nucleation of this latter polymer. The presence of double melting temperatures in the PLA/PHA blends corresponds to the melting of both the “as formed” and recrystallized polymer.10

According to Abdelwahab et al. and Ikehara et al., recrystallization strongly depends on the melting-temperature differences among the components of the mixture. When the $T_m$ difference is very large, the component with the higher melting temperature crystallizes first, and its spherulites contribute to fill all the volume.

The 20/80 blend exhibited a peak at 171.9 °C because of the melting of the PHA crystalline fraction and a shoulder at 148.4 °C corresponding to the melting of PLA. The 80/20, 60/40, and 40/60 blends exhibited two endothermic transitions; the enthalpy associated with the first event diminished with the incorporation of a higher proportion of PHA to the blend, whereas the enthalpy of the endothermic peak, characteristic of the PHA-crystalline phase, became more prominent (Figure 1a and Table 1). These findings were in accordance with a higher crystalline degree.

From the obtained DSC curves, two $T_g$ values were observed irrespective of the blend composition. These results suggest that the analyzed PLA/PHA blends are immiscible in the amorphous state (Figure 1c).

According to Lipatov and Alekseeva, the appearance of two transitions associated with the glass-transition temperatures supports the existence of a partially miscible system (i.e., materials with a heterogeneous biphasic structure).

During the cooling step, PHA exhibited a peak of crystallization at 58.7 °C with an associated enthalpy of 48.4 J g$^{-1}$, whereas the thermogram of PLA did not show this
Table 1. Thermal Analysis of Single and Blend Matrices with Different Proportions of PLA/PHA

| PLA/PHA | characteristic events of PHA | characteristic events of PLA | characteristic events of PHA |
|---------|-------------------------------|-----------------------------|-------------------------------|
|         | heating stage | cooling stage | heating stage | cooling stage | heating stage | cooling stage |
|         | $T_m$ (°C) | $\Delta H_m$ (J g$^{-1}$) | $T_m$ (°C) | $\Delta H_m$ (J g$^{-1}$) | $T_c$ (°C) | $\Delta H_c$ (J g$^{-1}$) |
| 0/100   | — | — | 147.1(1.0) a | 20.1(1.3) c | — | — |
| 80/20   | 170.4(1.2) a | 1.5(0.07) a | 150.3(1.9) a | 20.0(0.7) c | — | — |
| 60/40   | 169.9(0.6) a | 9.1(0.1) b | 149.8(0.6) a | 13.4(0.5) b | — | — |
| 40/60   | 170.3(0.4) a | 18.8(0.7) c | 149.5(0.9) a | 5.8(0.1) a | 65.6(0.5) b | 18.8(0.1) a |
| 20/80   | 171.9(0.8) a | 61.7(1.2) d | — | — | 65.9(3.8) b | 31.4(1.9) b |
| 0/100   | 172.7(0.1) a | 86.6(0.1) e | — | — | 58.8(0.5) a | 48.4(0.4) c |

*Different letters in the same column indicate significant differences ($p < 0.05$) among samples.*
estimated crystallinity degree was 14.3% (table insert in Figure 3). In contrast, PHA is a highly ordered polymer, and it is known to crystallize in an orthorhombic cell.\textsuperscript{10} X-ray-diffraction analysis was used to determine the crystalline structures and crystallinity degrees of the blends. The PHA spectrum showed diffraction peaks at $2\theta = 13.8$ and $17.5^\circ$, corresponding to the (020) and (110) planes, respectively.\textsuperscript{11} Additionally, reflections at $2\theta = 20.3, 22.4, 25.4$, and $30.8^\circ$ were detected, which were characteristics of the PHA polymer, its CD being $18.3\%$.\textsuperscript{14}

The inclusion of PHA in the blends increased the crystallinity of the materials. The highest crystallinity degrees of the 60/40 and 40/60 blends were confirmed by means of X-rays (table insert in Figure 3). The diffractograms showed peaks of higher intensity in relation to individual matrices. This behavior allows us to infer that PHA induces the recrystallization of PLA due to its capacity to act as an agent of nucleation. According to Furukawa et al.\textsuperscript{24} and Zhang and Thomas,\textsuperscript{11} it generates better packing density of the polymeric segments and promotes better adhesion and interaction at the interface level. However, the microstructure, porosity, and permeability of the matrix seem to depend on the PLA/PHA proportions, as presented below.

**SEM Observations.** From the macroscopic point of view, the blend of the two polymers appeared to be well mixed in the matrices with no apparent phase separation, although FTIR showed the immiscibility of both components. The average thickness of the films was $25 \mu m$, which was corroborated by microscopic analysis. As it can be seen in Figure 4, all matrices presented homogeneous appearances irrespective of the PLA/PHA ratio.

The films showed important differences when analyzed in the cross-sections of single or blend matrices. PLA-only films showed a homogeneous appearance, without pores and with good structural integrity. Addition of the PHA polymer led to films whose cross-section was rough, giving a structure with a fibrous appearance (Figure 4).

The cross-sections and surfaces of the 20/80 and 40/60 mixtures revealed the presence of an orderly structure, attributable to the growth and crystallization of the spherulites. Figure 4. Cross-section SEM micrographs of individual (PLA and PHA) and blend films with different proportions of PLA/PHA.
of PHA, proving to be a network formed by codomains corresponding to the different polymers with a granular, interspersed appearance and a repetitive pattern. It is important to remark that the highest proportion of PHA in the blends (PLA/PHA = 20/80) evidenced a porous microstructure as a result of the structural arrangement between the polymers. According to Abdelwahab et al., the interface interactions between the PHA and PLA phases could influence the nucleation phenomenon as supported by the XRD results.

These micrographs reinforced the results of immiscibility obtained by other techniques. As the PLA proportion increased, the morphology of the matrices became more homogeneous and less rough, until the 80/20 mixture presented an appearance where the PLA-enriched phase formed a continuous domain in which the PHA-enriched phase was dispersed and homogeneously distributed, as can be seen in Figure 4.

Water-Vapor Permeability. Table 2 shows the WVP values of the individual films and PLA/PHA blends. The formulation of the blend matrices improved the barrier properties of the materials, obtaining a reduction of 40% in the WVP values for the 40/60, 60/40, and 80/20 blends compared with the values of the individual films (Table 2). Meanwhile, the 20/80 blend did not show significant differences ($p > 0.05$).

According to Arrieta et al., the crystallization of PHA reduces the water-vapor permeability because the crystals decrease the volume of the amorphous phase, generating a path of greater tortuosity and reducing mass matter transfer.

The improvement of the barrier properties is related to the higher crystallinity of the PLA/PHA blend matrices, as observed by the X-ray diffraction technique and the MDSC thermal analysis.

Soil-Biodegradation Studies. The influence of the microstructure developed during the formulation of the blends on the biodegradation process was examined. A morphological study by SEM during soil-biodegradation experiments was complementary to visual examination as it helped to confirm the existence of structural modifications in the films, allowing a detailed evaluation of the degradation process.

The results showed that the degradation behavior of the biobased polymers followed different patterns regarding the morphological characteristic of each matrix. As can be seen in Figure 5a, the biodegradation occurred in both the PHA and PLA phases.

The biodegradation assay revealed that the PHA films exhibited remarkable biodegradation after 30 days, whereas the blend matrices (PLA/PHA) showed changes around 50 days, which indicated a delay in the process of biodegradation (Figure 5a). According to Weng et al., a PHA polymer could be biodegraded at a high rate under composting as well as soil-environment conditions; in contrast, although PLA was biodegradable under composting conditions, its degradation rate in soil was slow.

SEM micrographs show the fractured surface of the PLA/PHA matrices after a biodegradation process of 50 days (Figure 5a). It can be seen that the biodegradation was intensified with higher proportions of PHA in the blend system. As the proportion of PHA increased, particularly from 40/60 to 20/80, the matrices showed greater interstices or cavities (Figure 4), which could facilitate the biodegradation process. Zhang and Thomas explained that the inclusion of PHA improved the degradation degree of PLA at room temperature. The authors reported that PLA and PHA exhibit different degradation patterns. PHA is mainly degraded by the attack of various enzymes at the surface. According to Weng et al., the degradation of PHA can be attributed to erosion catalyzed by bacteria from the surface to the interior.

In contrast, PLA degradation is produced throughout the whole sample, starting with a nonenzymatic hydrolysis that leads to a reduction in the molecular weight. Then, low-molecular-weight PLA diffuses out of the bulk polymer and can be metabolized by microorganisms, producing water, carbon dioxide, and humus.

On the other hand, the thermograms of the 20/80, 40/60, and 60/40 blend matrices exposed to the biodegradation process for 50 days showed a decrease of the transition enthalpy, corresponding to the melting of the PHA crystalline fraction being more marked in the blends with the greatest proportion of PHA (Figure 5b). In this sense, Dharmalingam found that the changes of melting enthalpy ($\Delta H_m$) for a composite material based on PLA/PHB blends represent depolymerization. Consequently, this phenomenon could indicate a higher sensitivity to the degradation process in the presence of higher proportions of PHA, independent of the rearrangement formed between both polymers.

The chemical-structure changes of the matrices exposed to the biodegradation process were investigated by ATR-FTIR (Figure 5c).

ATR-FTIR spectra corroborated the changes caused in the structure of the polymers. After 50 days of exposure to the biodegradation process, ATR-FTIR spectra of the PHA and PLA blend films showed that the bands lost definition.

For all the samples assayed, the peaks in the 4000–3000 cm$^{-1}$ region became broadened after the biodegradation process (data not shown). According to Weng et al., this fact was attributable to the formation of hydroxyl and carboxylic groups. This was also confirmed by the shift of the absorption peak of the C=O stretching vibration after biodegradation.

Ludueña et al. pointed out that chemical and enzymatic hydrolysis are the main mechanisms of chain rupture during the degradation process. Then, biodegradation process depends on water availability, which produces hydrolysis, and microbial attack of the matrix. Water diffusion in the soil leads to a hydrolytic degradation of the material modifying the surface, resulting in a porous structure with evident signs of degradation. A similar explanation was proposed by Rocca-Smith et al.
The biodegradability of the blends was more marked in films formulated with increasing proportions of PHA; similar results were reported by Zhang and Thomas.\textsuperscript{11}

**Conclusions.** Thermal and microstructural studies revealed that blends of PLA/PHA-based systems were partially miscible. The formulation of blend matrices improved the crystallinity of PLA; additionally, it induced the polymer-recrystallization process, because crystallized PHA acted as a PLA-nucleating agent. This phenomenon explains the improvements in water-vapor-barrier film properties. Moreover, the blends exposed to a biodegradation process showed an intermediate behavior between those of PLA and PHA, leading to a consistent basis for designing systems tailored to a particular purpose or use. This work, therefore, contributes to the knowledge of microstructures, allowing one to develop and test materials with specific technological applications.

**Figure 5.** Monitoring of the behaviors of samples after they were submitted to biodegradation processes (buried for 50 days) through (a) SEM micrographs of the PLA/PHA blend matrices with enlarged sections showing the degradation (magnification is indicated in the micrographs), (b) MDSC analysis, and (b) FTIR-ATR studies.

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