

1 Microstructural Behaviors of Matrices Based on Polylactic Acid and 2 Polyhydroxyalkanoates

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

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

20 ■ INTRODUCTION

21 Polyhydroxyalkanoate (PHA) is a family of biopolyesters
 22 synthesized by microorganisms from various carbon sources;
 23 they are accumulated intracellularly under nutrient stress and
 24 act as carbon and energy reserves.¹ PHAs can be produced by
 25 both pure and mixed microbial cultures. Mixed cultures have
 26 the advantage that they do not need sterile conditions and are
 27 better able to adapt to complex substrates, such as industrial
 28 wastes, than pure cultures.² For this, wastes from the dairy
 29 industry, the sugar industry, forestry, and biodiesel production
 30 can be utilized.³ Cheese whey is a surplus material from the
 31 dairy industry that is mainly discharged to both soils and water
 32 bodies, causing serious environmental problems. PHA
 33 production from cheese whey could revalorize this dairy
 34 subproduct and, at the same time, solve the waste-disposal
 35 problems.

36 A relevant characteristic of PHA is its versatility, because
 37 there are more than a hundred different monomers, including
 38 hydroxyvalerate and butyrate among others. The properties of
 39 the synthesized polymer are modified depending on the
 40 position of its functional groups and degrees of polymerization.
 41 This chemistry allows PHAs to be tailored to provide similar
 42 properties to traditional thermoplastics, such as polyethylene
 43 (PE) and polypropylene (PP), while maintaining biodegrad-
 44 ability.⁴

45 Polylactic acid (PLA), a thermoplastic aliphatic polyester
 46 derived from lactic acid (2-hydroxy propionic acid), can be
 47 produced by condensation and polymerization directly from its
 48 basic building block, lactic acid, which is derived from the
 49 fermentation of sugars from carbohydrates sources, such as

corn starch; cassava root, chips, and starch; and sugar cane.⁵ 50
 Polylactic acid is produced at the largest industrial scale of all 51
 biodegradable polymers, and it is considered the most 52
 promising candidate for replacing conventional plastics.⁶ It is 53
 being used in biomedical applications, for bottle production, 54
 for filament production in 3D printing, and for compostable- 55
 food-packaging production. It is also being evaluated as a 56
 material for tissue engineering. Mass production has reduced 57
 the cost of PLA production, making it an economically viable 58
 choice for the fabrication of containers, plastic bags, and fibers. 59
 Commercial-scale plants today produce hundreds of thousands 60
 of tons of PLA per year.⁷ 61

By controlling the molecular architecture, suppliers are able 62
 to tailor the polymer to specific applications. Consequently, 63
 new and improved grades of bioplastic resins are constantly 64
 being introduced to the market. NatureWorks LLC focuses on 65
 a multistep procedure involving the condensation reaction of 66
 aqueous lactic acid for the production of a low-molecular- 67
 weight PLA prepolymer. It is converted into a blend of lactide 68
 stereoisomers in order to produce a large spectrum of PLA 69
 grades.⁸ The films based on PLA have excellent optics and 70
 good machinability, barrier, and mechanical properties.⁵ 71

PLA and PHA polymers are polyesters and are used in 72
 consumer products by a wide industrial sector as a result of 73
 their biocompatibility and sustainability.⁹ They have thermal 74

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75 behaviors comparable to those of some conventional polymers,
76 and this has generated much interest in exploring their physical
77 and structural properties to identify potential applications.¹⁰

78 The combination of the two polymers allows the design of
79 new materials with tailorable properties differing meaningfully
80 from those of each component by adjusting the advantages of
81 each polymer in order to obtain materials for different
82 applications. In this sense, the formulation of blend systems
83 is easier and faster than copolymerization methods.¹¹ There
84 are many studies focused on PLA modification, such as the
85 addition of modifiers and copolymerization.¹² The addition of
86 a highly ordered stereochemical structure, such as that of PHA,
87 could improve the film properties of PLA.^{13,14} In this sense,
88 blending PLA with another biobased and biodegradable
89 material, PHA, in order to obtain tailor-made materials
90 constitutes a promising alternative.

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

96 ■ MATERIALS AND METHODS

97 Polylactic acid (PLA), grade 4043D in pellet form (98% L-lactide with
98 a D-isomer content of approximately 2%) and designed for the
99 production of films, was purchased from Natureworks under the
100 trademark Ingeo. As is well-known, the production of PLA involves
101 the conversion of starch in dextrose via a hydrolysis process and
102 fermentation by microorganisms to synthesize the chain of the
103 polylactide polymer.

104 Polyhydroxyalkanoate (PHA) was obtained from activated sludges
105 from a wastewater-treatment system at the laboratory scale (CIDCA).
106 A two-stage biological system was proposed to produce PHA by
107 aerobic mixed culture from hydrolyzed cheese whey. The first step
108 involved the selection of PHA-accumulating organisms using an
109 aerobic sequencing batch reactor (SBR) operated under a feast–
110 famine regime. Then, there was the stage of PHA accumulation in an
111 aerobic batch reactor that was inoculated with biomass taken from
112 SBR enriched with PHA-accumulating bacteria.

113 **Extraction and Quantification of PHA.** Extraction and
114 characterization of PHA from the batch-reactor biomass were
115 performed following the method proposed by Venkateswar Reddy
116 et al.¹⁵ A hydroxybutyrate–hydroxyvalerate (HB–HV) copolymer
117 with a purity of 96% and a molar relation 95:5 HB–HV was obtained.

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

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

130 Film thickness was measured by means of a coating-thickness gauge
131 (Check Line DCN-900) for nonconductive materials on nonferrous
132 substrates. For each specimen, at least 14 measurements at different
133 positions were taken.

134 **Water-Vapor Permeability.** Water-vapor-permeability (WVP)
135 tests were carried out according to the technique described by Rivero
136 et al.¹⁶ based on a modified version of ASTM¹⁷ method E96. A
137 permeation cell maintained at 20 °C was used for the assays. Eight
138 measurements were performed once steady-state conditions were
139 reached. All measurements were performed at least four times for each
140 specimen.

Thermal Analysis by MDSC. Thermal analysis of the samples
141 was conducted by the modulated-differential-scanning-calorimetry
142 (MDSC) technique. Q100 (TA Instruments) controlled by a TA
143 5000 module (TA Instruments) and equipped with a cryogenic-
144 quench-cooling accessory was used under a N₂ atmosphere. This
145 technique allowed us to measure the calorific capacity of the sample
146 and simultaneously differentiate between the reversible (dependent
147 on the calorific capacity) and irreversible events (dependent on the
148 time and temperature) that the sample experienced. Likewise, it
149 allowed the resolution of complex transitions.

150 A standard heating ramp of 10 °C min⁻¹ with a modulation-
151 temperature amplitude of 0.5 °C and a modulation period of 60 s was
152 used. The first scan (heating) was performed in order to delete the
153 thermal story from –50 °C up to 200 °C. Once the first scan was
154 completed, the sample was cooled to –80 °C, and then a second
155 heating scan was recorded. Informed results were the averages of two
156 replicates to ensure reproducibility of the results.

157 The results were analyzed by using the Universal Analysis V1.7F
158 software (TA Instruments). Different parameters were determined
159 from the obtained thermograms: melting temperature (T_m), enthalpy
160 corresponding to the area of the endothermic peak (ΔH_m),
161 crystallization temperature during the cooling stage (T_c), crystal-
162 lization enthalpy (ΔH_c), and glass-transition temperature (T_g)
163 determined from the reversible signal.

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

173 **X-ray Diffraction.** X-ray diffractograms of individual PVA and
174 PLA films and their blends were evaluated by using an X'Pert Pro P
175 Analytical Model PW 3040/60 (Almelo) operated at room temper-
176 ature. The Cu K α radiation (1.542 Å) was generated at 30 mA and 40
177 kV. Scattered radiation was detected in an angular range of 3–60°
178 (2 θ) at a step size of 0.02°. The crystallinity degree (CD) was
179 calculated following the procedure described in previous works.^{18,19}

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

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

199 In accordance with the described methodology in ASTM D5988-
200 03,²¹ a ratio of 1 g of compost per 25 g of soil was used. Studies of the
201 morphology of the degraded films were performed by means of SEM,
202 MDSC, and ATR-FTIR analysis.

203 **Statistical Analysis.** For statistical analysis, version 10.0 of Systat-
204 software (Systat, Inc.) was used. Analysis of variance (ANOVA),
205 linear regressions, and Fisher's least-significant-difference test for
206 mean comparison were performed. The significance level used was
207 0.05.

209 ■ RESULTS AND DISCUSSION

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

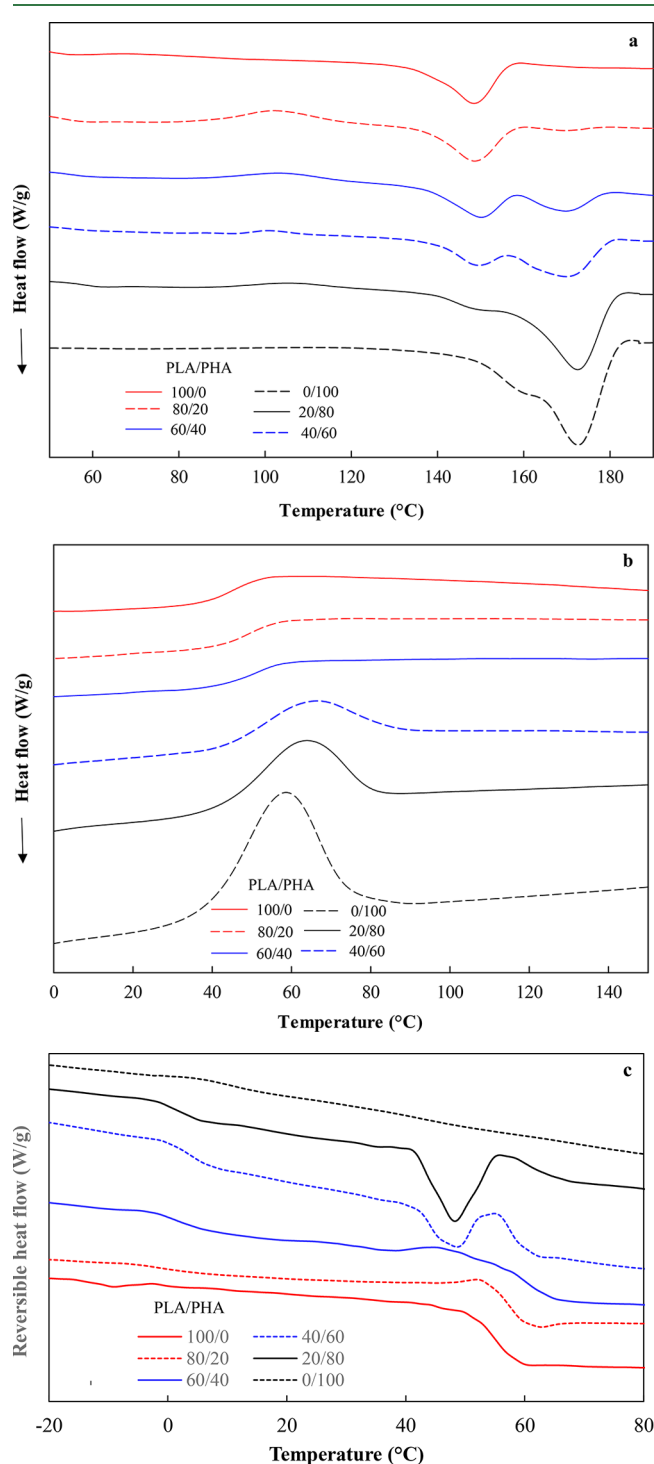


Figure 1. MDSC curves of individual (PLA and PHA) and blend films with different proportions of PLA/PHA showing (a) heating stage, (b) cooling stage, and (c) reversing heat flow (W g^{-1}), evidencing the glass-transition temperatures (T_g) of each component.

and cooling stages obtained from MDSC curves are 215 t1
summarized in **Table 1**. 216 t1

As it is possible to see in **Figure 1a**, the thermal analysis 217
allowed us to observe a peak for each individual film, 218
attributable to the melting of the crystalline domains 219
corresponding to PLA and PHA at 147.7 and 172.7 $^{\circ}\text{C}$, with 220
the associated enthalpies of 20.1 and 86.6 J g^{-1} , respectively. 221
The intensity of the melting peak is related to the number of 222
crystals or crystalline populations (crystalline fraction) that 223
exist in the material when the melting occurs. Using MDSC, 224
Thellen et al.⁴ reported that crystal melting is produced at 225
higher temperatures in samples of PHA containing lower 226
percentages of valerate, because as the valerate content 227
increases, the onset of crystal melting occurs at lower 228
temperatures. In the present study, the PHA thermograms 229
evidenced the presence of a peak with a shoulder, which could 230
represent the melting of crystal lamellae, as was reported by 231
Thellen et al.⁴ for extruded PHA. 232

On the other hand, PHA films exhibited a T_g at -4.7°C , 233
whereas PLA showed a marked transition at 58.1°C (**Figure** 234
1c). Glass-transition temperatures ranging from 2.7 to -4.4°C 235
for a PHA matrix obtained by casting were reported by da Silva 236
et al.²² 237

The thermograms of all the mixtures exhibited PLA- 238
recrystallization peaks at 107°C ; this transition was more 239
evident with higher PLA proportions in the mixture (**Figure** 240
1a). These results indicate that the incorporation of PHA 241
contributes to the process of recrystallization of PLA in all the 242
blend formulations. This effect was more marked in the 80/20 243
blend, a behavior that could be explained by bearing in mind 244
that a low proportion of crystalline domains of PHA dispersed 245
in a continuous matrix of PLA induced the phenomenon of 246
nucleation of this latter polymer. The presence of double 247
melting temperatures in the PLA/PHA blends corresponds to 248
the melting of both the “as formed” and recrystallized 249
polymer.¹⁰ 250

According to Abdelwahab et al.¹⁰ and Ikehara et al.,²³ 251
recrystallization strongly depends on the melting-temperature 252
differences among the components of the mixture. When the 253
 T_m difference is very large, the component with the higher 254
melting temperature crystallizes first, and its spherulites 255
contribute to fill all the volume. 256

The 20/80 blend exhibited a peak at 171.9°C because of the 257
melting of the PHA crystalline fraction and a shoulder at 148.4 258
 $^{\circ}\text{C}$ corresponding to the melting of PLA. The 80/20, 60/40, 259
and 40/60 blends exhibited two endothermic transitions; the 260
enthalpy associated with the first event diminished with the 261
incorporation of a higher proportion of PHA to the blend, 262
whereas the enthalpy of the endothermic peak, characteristic of 263
the PHA-crystalline phase, became more prominent (**Figure 1a** 264
and **Table 1**). These findings were in accordance with a higher 265
crystalline degree. 266

From the obtained DSC curves, two T_g values were observed 267
irrespective of the blend composition. These results suggest 268
that the analyzed PLA/PHA blends are immiscible in the 269
amorphous state (**Figure 1c**). 270

According to Lipatov and Alekseeva,²⁴ the appearance of 271
two transitions associated with the glass-transition temper- 272
atures supports the existence of a partially miscible system (i.e., 273
materials with a heterogeneous biphasic structure). 274

During the cooling step, PHA exhibited a peak of 275
crystallization at 58.7°C with an associated enthalpy of 48.4 276
 J g^{-1} , whereas the thermogram of PLA did not show this 277

Table 1. Thermal Analysis of Single and Blend Matrices with Different Proportions of PLA/PHA^a

PLA/PHA	heating stage				cooling stage	
	characteristic events of PHA		characteristic events of PLA		characteristic events of PHA	
	T_m (°C)	ΔH_m (J g ⁻¹)	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_c (J g ⁻¹)
100/0	—	—	147.7(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

^aDifferent letters in the same column indicate significant differences ($p < 0.05$) among samples.

278 transition (Figure 1b and Table 1). Taking these results into
279 account, it is possible to infer that the crystallinity of PHA is
280 greater than that of PLA.

281 The thermal analysis of the PLA/PHA mixtures showed that
282 the peak of crystallization attributable to PHA was observed
283 only in the 20/80 and 40/60 mixtures, with a minor associated
284 enthalpy regarding a single PHA matrix (Figure 1b). On the
285 other hand, the thermograms of the individual PLA film and
286 the 60/40 and 80/20 mixtures did not exhibit this thermal
287 transition (Figure 1b). Nevertheless, an event was observed at
288 57.7 °C attributable to the glass-transition temperature of the
289 PLA-enriched phase. Similar results were informed by Arrieta
290 et al.,¹² Furukawa et al.,²⁵ and Zhang and Thomas,¹¹ indicating
291 that these results are a signal of the fact that the PHA in the
292 mixtures does not crystallize during the cooling stage when it is
293 the minor proportion.

294 **Microstructural Analysis. FTIR Analysis.** From the ATR-
295 FTIR spectra, the functional characteristic groups of PLA and
296 PHA were identified (Figure 2a,b). They are consistent with
297 those reported in the literature.^{5,26,27}

298 In the PLA spectrum, the band located at 1746 cm⁻¹ is a
299 strong peak that corresponds to the stretching of the carbonyls'
300 amorphous phase.⁵ The bands located at 1180 and 1080 cm⁻¹
301 belong to the asymmetric and symmetric stretching vibrations
302 of C—O—C. As is known, PLA is a hydrophobic polymer
303 because of the presence of —CH side groups. The peaks at
304 about 2997 and 2946 cm⁻¹ correspond to the asymmetric and
305 symmetric stretching vibrations of the —CH groups in the side
306 chains, respectively (data not shown).

307 On the other hand, in the PHA spectrum, the peak at 1719
308 cm⁻¹ is attributable to the stretching of the crystalline carbonyl
309 group, and the stretching of the carbonyl group of the
310 amorphous phase is virtually imperceptible. The 40/60 and
311 20/80 samples exhibited peaks at 1748 and 1755 cm⁻¹ (Figure
312 2b), which were assigned to the amorphous and crystalline
313 bands of PLA, respectively.²⁴

314 Furthermore, Figure 2a,b depicts the ATR-FTIR spectra of
315 the PLA/PHA blend matrices. The spectra of the 80/20 and
316 60/40 compositions followed a similar pattern to that of the
317 pristine PLA, whereas the 40/60 and 20/80 mixtures were
318 identified mainly with the PHA spectrum. All of them unfolded
319 both bands corresponding to the stretching of carbonyls
320 located at 1746 and 1719 cm⁻¹ due to PLA and PHA phase,
321 respectively (Figure 2a,b).

322 In the cases of the 80/20, 60/40, and 40/60 blends, the
323 bands in the C—O—C and C—C stretching and CH
324 deformation mode region (1300–1000 cm⁻¹) are visualized
325 at about the same wavenumbers as those of pure PHA (Figure
326 2a,b).

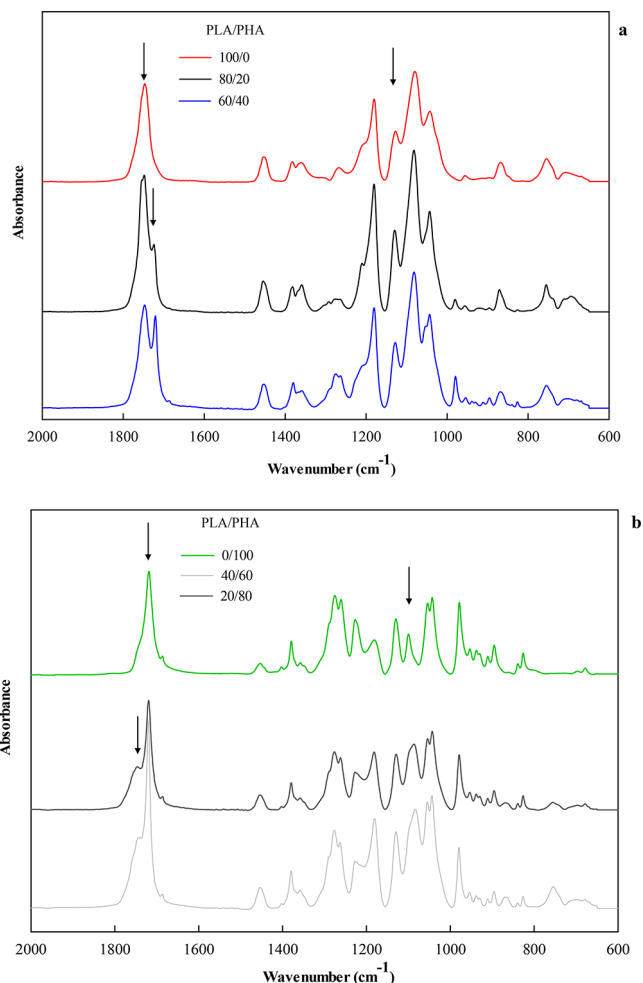


Figure 2. ATR-FTIR spectra of individual (PLA and PHA) and blend matrices with different proportions of PLA/PHA.

It is noteworthy that the intensities of these bands were
interdependent and mutually dependent, one being increased
at the expense of the other, meaning that the ratio of intensities
of these two bands changed in agreement with the ratio of the
individual components. These results allowed us to infer the
immiscibility of these components and that there were no
strong molecular interactions between the polymers.

X-ray Diffraction. The typical diffraction patterns of
individual PHA and PLA and those of the composite films
are depicted in Figure 3. The X-ray diffractogram of the PLA
films exhibited a pattern corresponding to an amorphous
material with a peak located at $2\theta = 17^\circ$, which was associated
with the reflection of the crystals of the polymer;

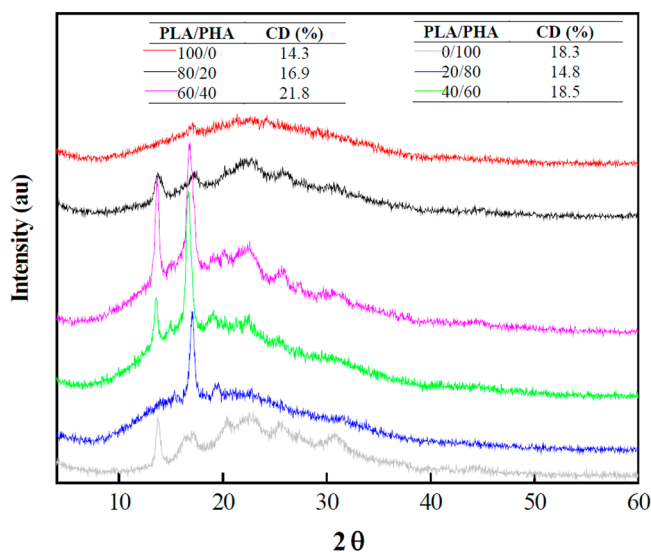


Figure 3. X-ray diffractograms of individual (PLA and PHA) and blend films with different proportions of PLA/PHA. Table inset shows the crystallinity degrees (%) of the samples.

340 estimated crystallinity degree was 14.3% (table insert in [Figure](#)
341 [3](#)). In contrast, PHA is a highly ordered polymer, and it is
342 known to crystallize in an orthorhombic cell.¹⁰
343 X-ray-diffraction analysis was used to determine the
344 crystalline structures and crystallinity degrees of the blends.
345 The PHA spectrum showed diffraction peaks at $2\theta = 13.8$ and
346 17° , corresponding to the (020) and (110) planes,
347 respectively.¹¹ Additionally, reflections at $2\theta = 20.3, 22.4,$

25.4, and 30.8° were detected, which were characteristics of 348
the PHA polymer, its CD being 18.3%.¹⁴ 349

The inclusion of PHA in the blends increased the 350
crystallinity of the materials. The highest crystallinity degrees 351
of the 60/40 and 40/60 blends were confirmed by means of X- 352
rays (table insert in [Figure 3](#)). The diffractograms showed 353
peaks of higher intensity in relation to individual matrices. 354

This behavior allows us to infer that PHA induces the 355
recrystallization of PLA due to its capacity to act as an agent of 356
nucleation. According to Furukawa et al.²⁴ and Zhang and 357
Thomas,¹¹ it generates better packing density of the polymeric 358
segments and promotes better adhesion and interaction at the 359
interface level. However, the microstructure, porosity, and 360
permeability of the matrix seem to depend on the PLA/PHA 361
proportions, as presented below. 362

SEM Observations. From the macroscopic point of view, 363
the blend of the two polymers appeared to be well mixed in the 364
matrices with no apparent phase separation, although FTIR 365
showed the immiscibility of both components. The average 366
thickness of the films was $25 \mu\text{m}$, which was corroborated by 367
microscopic analysis. As it can be seen in [Figure 4](#), all matrices 368
presented homogeneous appearances irrespective of the PLA/ 369
PHA ratio. 370

The films showed important differences when analyzed in 371
the cross-sections of single or blend matrices. PLA-only films 372
showed a homogeneous appearance, without pores and with 373
good structural integrity. Addition of the PHA polymer led to 374
films whose cross-section was rough, giving a structure with a 375
fibrous appearance ([Figure 4](#)). 376

The cross-sections and surfaces of the 20/80 and 40/60 377
mixtures revealed the presence of an orderly structure, 378
attributable to the growth and crystallization of the spherulites 379

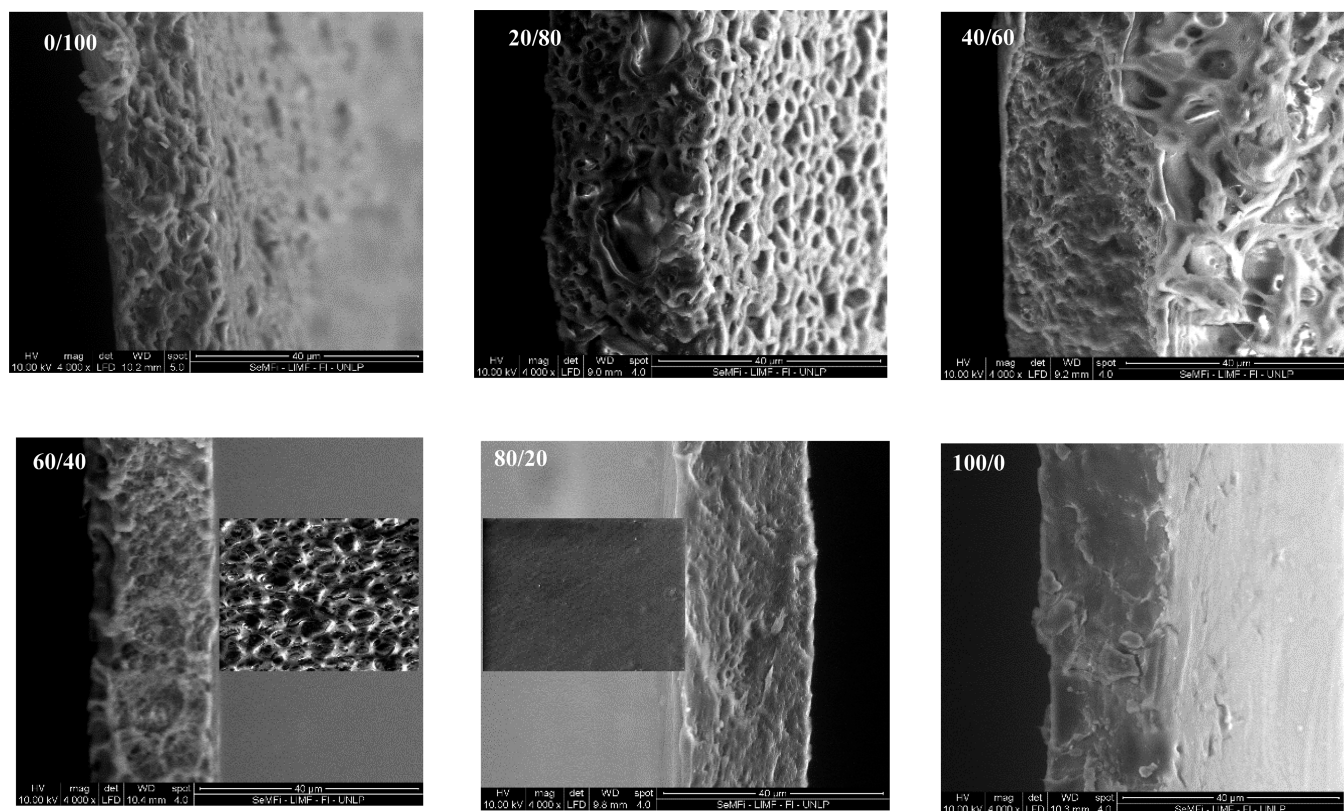


Figure 4. Cross-section SEM micrographs of individual (PLA and PHA) and blend films with different proportions of PLA/PHA.

380 of PHA, proving to be a network formed by codomains
381 corresponding to the different polymers with a granular,
382 interspersed appearance and a repetitive pattern. It is
383 important to remark that the highest proportion of PHA in
384 the blends (PLA/PHA = 20/80) evidenced a porous
385 microstructure as a result of the structural arrangement
386 between the polymers. According to Abdelwahab et al.,¹⁰ the
387 interface interactions between the PHA and PLA phases could
388 influence the nucleation phenomenon as supported by the
389 XRD results.

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

398 **Water-Vapor Permeability.** Table 2 shows the WVP values
399 of the individual films and PLA/PHA blends. The formulation

Table 2. Water-Vapor-Barrier Properties of the Individual (PLA and PHA) and Blend Films with Different Proportions of PLA/PHA^a

PLA/PHA	WVP ($\times 10^{11}$ g s ⁻¹ m ⁻¹ Pa ⁻¹)
100/0	1.73(0.25) b
80/20	0.62(0.06) a
60/40	0.68(0.07) a
40/60	0.72(0.05) a
20/80	2.22(0.38) b
0/100	2.24(0.30) b

^aDifferent letters indicate significant differences ($p < 0.05$) among samples.

400 of the blend matrices improved the barrier properties of the
401 materials, obtaining a reduction of 40% in the WVP values for
402 the 40/60, 60/40, and 80/20 blends compared with the values
403 of the individual films (Table 2). Meanwhile, the 20/80 blend
404 did not show significant differences ($p > 0.05$).

405 According to Arrieta et al.,¹² the crystallization of PLA
406 reduces the water-vapor permeability because the crystals
407 decrease the volume of the amorphous phase, generating a
408 path of greater tortuosity and reducing mass matter transfer.

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

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

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

425 The biodegradation assay revealed that the PHA films
426 exhibited remarkable biodegradation after 30 days, whereas the
427 blend matrices (PLA/PHA) showed changes around 50 days,

which indicated a delay in the process of biodegradation 428
(Figure 5a). According to Weng et al.,²⁷ a PHA polymer could 429
be biodegraded at a high rate under composting as well as soil- 430
environment conditions; in contrast, although PLA was 431
biodegradable under composting conditions, its degradation 432
rate in soil was slow. 433

SEM micrographs show the fractured surface of the PLA/ 434
PHA matrices after a biodegradation process of 50 days 435
(Figure 5a). It can be seen that the biodegradation was 436
intensified with higher proportions of PHA in the blend 437
system. As the proportion of PHA increased, particularly from 438
40/60 to 20/80, the matrices showed greater interstices or 439
cavities (Figure 4), which could facilitate the biodegradation 440
process. Zhang and Thomas¹¹ explained that the inclusion of 441
PHA improved the degradation degree of PLA at room 442
temperature. The authors reported that PHA and PLA exhibit 443
different degradation patterns. PHA is mainly degraded by the 444
attack of various enzymes at the surface. According to Weng et 445
al.²⁷ the degradation of PHA can be attributed to erosion 446
catalyzed by bacteria from the surface to the interior. 447

In contrast, PLA degradation is produced throughout the 448
whole sample, starting with a nonenzymatic hydrolysis that 449
leads to a reduction in the molecular weight.¹¹ Then, low- 450
molecular-weight PLA diffuses out of the bulk polymer and can 451
be metabolized by microorganisms, producing water, carbon 452
dioxide, and humus.²⁹ 453

On the other hand, the thermograms of the 20/80, 40/60 454
and 60/40 blend matrices exposed to the biodegradation 455
process for 50 days showed a decrease of the transition 456
enthalpy, corresponding to the melting of the PHA crystalline 457
fraction being more marked in the blends with the greatest 458
proportion of PHA (Figure 5b). In this sense, Dharmalingam³⁰ 459
found that the changes of melting enthalpy (ΔH_m) for a 460
composite material based on PLA/PHA blends represent 461
depolymerization. Consequently, this phenomenon could 462
indicate a higher sensitivity to the degradation process in the 463
presence of higher proportions of PHA, independent of the 464
rearrangement formed between both polymers. 465

The chemical-structure changes of the matrices exposed to 466
the biodegradation process were investigated by ATR-FTIR 467
(Figure 5c). 468

ATR-FTIR spectra corroborated the changes caused in the 469
structure of the polymers. After 50 days of exposure to the 470
biodegradation process, ATR-FTIR spectra of the PHA and 471
blend films showed that the bands lost definition. 472

For all the samples assayed, the peaks in the 4000–3000 473
cm⁻¹ region became broadened after the biodegradation 474
process (data not shown). According to Weng et al.,²⁷ this 475
fact was attributable to the formation of hydroxyl and 476
carboxylic groups. This was also confirmed by the shift of 477
the absorption peak of the C=O stretching vibration after 478
biodegradation. 479

Ludueña et al.³¹ pointed out that chemical and enzymatic 480
hydrolysis are the main mechanisms of chain rupture during 481
the degradation process. Then, biodegradation process 482
depends on water availability, which produces hydrolysis, and 483
microbial attack of the matrix. Water diffusion in the soil leads 484
to a hydrolytic degradation of the material modifying the 485
surface, resulting in a porous structure with evident signs of 486
degradation. A similar explanation was proposed by Rocca- 487
Smith et al.³² 488

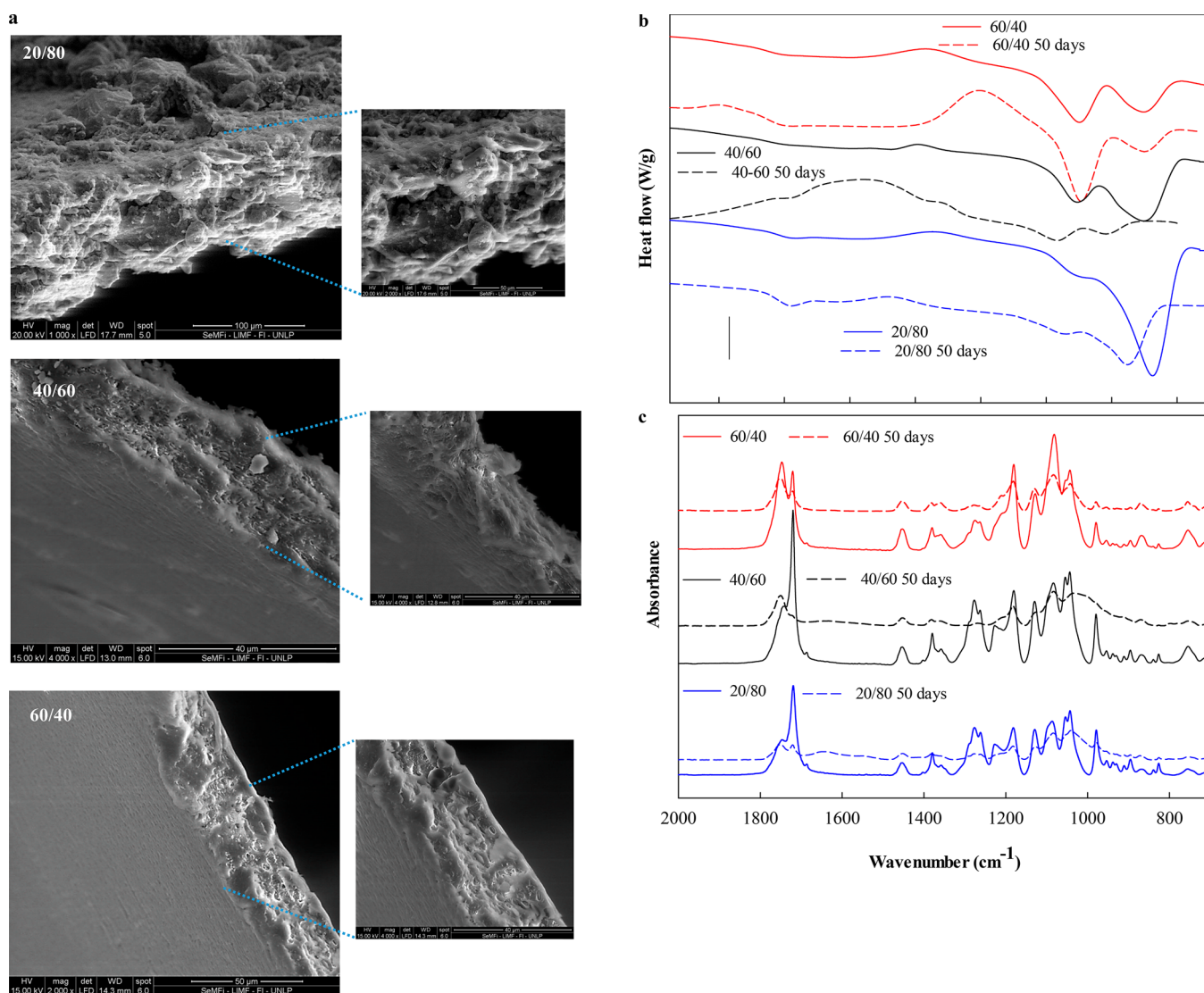


Figure 5. Monitoring of the behaviors of samples after they were submitted to biodegradation processes (buried for 50 days) through (a) SEM micrographs of the PLA/PHA blend matrices with enlarged sections showing the degradation (magnification is indicated in the micrographs), (b) MDSC analysis, and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

489 The biodegradability of the blends was more marked in films
490 formulated with increasing proportions of PHA; similar results
491 were reported by Zhang and Thomas.¹¹

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

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