Miscibility and degradation of polymer blends based on biodegradable poly(butylene adipate-*co*-terephthalate)

Ainara Sangroniz[1], Alba Gonzalez[1], Loli Martin[2], Lourdes Irusta[1], Marian Iriarte[1], Agustin Etxeberria[1,*]

[1]POLYMAT, Department of Polymer Science and Technology, Faculty of Chemistry, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, Donostia 20018, Spain.

[2]Macrobehavior–Mesostructure–Nanotechnology General Research Service (SGIker), University of the Basque Country (UPV/EHU), Donostia-San Sebastian, Spain

Correspondence to: Agustin Etxeberria (E-mail: agustin.etxeberria@ehu.es)

Abstract

The aim of this work is to analyse the effect of the preparation method on the miscibility of poly(butylene adipate-*co*-terephthalate) (PBAT) and poly(hydroxy ether of bisphenol A) (PH) blends and to provide a better understanding on the effect of a non-degradable component (PH) in the degradation of biodegradable PBAT. Blends have been prepared by different methods and the miscibility has been studied in a deeper way by means of differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and infrared spectroscopy (FTIR). Depending on the preparation method miscible or partially miscible blends are obtained. Furthermore, for miscible blends the hydrolytic degradation has been carried out for 405 days. It has been observed that adipate sequences on poly(butylene adipate-*co*-terephthalate) copolymer are more prone to degradation which leads to changes on glass transition temperature, crystallinity and chemical structure. The degradation rate is decelerated with the addition of PH, however the rate is similar or higher than other biodegradable polymers. Therefore the degradation rate can be controlled varying the composition of the blend and tailored materials with adequate properties can be obtained.

Keywords: Biodegradable polymer; polymer blend; miscibility; hydrolytic degradation

1.Introduction

The growing awareness of the environmental problems together with the government regulations has increased the interest on biodegradable polymers. These polymers are a potential solution for the waste problems associated with commodity polymers such as poly(propylene), poly(ethylene), poly(ethylene terephthalate) and poly(styrene) [1].

Biodegradable polymers such as poly(lactide) or poly(caprolactone) have been widely studied in literature [1-3]. However, this kind of materials presents a poor mechanical performance and low barrier character that limits their applications. In the search of new biodegradable polymers that will be suitable for packaging applications poly(butylene adipate-*co*-terephthalate) (PBAT) (known under the trade name Ecoflex) has attracted a great interest. PBAT presents good mechanical properties that are similar to polyethylene, therefore it is an adequate polymer for packaging applications [4]. However, it also has a low barrier character that must be improved.

Great efforts have been done to improve the barrier character of biodegradable polymers, such as blending biodegradable polymers with polymers that present good barrier character. The miscibility of the blend is of great importance since it will determine the properties of the system. There are few miscible blends due to the high molecular weight and the weak interactions between them. The miscibility of the blends depends on the mixing enthalpy, since the mixing entropy is negligible. Usually favourable specific interactions are needed to guarantee the miscibility of the blends [5, 6].

The miscibility is greatly influenced by the preparation conditions of the blend leading to immiscible, partially miscible and miscible blends. For blends prepared by casting, phase separation can occur due to the differences in the solvent-polymer 1 and solvent-polymer 2 interactions. The solvent could interact more favourably with one polymer excluding the other one. Although a polymer pair can be thermodynamically miscible, the use of a solvent can lead to phase separation, which is known as the solvent-induced phase separation or $\Delta\chi$ effect [7-10]. Despite the great importance of the preparation method on the blend miscibility [11-13], the studies analysing this phenomena are not abundant.

Poly(hydroxy ether of bisphenol A) (Phenoxy) has excellent barrier character and also contains hydroxyl groups that could form strong specific interactions. It forms miscible blends with a wide range of polymer families: polyoxides [14], polyesters [15], poly(vinyl ether)s [16], polyamides [17] and polysulphones [18], among others.

Poly(1,4-butylene adipate)/phenoxy blends [15] and poly(butylene terephthalate)/phenoxy [19] blends are miscible, therefore it is expected that the copolymer poly(butylene adipate-*co*-terephthalate) would be miscible with phenoxy, as it has been demonstrated by Su et al. [20]. They prepared the blends by melt processing and miscibility was achieved for the studied compositions, as it has been corroborated by means of thermal analysis and infrared spectroscopy.

The first purpose of this study is to provide a deeper analysis about the effect of the preparation conditions on the miscibility of PBAT/PH blends. Blends of PBAT/PH have been prepared i) by solution/evaporation, ii) by solution/evaporation and annealed, iii) by solution/precipitation and iv) in the molten state, and the influence of the blending method in the miscibility has been studied. First of all, thermal properties were characterized by differential scanning calorimeter and the transparency of the films was examined. Additional measurements for evaluating the miscibility were carried out by infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

Taking into account the potential application of these blends for packaging the hydrolytic degradation has been studied for more than a year for the blends prepared by melt processing. In this way the degradation of the blends has been deeply analysed characterizing the molecular weight, thermal properties, water absorption, weight loss, microstructure and macroscopic appearance.

In the future the free volume and transport properties of this system will be studied in order to gain insight into the factors involving the improvement of the permeability of a biodegradable polymer that will help in the search of new systems for packaging applications.

2. Experimental part

2.1. Materials

PBAT was supplied by Basf with an average molecular weight (Mw = 75000 g/mol) and phenoxy resin was supplied by Union Carbide with an average molecular weight (Mw = 50700 g/mol). The relation between adipate/terephthalate units is 53/47 in mole fraction. Chloroform was purchased from Panreac, PRS grade, and n-hexane from Lab-Scan, HPCL grade. All the products were used without further purification. Phosphate buffered saline (pH 7.4) was obtained from Sigma-Aldrich.

2.2. Sample preparation

The blends were prepared by four different methods: i) by casting employing chloroform as a solvent (5 %), ii) by casting and annealed at 200 °C for 15 min, iii) by solution/precipitation using n-hexane as precipitant and iv) by melt processing employing a Model CS-183 MMX mixer operating at 40 rpm at 190 °C.

The blends prepared by melt processing were used to prepare the films for hydrolytic degradation. Films were obtained by hot-pressing in a Graseby Specac device at 190 °C and the thickness was about 200 μm.

2.3. Thermal analysis

Thermal analysis was carried out on a differential scanning calorimeter from TA Instrument, model Q2000 V24. Approximately 5 mg sample were encapsulated in aluminium pans. Two scans were carried out: first from -80 °C to 200 °C to eliminate the thermal history. Then, the sample was cooled to -80 °C at 10 °C/min cooling rate and then another scan was recorded at 10 °C/min heating rate up to 200 °C. In order to analyse the miscibility depending on the preparation method the glass transition temperature was obtained from the first heating scan. Once elucidated the miscibility, for the blends prepared by melt processing the crystallinity of the samples was analysed in the first scan and the glass transition temperature was analysed as usual in the second scan of the thermogram. For the degraded samples, in order to avoid the possible effect of

heating the sample from -80 °C to room temperature, that could change the crystallinity of the sample due to the low T_g, the first scan was carried out starting at 25 °C. For modulated temperature differential scanning calorimetry (MTDSC) the scan was performed from -80 °C to 190 °C at 2 °C/ min heating rate, period of 60 s and amplitude of 0.32 °C.

2.4. Thermal degradation

Thermal degradation was determined by thermal gravimetric analysis employing a TGA Q 500 instrument (TA instruments). Samples of about 3 mg were heated from room temperature to 800 °C at 10 °C/min heating rate under nitrogen flux of 100 mL/min.

2.5. Infrared spectroscopy

Infrared spectroscopic measurements were recorded in a Nicolet model Magna 560 FTIR spectrometer at a resolution of 2 cm^{-1}. Analysed samples were prepared by casting, by casting and annealed at 200 °C for 15 min and by hot-pressing.

2.6. Scanning electron microscopy

The SEM analysis was performed using a Hitachi S-2700 microscope with accelerating voltages of 15 kV. The morphology was observed in the surface of the cross section of the films fractured in liquid nitrogen. A Bio-Rad Microscience Division SC500 sputter Coater was employed for gold sputtering of the samples.

2.7. Hydrolytic degradation

The hydrolytic degradation was carried out with PBAT and blends rich in PBAT (75 PBAT/ 25 PH and 50 PBAT/ 50 PH) that are the most interesting blends from the point of view of the application. The blends prepared by melt processing were used to obtain films for the in vitro degradation study with 8.5 x 8.5 mm size, about 200 μm thickness and 13-17 mg weight (W_0). The samples were placed in Falcon tubes containing 13 mL of solution, maintaining a surface area to volume ratio equal to 0.1 cm^{-1}. The degradation study was carried out in a shaking incubator at 30 rpm and at 60 °C in distilled water or at 37 °C in

phosphate buffer solution. Four samples of each blend were removed at different degradation times from the tubes and weighed (W_w) after wiping the surface with filter paper in order to absorb the surface water. Then the samples were dried at 70 °C and in vacuum for 48 hours and they were weighed (W_d) obtaining the weight loss. Water absorption (% WA) and remaining weight (% RW) were calculated by the equations 1 and 2,

$$\% \, WA = \frac{W_w - W_d}{W_d} \times 100 \tag{1}$$

$$\% \, RW = \frac{W_d}{W_0} \times 100 \tag{2}$$

The apparent degradation rate have been obtained from the exponential relationship between the molecular weight (M_w) and degradation time (t),

$$\ln M_w = \ln M_{w0} - K_{M_w} \times t \tag{3}$$

where M_w is the weight-averaged molecular weight and M_{w0} is the initial weight-averaged molecular weight. The half degradation time $t_{1/2}$ is calculated employing the following expression,

$$t_{1/2} = \ln 2 / K_{M_w} \tag{4}$$

2.8. pH measurements

The pH measurements were performed at 23 °C using a digital pH-meter (Crison pH-meter Basic 20) for the degradation study carried out at 60 °C in distilled water.

2.9. Gel permeation chromatography

The molecular weights of the samples degraded at 60 °C in distilled water were determined by Size Exclusion Chromatography (SEC) using a Waters 717 autosampler with a differential refractometer (Waters 2410), a pump (LC-20A Shimadzu) and three Waters Styragel columns (HR2, HR4 and HR6). The measurements were performed in tetrahydrofuran (THF) at a flow rate of 1 mL/min and 35 °C. The calibration was made employing polystyrene narrow standards (ranging from 580 to 395×10^3 g/mol) to obtain a primary calibration curve.

For the samples degraded at 37 °C in buffered phosphate saline the molecular weights were determined by Size Exclusion Chromatography (SEC, Thermo Scientific), a pump (Dionex Ultimate 3000), refractive index detector (RI, Refracg-to Max 521) and four Phenogel GPC columns (Phnenomenex) with 5 μm particle size and 10^5, 10^3, 100 and 50 A porosities. The measurements were performed in THF at a flow rate of 1 mL/min and 30 °C. The molecular weights were calculated referred to polystyrene standards.

3. Results and discussion

3.1. Influence of the method in the miscibility

3.1.1. Optical properties

Transparency of the samples could be taken as a first macroscopic proof of miscibility. However, it should be considered with caution: the presence of a crystalline phase in miscible mixtures leads to opacity. As opposite case, when both components have similar refraction index, their immiscible blend could appear transparent.

The films obtained from the blends prepared in the molten state are highly transparent in all the compositions (see Figure S1 in supporting information); this is a first indication of the miscibility of the system. The most transparent film is obtained for pure PH and as the PBAT content increases a more translucent film is obtained, probably due to the semicrystalline nature of PBAT. In Figure 1 a) an image of 25 PBAT/75 PH film prepared by melt blending is shown. For the blends prepared by casting the biphasic nature of the blends is clear for 50 PBAT/ 50 PH and 25 PBAT/ 75 PH blends (see Figure S2 in supporting information and Figure 1b). For 75 PBAT/ 25 PH blend opaque films are obtained (see Figure S2). Finally for films prepared by casting and heated up to 200 °C for 15 min all the films became clear (see Figure S3). The samples obtained by solution/precipitation method are white. Moreover, due to the presence of bubbles is not appropriate to use the optical properties as a criterion for miscibility. Anyway, the transparency of the blends is not a sufficient proof of miscibility and it must be characterized by other measurements.
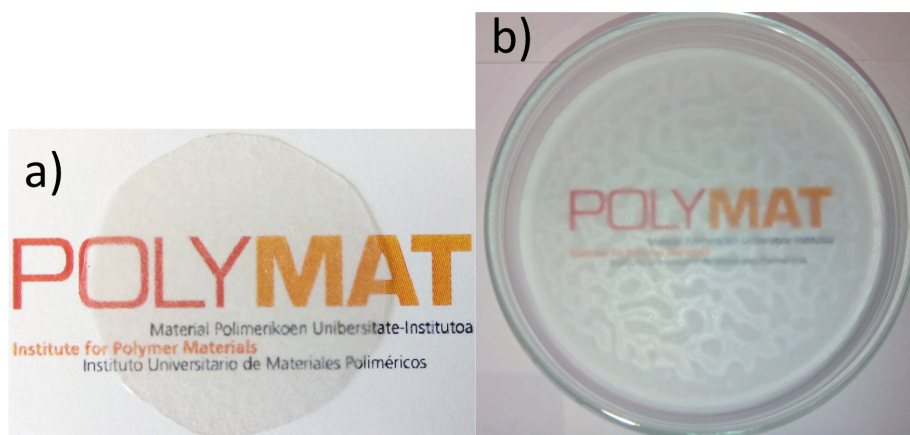
Figure 1. Photographs of 25 PBAT/ 75 PH films for a) blend prepared in the molten state and b) blend prepared by casting.

3.1.2. Thermal analysis

The characterization of the glass transition temperature is the most employed method to determine the miscibility, even though its macroscopic character. Miscible polymer blends will show a single glass transition temperature between those of the pure components. Whereas immiscible blends will show two transitions near of the pure components [5]. In some cases, the blend preparation method could affect the phase behaviour [11-13]. In this sense, PBAT/ PH blends were prepared by casting, casting and annealed, solution/precipitation and melt processing.

Poly(butylene adipate-*co*-terephthalate) shows the glass transition temperature at -27 °C and poly(hydroxy ether of bisphenol A) at 91 °C on the first heating scan. Blends prepared in the molten state show a single glass transition temperature. The values are reported in Table 1, indicating that miscibility is achieved for the studied compositions.

For the blends prepared by casting the thermograms show two glass transition temperatures. The obtained transitions are displaced from those of the pure components, therefore partial miscibility could be supposed. For 75 PBAT/ 25 PH a single transition is observed due to the presence of cold crystallization. These results indicate that phase separation occurs during solvent evaporation due to polymer-solvent interactions that are more favourable for one polymer than for the other, the so-called Δχ effect [7-9].

For the blends prepared by casting and heated up to 200 °C for 15 min a single glass transition temperature is observed. However, we can not state that the

blend is miscible since the second transition could be overlapped with both, the melting enthalpy and cold crystallization, which appear in the same temperature region. For all the blends the thermal treatments favours the phase separation since the glass transition temperatures are nearer from the pure components. Therefore, it indicates that the thermal treatment is not enough to miscibilize the two phases. In order to elucidate the miscibility of the blends prepared by casting and annealed further experiments have been performed employing modulated temperature differential scanning calorimetry (MTDSC). The heat capacity of the blends are shown in Figure S4 in supporting information. As can be seen 25 PBAT/ 75 PH blend shows clearly two transitions, however for the other blends, due to the melting of the crystals the transitions are overlapped, therefore just one transition can be observed.

PBAT/ PH blends were prepared also by solution precipitation process. The blends show glass transition temperatures that are nearer from the T_g-s of the pure components. For 75 PBAT/ 25 PH and 50 PBAT/ 50 PH blends a single glass transition temperature is observed due to the presence of cold crystallization and melting enthalpy. The slight changes observed in the T_g's indicate that the blends are not completely immiscible and partial miscibility is achieved.

In order to calculate the composition of each phase Fox equation has been applied supposing that this equation is valid for partially miscible blends.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{5}$$

Where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} correspond to the glass transition temperatures of neat polymers and w_1 and w_2 are the weight fractions of each polymer.

The composition of each phase is given in Table S1 in supporting information. Anyway, the composition calculated with Fox equation is a qualitative approximation. As mentioned above, most of the blends show just one glass transition temperature, since the second one could be overlapped with cold crystallization or melting enthalpy, therefore just the phase of PBAT can be analysed for all the blends. Focusing on the sample that shows only one T_g, 75 PBAT/ 25 PH, the composition rich in PBAT is practically equal to the overall composition. For the samples where two glass transition temperatures are

observed the phase rich in PBAT has a composition similar to the overall composition while the phase rich in PH has lower quantities of PBAT. Thus, it can be concluded that PBAT has a higher ability to incorporate phenoxy.

To summarize, blends prepared by i) casting, ii) casting and annealed and iii) by solution/ precipitation are partially miscible whereas the blends prepared in the molten state are miscible. The employed solvents lead to solvent induced phase separation, so it can be considered that the blends prepared by casting and solution/precipitation methods are not in an equilibrium state but they can be in a metastable situation. Finally it can be stated that the preparation method, as well as the solvents employed, have a great effect on the miscibility of the system which leads to miscible and partially miscible blends, as it has been reported in other polymer blends [11-13].

Table 1. Glass transition temperatures of PBAT/ PH blends prepared by casting, prepared by casting and annealed at 200 °C for 15 min, prepared by solution/precipitation and by melt processing.

PBAT/PH	T_g (°C) Casting	T_g (°C) Casting and annealed	T_g (°C) Solution/ precipitation	T_g (°C) Melt processing
75/25	-7, *	-4, *	-6, *	-2
50/50	16, 91	5, *	8, *	27
25/75	24, 75	-5, *	9, 91	60

* In this case the second T_g cannot be determined due to the cold crystallization.

Miscibility is achieved for blends prepared in the molten state, therefore the whole composition range has been studied. Table 2 shows the glass transition temperature, T_g, of the blends obtained from the second DSC heating scan and the melting temperature, T_m, the crystallinity of the sample, $X_{c\ sample}$ (%), and the crystallinity referred to PBAT phase, $X_{c\ PBAT}$ (%), obtained from the first scan. For the DSC heating scan see Figure S5 in supporting information.

Table 2. Thermal properties of PBAT/ PH blends.

PBAT/PH	T_g (°C)	T_m (°C)	$X_{c\ sample}$ (%)	$X_{c\ PBAT}$ (%)
100/0	-27	90, 122	14	14
80/20	-8	91, 119	11	14

75/25	-2	87, 120	11	15
60/40	14	92, 115	8	13
50/50	27	92, 115	5	10
40/60	40	102, 118	3	8
25/75	60	-	-	-
20/80	67	-	-	-
0/100	99	-	-	-

The results indicate that PBAT/ PH system is miscible over the entire composition range since a single T_g is reported for all the blends between those of the pure components. As shown in Figure 2 a) the blends exhibit negative deviation from the prediction of the mixture rule. This is usual in blends where the conformational entropy contribution is predominant, due to the weakening of the interactions between the chain segments of the substance with the highest T_g and the segments of the substance with lower T_g [21].
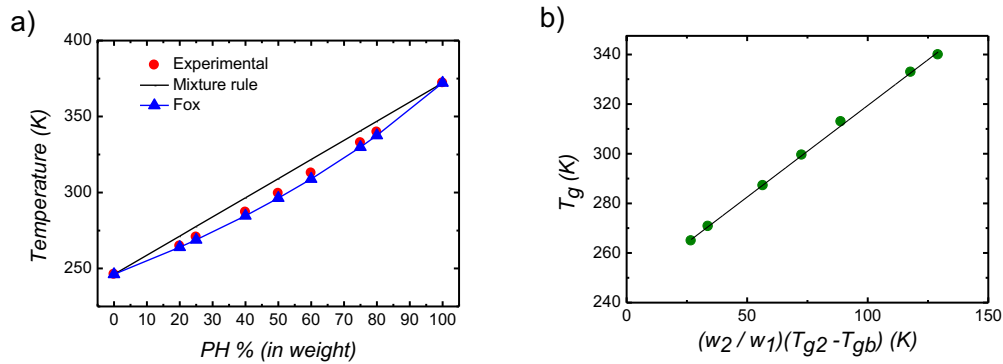

Figure 2. a) T_g vs composition for different PBAT/ PH blends and b) the determination of Gordon-Taylor parameter.

There are several equations to predict the composition dependence of the T_g for miscible polymer blends: mixture rule, Fox (see equation 5) and Gordon-Taylor which is given by [5]:

$$T_g = T_{g1} + K\frac{w_2}{w_1}\left(T_{g2} - T_g\right) \tag{6}$$

where K is the Gordon-Taylor parameter.

In Figure 2 a) it can be seen that the experimental data is well fitted to Fox rule. In Figure 2 b) it can be observed that the Gordon-Taylor equation describes well the experimental glass transition temperature behaviour of the blends. From the slope K parameter, Gordon-Taylor parameter, is obtained: 0.74. For the same blend Su et al. [20] obtained a lower value for K parameter: 0.6. Belorgey and Prud´homme suggested that K parameter could be considered as a semiquantitative measure of the strength of the interaction between the components of the blend [22]. For blends with stronger interactions higher values of K are obtained, for example for poly(butylene terephthalate)/phenoxy Eguiazabal et al. [23] reported a value of 0.47. In this case a value of 0.74 would indicate stronger interactions.

The crystallinity of the samples is shown in Table 2 for the blends prepared in the molten state. Two melting endotherms are observed for neat PBAT at 90 °C and 122 °C, which is the melting endotherm corresponding to poly(butylene terephthalate) (PBT) sequence. In literature neat PBT also presents multiple melting endothermic peaks corresponding to two crystalline structures: α and β form, which undergo melting-recrystallization process during heating [24]. In the range of 40-62 °C another endothermic peak is observed, see Figure S4 in supporting information, corresponding to adipate sequences. In literature poly(butylene adipate) homopolymer presents also multiple melting endotherm attributed again to the crystalline reorganization during heating [25]. This last endotherm is very small comparing to the PBT endotherm and therefore is considered for the calculation of the crystallinity of the sample but its melting temperature is not given in the table. In order to calculate crystallinity $\Delta H_m^0 = 142 \, J/g$ is considered [26] for PBT and $\Delta H_m^0 = 135 \, J/g$ is considered [25] for PBA sequence.

The crystallinity degree of pure PBAT is 14 % (20.5 J/g) and the melting temperature 90 °C and 122 °C, both values are within the typical range for this polymer [27]. The addition of phenoxy decreases slightly the melting temperature range of the blends since less ordered crystals are formed, which is the usual behaviour in miscible blends [28]. Furthermore 50 PBAT/ 50 PH blend shows two melting endotherms located at 92 °C and 114 °C.

Increasing phenoxy content the crystallinity degree referred to PBAT component decreases over the composition range. The data show that the second component hinders the crystallization of PBAT, this is also a usual behaviour for miscible blends [28].

3.1.3. FTIR analysis

FTIR spectroscopy is a powerful technique to analyse the miscibility of polymer blends in which the miscibility is driven by specific interactions such as hydrogen bonds [29]. In literature the miscibility of phenoxy with different polymer families have been widely studied [30, 31]. In this blend hydrogen bonds are expected between carboxyl groups of PBAT and hydroxyl groups of phenoxy.

Figure 3 a) shows the carbonyl-stretching band of PBAT/ PH blends prepared by casting. Pure PBAT shows a broad band at about 1709 cm^{-1} and a shoulder at about 1731 cm^{-1}, corresponding to the carbonyl-stretching band of amorphous and crystalline phases (see table S2 for the carbonyl stretching band wavenumber values). All blends show similar trend compared to pure polymer, therefore miscibility is not achieved.
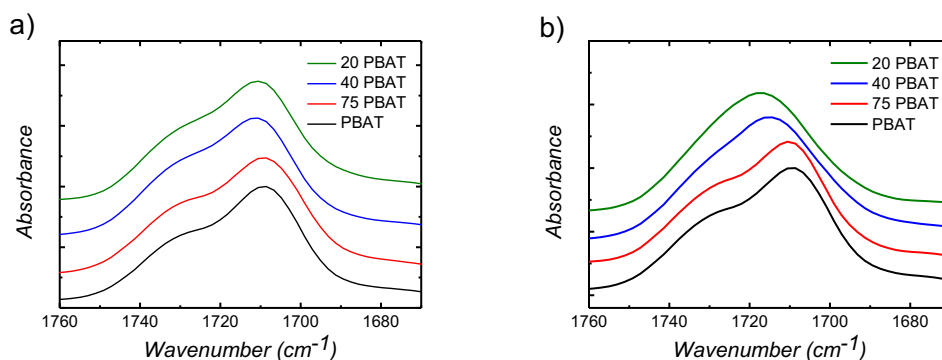

Figure 3. Carbonyl stretching region for PBAT/ PH blends a) prepared by casting and b) prepared in the molten state.

The infrared spectra in the carbonyl stretching region of the blends prepared in the molten state are shown in the Figure 3 b). As in the case of the samples prepared by casting, all the blends show two carbonyl contributions. Nonetheless and, contrary to what happens in the samples prepared by casting, in the blends prepared by melting, the peak at lower wavenumber shifts to higher frequencies when increasing the PH content of the blend. Similar

behaviour has been observed in PVC/PBAT miscible blends where C=O band of pure PBAT at 1714 cm^{-1} shifts to 1718 cm^{-1} in the blends [32]. Hexig et al. [33] studied the infrared spectra of miscible blends of PBAT and a phenolic compound. They found that the blends, in addition to the bands assigned to amorphous and crystalline carbonyl stretching, presented a new band attributed to the carbonyls linked by hydrogen bond with the phenolic hydroxyls. This new band, whose frequency is lower than that of the bands attributed to amorphous and crystalline carbonyls was related to the blend miscibility. Taking in mind this argument, the infrared shift we have observed in the samples prepared by melting is indicative of the blend miscibility. Thus, it can be argued that the miscible blends must contain a new band related to the hydrogen bonding association. In our case, as the hydroxyl is aliphatic, the hydrogen bond is weaker than the reported by Hexig et al. and therefore the new band appears at higher wavenumbers, very close to the band assigned to crystalline carbonyls. This new band is in the origin of the shift observed in the samples obtained by melting, that are miscible. However, the carbonyl of the samples obtained by casting do not show any change which means that these blends are not miscible.

For blends prepared by casting and annealed at 200 °C for 15 min (Figure 4), a slight shift is observed in the lower frequency carbonyl stretching. However, this shift does not depend on blend composition. DSC results have proven that the annealing treatment is not enough to miscibilize the phase separated samples. Nevertheless, infrared results show that the annealing has some effect on the phase behaviour as a change in the carbonyl stretching frequency is observed, although this change is not composition dependent. Therefore, it can be concluded that the annealing treatment imparts partial miscibility to the blend but is not enough to get total miscibility.
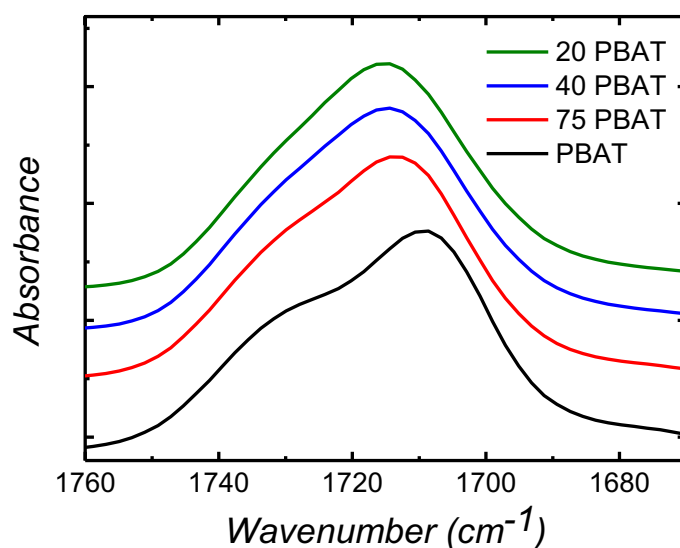
Figure 4. Carbonyl stretching region for PBAT/ PH blends prepared by casting and heated up to 200 °C for 15 min.

3.1.4. Morphological characterization

The morphology of the cryofractured surfaces was analysed by scanning electron microscopy. In Figure 5 a) the morphology of 50 PBAT/ 50 PH blend prepared by casting can be observed: it shows a cocontinuous morphology. This kind of morphology has been attributed to phase inversion composition. In the Figure 5 b) the morphology of 25 PBAT/ 75 PH is shown and exhibits a biphasic structure, being the adhesion between two components very good, however miscibility is not achieved. In the case of 75 PBAT/ 25 PH blend the micrograph does not show a biphasic structure (micrograph not shown). However, taking into account the previous results we cannot conclude that the blend is miscible. In our opinion, the poor contrast between both phases could explain why the phase separation is not observed.

On the other hand, for blends prepared in the molten state (micrographs not shown) a homogeneous and monophasic phase is observed.
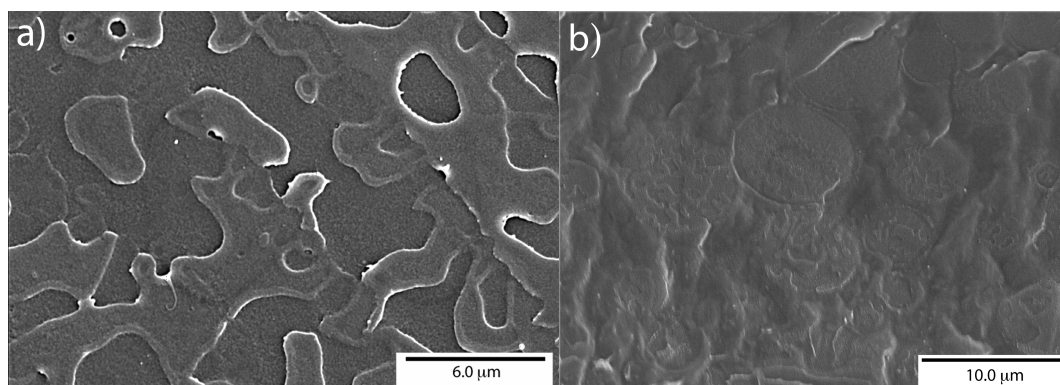
Figure 5. SEM micropraphs of cryofractured surfaces of a) 50 PBAT/ 50 PH prepared by casting and b) 25 PBAT/ 75 PH prepared by casting.

3.2. Hydrolytic degradation study

3.2.1. Water absorption and weight loss

In Figure 6 a) and b) the results obtained for water absorption and weight loss for PBAT/ PH blends, prepared in the molten state, degraded in distilled water at 60 °C are shown. As can be seen the samples absorb water from the first 21 days of degradation. However, the absorption is very low for all the samples, without reaching the 3 %. At 174 days the water absorption increases slightly for all the samples. 50 PBAT/ 50 PH is the blend that absorbs more water at early stages, it has to be considered that this blend is amorphous before degradation and although it crystalizes over degradation the crystallinity level is low. Since the polymer chains are less packed in amorphous regions than in crystallines ones, the water can penetrate more easily and this leads to an increase in water absorption. At 342 days PBAT shows an unexpected increase in the water absorption, however this result has to be considered carefully due to the high standard deviation. This great increase in the water absorption results from the lower glass transition temperature and the possible presence of new functional groups or more hydrophilic character.

Concerning the weight loss of the samples, a little change is observed during the first 90 days where the remaining weight is higher than 90 %. From that moment a huge decrease in the remaining weight is observed, especially for PBAT. The degradation rate decreases with phenoxy content being the weight loss of about 50 % for PBAT, 35 % for 75 PBAT/ 25 PH and 20 % for 50 PBAT/

16

50 PH after 405 days.

In this case the crystallinity of the samples does not play an important role in the degradation, since the water absorption increases considerably even though the crystallinity rises, and both the lower glass transition temperature of PBAT and the less packed chains increase the water absorption and the loss of weight.
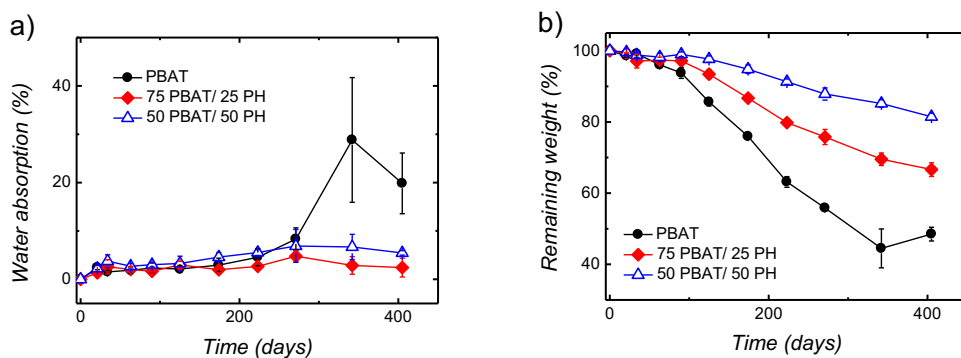

Figure 6. Evolution of a) the water absorption and b) remaining weight over degradation for PBAT and PBAT/ PH blends.

pH measurements

The pH of the samples was measured over degradation time, the values obtained are shown in Figure 7. Before the degradation the distilled water has a pH value of 6.25. For all the blends the pH decreases considerably over degradation. The behaviour of the pH is similar to that obtained for the molecular weight, which will be shown later, and indicates that water soluble oligomers and monomers are being released. After 190 days of degradation, the decrease of the pH is less pronounced since the rate of the weight loss and molecular weight is decreased. The greatest pH decrease is found for PBAT and as the content of phenoxy increases the pH change is less pronounced.
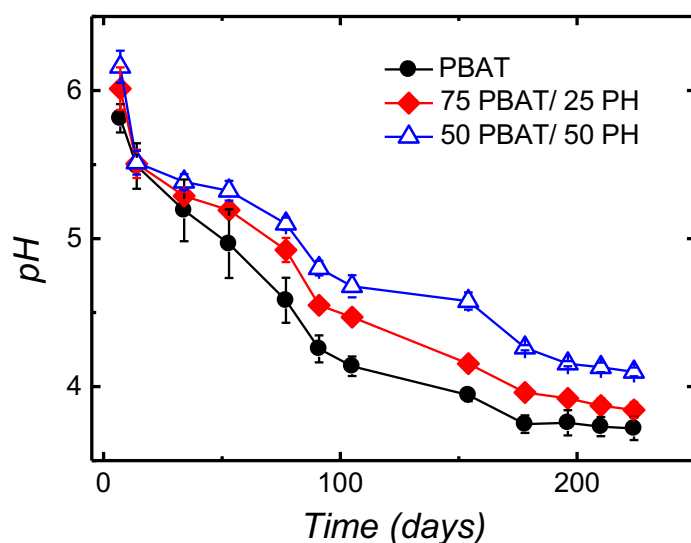
Figure 7. pH measurements of the degrading medium over time.

3.2.2. Thermal analysis

Table 3 shows the thermal properties obtained for PBAT and PBAT/ PH blends over degradation, for DSC heating thermograms see Figure S6 in supporting information. The glass transition temperature of the samples decreases over degradation on the first months, especially in the case of PBAT (see Figure 8). However, after 90 days approximately, the glass transition temperature starts to increase (thermogram not shown in Figure S6).

Glass transition temperature decreases initially due to a lower molecular weight over degradation that leads to an easier chain mobility. After that, it rises considerably and this is mainly due to two effects: regarding PBAT the degradation occurs preferentially in adipate units (this will be discussed later based on NMR measurements) becoming the remaining copolymers richer on terephthalate, therefore, the T_g raises. On the other hand, the disappearance of the adipate units facilitates the crystallization of terephthalate units leading to the increase of the crystallinity degree, and this hinders the mobility of the polymer chains [34].

18

Table 3. Evolution of the thermal properties of PBAT and PBAT/ PH blends over degradation.

|	Time (days)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PBAT	0	-28	120	24
	21	-31	124	26
	34	-33	125	29
	63	-34	126	29
	90	-33	103, 128	32
	125	-32	103, 131	35
	174	-31	106, 142	42
	223	-23	110, 143	46
	271	-13	112, 152	57
	342	-6	121, 152	54
	405	-13	119, 153	57
75 PBAT	0	-4	119	13
	21	-3	121	18
	34	-3	125	14
	63	-5	128	20
	90	-6	107, 128	20
	125	-5	106, 131	21
	174	-6	106, 139	21
	223	-2	110, 143	24
	271	28	106, 152	29
	342	30	115, 148	26
	405	31	119, 150	30
50 PBAT	0	27	-	-
	21	26	91, 113	10
	34	26	93, 112	10
	63	25	90, 115	11
	90	24	92, 111, 131	11
	125	25	92, 111, 134	11
	174	26	89, 112, 142	14
	223	30	95, 115, 142	11
	271	33	117, 143	11
	342	38	117, 144	10
	405	43	123, 148	12
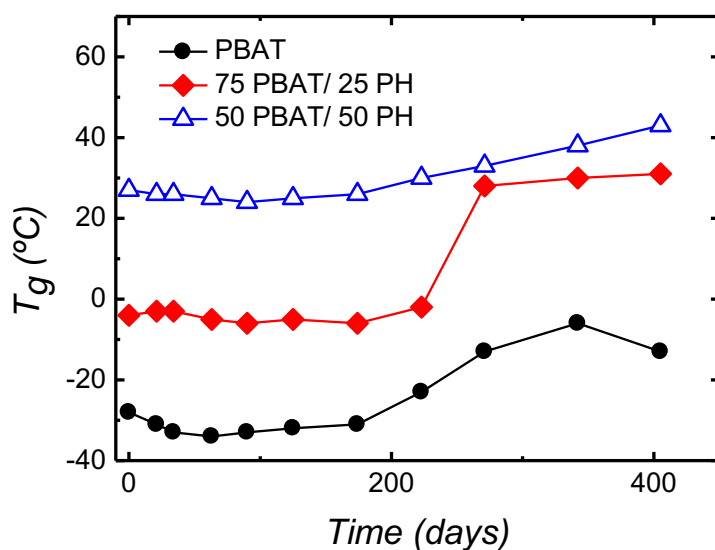
Figure 8. Glass transition temperature of PBAT and PBAT/ PH blends over degradation.

Regarding the melting temperature of PBAT and 75 PBAT/ 25 PH it increased over degradation and at day 90 it splits into two peaks (thermogram not shown in Figure S6). The melting enthalpy also rises considerably. The increase is more noticeably in neat PBAT and 75 PBAT/ 25 PH that without degradation show a melting enthalpy of 23.6 J/g and it increases to 57.0 J/g and for the blend the melting enthalpy increases from 12.7 J/g to 30.0 J/g, respectively. For 50 PBAT/ 50 PH blend two melting peaks can be observed in Figure S6. The melting temperatures decrease slightly over degradation until 223 day when it starts to increase. No great changes are observed in the melting enthalpy that is maintained practically constant.

The melting peak increases over degradation (see Figure 9), this may arise due to the lower molecular weight of the chains which have increased mobility that could provoke the thickening of the crystals [35]. In relation to the split of the melting endotherm into two peaks it could be due to the appearance of polymorphisms. In this sense, poly(butylene terephthalate) homopolymer presents also multiple melting endothermic peaks corresponding to two crystalline structures: α and β form, which undergo melting-recrystallization process during heating [24]. The melting enthalpy increases since the degradation occurs preferentially in the amorphous region at the first stage. Furthermore, since the samples are at 60 °C, they are above their T_g and

therefore the chains have enough mobility to crystallize. The different behaviour of 50 PBAT/ 50 PH blend on the crystallinity compared to the other two samples can be due to the composition of the blend, since this blend is richer in PH the crystallization of PBAT could be more hindered.
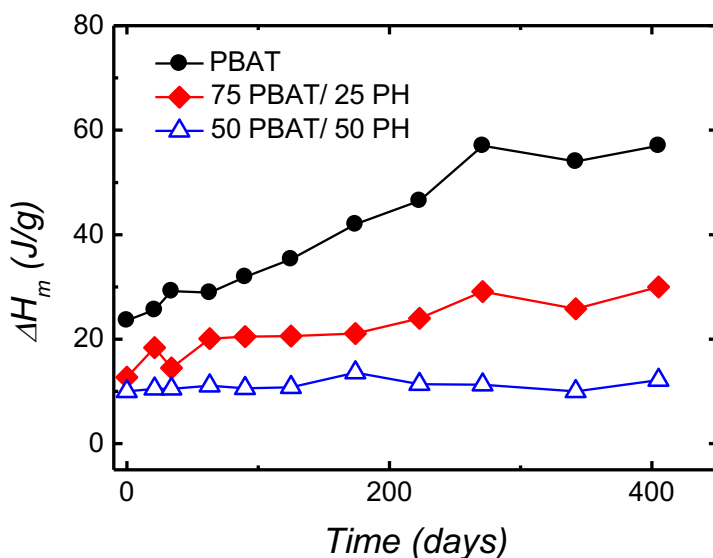

Figure 9. Melting fusion enthalpy of PBAT and PBAT/ PH blends over degradation.

3.2.3. Thermogravimetric analysis

The thermal stability of the blends over degradation is shown in Table 4, for the thermogravimetric graphs see Figure S7 in supporting information. The thermal stability of neat PBAT is decreased over degradation, especially after 405 days. On the other hand, the blends degraded for 405 days start to degrade later than the samples degraded for 174 days. This effect could arise from the fact that the blends degraded for 405 days are richer in PH, as it will be analysed in the next section, which has a higher thermal stability.

Table 4. Thermodegradation temperatures for PBAT/ PH blends at different degradation times.

Time (days)	PBAT $T_{5\%}$ (°C)	75 PBAT $T_{5\%}$ (°C)	50 PBAT $T_{5\%}$ (°C)
0	331.4	324.8	351.4
174	328.9	277.6	329.4
405	293.6	315.4	333.2

3.2.4. Nuclear magnetic resonance

Taking into account the non-degradable character of phenoxy it is interesting to analyse the composition of the blends over degradation since it is possible that PBAT will degrade faster and the composition of the blends will be richer in phenoxy. Furthermore PBAT, being a copolymer, can also suffer drastic changes in its composition since terephthalate and adipate sequences will be degrading with different rates.

In Figure S8 (see supporting information) the ^{1}H NMR spectrum of 75 PBAT / 25 PH at 0 and 405 days are shown. The aromatic protons corresponding to terephthalate sequence appear at 8.13 ppm and the aromatic protons of phenoxy at 7.13 and 6.85 ppm. The signals at 4.47, 4.41, 4.18 and 4.13 ppm correspond to butanediol sequences: TBT, TBA, ABT and ABA, respectively. At 2.36 ppm appears the signal corresponding to the methylenes of adipate.

In Table 5 the PBAT molar fraction change in the blends, (Δf_{PBAT}), and the fraction of terephthalate respect to adipate, (f_T), are shown that are calculated according to equation 7 and 8, respectively, where f_{PBAT} and f_{PH} are the molar fractions of PBAT and PH and A_T and A_A are the areas of terephthalate and adipate sequences. For the calculations the following signals of the NMR sprectrum were used: f_{PBAT} signal at 8.13 and at 2.36 ppm and for f_{PH} signals at 7.13 and 6.85 ppm. For A_T the signal at 8.13 ppm and for A_A the signal at 2.36 ppm. As can be observed the changes in PBAT/ PH composition are small for 174 days. However, after 405 days PBAT has degraded faster than PH and the remaining blends are clearly richer in PH.

$$\Delta f_{PBAT} = \frac{f_{PBAT}}{f_{PBAT}+f_{PH}} \tag{7}$$

$$f_T = \frac{A_T}{A_T+A_A} \tag{8}$$

Regarding the degradation of PBAT in PBAT/ PH blends it is clear that adipate units are more prone to degradation than terephthalate units that contain aromatic rings, which leads to a considerable change in composition and perhaps in other properties. This raises the glass transition temperature, as mentioned previously, since PBT shows a lower chain mobility being its T_g higher than the T_g of PBA as well as the crystallinity.

Table 5. The change of PBAT composition respect PH, Δf_PBAT, and PBT % composition respect PBA, f_T, over degradation study.

	Time (days)	Δf_{PBAT}	f_T
75 PBAT	0	0	0.49
	174	-0.052	0.54
	405	-0.204	0.68
50 PBAT	0	0	0.49
	174	0.008	0.51
	405	-0.178	0.61

The parameters of PBAT microstructure over degradation study are shown in Table 6, where f_A and f_T are adipate and terephthalate mole fractions, respectively. P_{TA} and P_{AT} are the probability to find a terephthalate unit in AB sequence and the probability to find an adipate unit next to TB sequence (equations 9 and 11 respectively). And finally L_T and L_A are the number average sequence length of terephthalate and adipate blocks and η is the random character of the copolymer (equations 10, 12 and 13) [36].

$$P_{AT} = \frac{f_{AT}}{f_A} \quad (9) \quad L_{nA} = \frac{1}{P_{AT}} \quad (10) \quad P_{TA} = \frac{f_{TA}}{f_A} \quad (11) \quad L_{nT} = \frac{1}{P_{TA}} \quad (12)$$

$$\eta = \frac{(f_{AT}+f_{TA})}{2(f_A)(f_T)} \quad (13)$$

Table 6. PBAT microstructure parameters over degradation study.

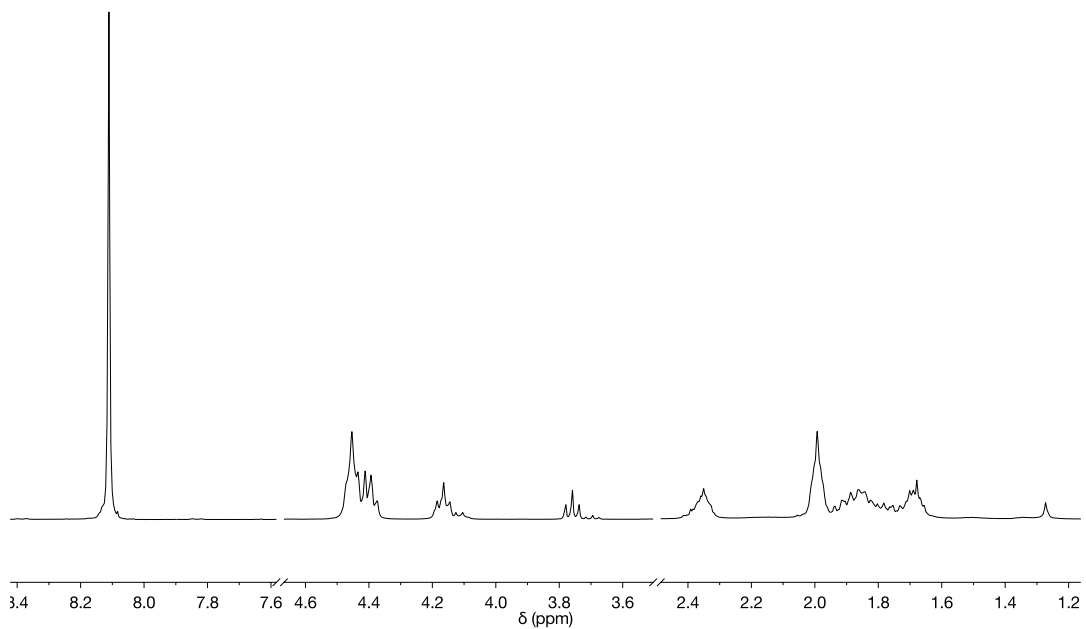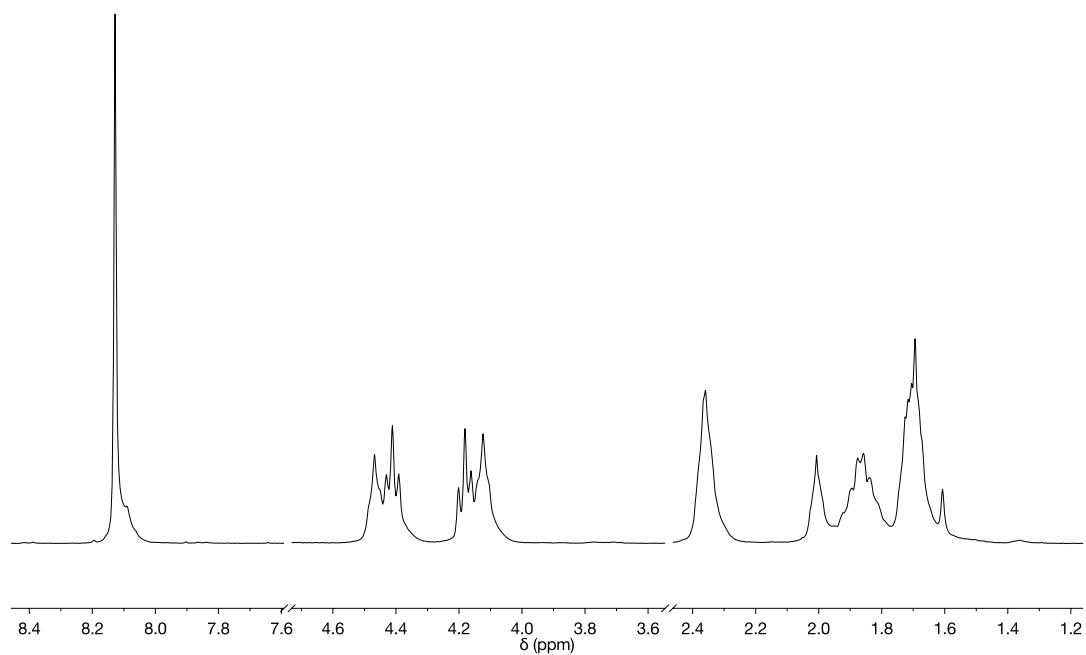| Days	f_A	f_T	P_{TA}	P_{AT}	L_T	L_A	η
0	0.53	0.47	0.60	0.43	1.67	2.32	1.02
174	0.43	0.57	0.47	0.64	2.13	1.56	1.09
405	0.26	0.74	0.36	0.83	2.78	1.21	2.01

Figure 10.¹H NMR spectrum of a) PBAT before the degradation and b) PBAT after 405 days of degradation.

As can be seen in Figure 10 adipate units are more prone to degradation than terephthalate units, leading to a great increase of terephthalate composition

by the end of the degradation study. The length of terephthalate blocks increases over degradation and the length of adipate block decreases, which is in accordance with the changes observed in composition. The same result has been obtained by Herrera et al. [27]. The character of the copolymer changes from random to alternating copolymer over degradation, this behaviour can be attributed to the disappearance of adipate sequences, that are more prone to degradation, and the remaining adipate units will be isolated between terephthalate sequences. Neat PBAT and PBAT/ PH blends that have been degraded show small peaks centred at 3.69 and 3.76 ppm, related to CH_2OH groups in butanediol units next to adipate and terephthalate units, respectively [27]. However, for the blends it is not possible to analyse deeply the microstructure due to signal overlaps between PBAT and PH but a similar behaviour would be expected, see Figure S7 in supporting information.

3.2.5. Optical analysis of the remnants

In Figure 11 the pictures of the samples at different degradation times are shown. As can be seen all the samples undergo changes in colour and in shape. The blends become yellowish, opaque and brittle as the degradation occurs. The samples start also to bend and the size is reduced considerably.

PBAT is the sample with the highest change in colour and size, the reduction of the area is of 42 % after 405 days of degradation. 75 PBAT/ 25 PH blend takes a yellowish colour and a slight reduction of the size is observed, 32 %. It also shows a major fragility although it maintains its original shape. For 50 PBAT/ 50 PH blend the changes in colour are also noticeably although the fragility and size reduction, 20 %, is less pronounced.
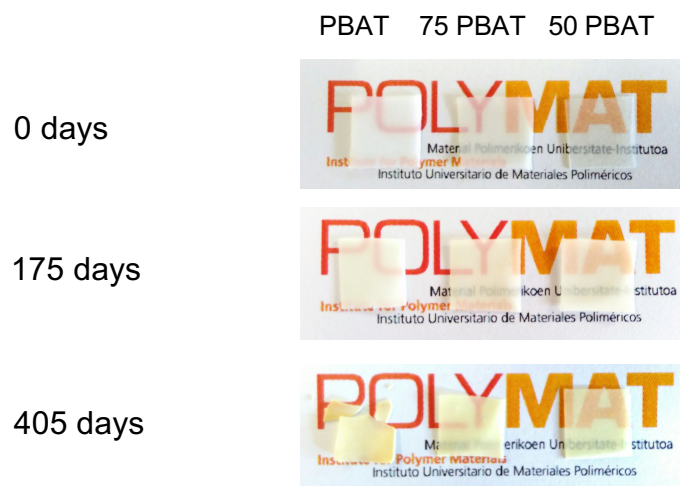
PBAT   75 PBAT   50 PBAT

0 days

175 days

405 days

Figure 11. PBAT, 75 PBAT/ 25 PH and 50 PBAT/ 50 PH blends at 0, 174 and 405 days of degradation at 60 °C in distilled water.

3.2.6. Molecular weight

In previous sections it has been shown that over degradation the samples loss weight and absorb water. The glass transition temperature decreases at early stages due to higher chain mobility, although for longer times it increases due to changes on composition, and the crystallinity also rises. Finally, in the optical properties it have been seen that samples become more brittle over degradation. The obtained results clearly indicate that the molecular weight of the samples decreases as degradation occurs, therefore it is essential to measure the molecular weight of PBAT and PBAT/ PH blends. In Figure 12 the molecular weight progress versus degradation time is shown. The molecular weight decreases over degradation and the dispersity of the samples increases indicating a broader distribution of the polymer chain length (see Figures S9, S10 and S11 in supporting information). After 90 days the chromatograms for PBAT/ PH blends show two peaks (see Figures S10 and S11 in supporting information) therefore the molecular weight for those blends have been calculated by deconvolution employing Origin Software 8.0. For 75 PBAT/ 25 PH when the peak starts to split into two peaks the deconvolution is complicated leading to nonsense values for PH fraction, therefore for 90 and 125 days this points are not shown. In Figure 12 the molecular weight of PBAT fraction is shown, for the fraction of PH see Figure S12 in supporting information. The reduction of the molecular weight provokes a major mobility of the chains and a

reduction on the entanglements which leads to a reduced glass transition temperature at early stages of the degradation that is corroborated by DSC measurements. At early stages the molecular weight of the PBAT fraction decreases considerably, but after 125 days the slope changes being the reduction of the molecular weight less pronounced which indicates that the degradation mechanism is changing from that in which the random scission plays a major role to another mechanism that is controlled by chain end scission [37]. For PH fraction a similar behaviour is observed (see Figure S12 in supporting information), in this case the decrease of the molecular weight is slower but by the end of the study the reduction of the molecular weight is about 50 %.
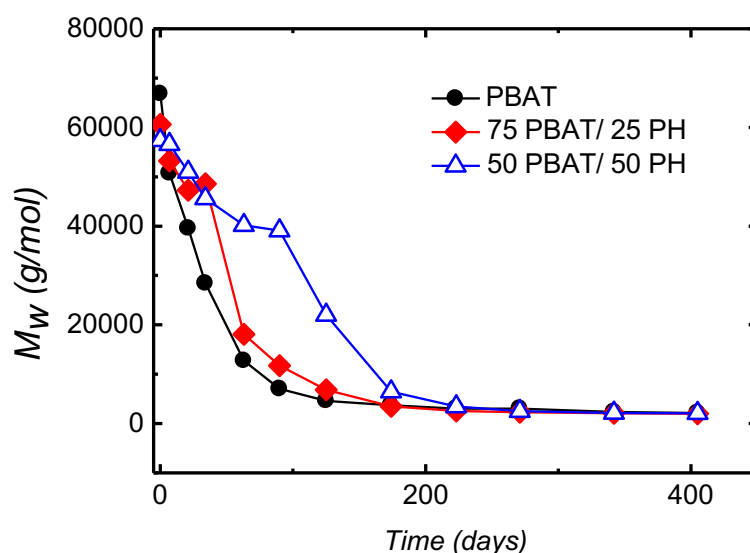

Figure 12. Molecular weight of PBAT and PBAT fraction of PBAT/ PH blends over hydrolytic degradation at 60 °C in distilled water.

In order to compare the degradation rate with other polymers studied in literature the degradation was carried out at 37 °C in phosphate buffered solution. The values of the molecular weight are in Table S3 in supporting information and the parameters obtained are shown in Table 7. The addition of phenoxy reduces the apparent degradation rate of PBAT and increases the half degradation time. However, the degradation rate of the blends are high comparing to other biodegradable polymers such as polycaprolactone (K_{MW} = 0.0010 days^{-1}) which has a very low apparent degradation rate and some lactide caprolactone copolymers, among others [38]. Furthermore, 75 PBAT/ 25 PH

blend has an apparent degradation rate similar to polylactide [39] with K_{MW} = 0.0112 days^{-1}.

Table 7. Apparent degradation rate and half degradation time values for PBAT/ PH blends degraded at 37 °C in phosphate buffered saline.

PBAT/ PH	K_{Mw} (day^{-1})	$t_{1/2}$ (days)
100/ 0	0.0221	31
75/ 25	0.0099	70
50/ 50	0.0039	178

Conclusions

The influence of the blending method on the miscibility of poly(butylene adipate-*co*-terephthalate)/phenoxy system has been clarified. For blends prepared in the molten state differential scanning calorimetry results show that miscibility is achieved, whereas for blends prepared by casting and solution/precipitation process partially miscible or immiscible blends are obtained, even an annealing process was applied without reaching the miscibility. These results are corroborated by FTIR measurements and scanning electron microscopy micrographs. For the blends prepared by casting and annealed DSC measurements show that partially miscible blends are obtained whereas FTIR measurements indicate that miscibility is achieved since it has a lower sensitivity.

Regarding the hydrolytic degradation of the blends prepared by melt processing it has been shown that water absorption and the weight loss are higher in blends rich in PBAT. Thermal analysis shows that the glass transition temperature decreases on the first months whereas it increases for longer periods. Regarding the melting temperature and crystallinity they increase due to different factors. NMR measurements indicate that PBAT becomes richer in terephthalate since adipate units are more prone to degradation and in the blends it is shown that the degradation of phenoxy is slower than PBAT. The deconvolution of chromatograms was carried out observing that the molecular weight decreases considerably for both, PBAT and PH fraction. Finally, the

28

degradation rate of PBAT/ PH blends is higher or similar to other biodegradable polymers, therefore depending on the final application an adequate composition can be selected that fulfils the final requirements.

Bibliography

[1] V. Siracusa, P. Rocculi, S. Romani, M.D. Rosa, Biodegradable polymers for food packaging: a review, Trends Food Sci. Technol. 19 (2008) 634-643.

[2] K. Madhavan Nampoothiri, N.R. Nair, R.P. John, An overview of the recent developments in polylactide (PLA) research, Bioresour. Technol. 101 (2010) 8493-501.

[3] R. Auras, B. Harte, S. Selke, An overview of polylactides as packaging materials, Macromol. Biosci. 4 (2004) 835-64.

[4] I. Vroman, L. Tighzert, Biodegradable polymers, Materials 2 (2009) 307-344.

[5] O. Olabisi, L.M. Robeson, M.T. Shaw, Polymer-polymer miscibility, Academic Press, New York, 1979.

[6] D.R. Paul, S. Newman, Polymer blends, Academic Press, New York, 1978.

[7] M. Bank, J. Leffingwell, C. Thies, The influence of solvent upon the compatibility of polystyrene and poly(vinyl methyl ether), Macromolecules 4 (1971) 43-46.

[8] L. Zeman, D. Patterson, Effect of the solvent on polymer incompatibility in solution, Macromolecules 5 (1972) 513-516.

[9] L.W. Kelts, C.J.T. Landry, D.M. Teegarden, Two-dimensional NMR of synthetic polymers: polymer blend miscibility at the molecular level, Macromolecules 26 (1993) 2941-2949.

[10] W.B. Liau, C.F. Chang, Casting solvent effect on crystallization behavior and morphology of poly(ethylene oxide)/poly(methyl methacrylate), J. Appl. Polym. Sci. 76 (2000) 1627-1636.

[11] M. Alberdi, E. Espi, M.J. Fernandez-Berridi, J.J. Iruin, Influence of the blending method and poly(methyl methacrylate) tacticity in its miscibility with poly(hydroxy ether of bisphenol A, phenoxy), Polym. J. 26 (1994) 1037-1046.

[12] A. Etxeberria, S. Guezala, J.J. Iruin, J.G. De la Campa, J. De Abajo, Blends of poly(ether imide) and an aromatic poly(ether amide): Phase Behavior and CO_2 Transport Properties, J. Appl. Polym. Sci. 68 (1998) 2141-2149.

[13] A. Etxeberria, J.J. Iruin, A. Unanue, P.J. Iriondo, M.J. Fernandez-Berridi, A. Martinez de Ilarduya, Miscibility windows of poly(vinyl methyl ether) with modified phenoxy resin, Eur. Polym. J. 37 (2001) 1943-1950.

[14] L.M. Robeson, W.F. Hale, C.N. Merriam, Miscibility of the poly(hydroxy ether) of bisphenol A with water-soluble polyethers, Macromolecules 14 (1981) 1644-1650.

[15] J.E. Harris, S.H. Goh, D.R. Paul, J.W. Barlow, Miscible binary blends containing the polyhydroxy ether of bisphenol-a and various aliphatic polyesters, J. Appl. Polym. Sci. 27 (1982) 839-855.

[16] C. Uriarte, J.I. Eguiazábal, M. Llanos, J.I. Iribarren, J.J. Iruin, Miscibility and phase separation in poly(vinyl methyl ether)/poly(bisphenol A hydroxy ether) blends, Macromolecules 20 (1987) 3038-3042.

[17] J.I. Eguiazábal, J.J. Iruin, M. Cortazar, G.M. Guzmán, Glass transition temperature in blends of poly(N-vinyl-2-pyrrolidone) with a copolymer of bisphenol A and epichlorohydrin or with poly(vinyl butyral), Macromol. Chem. Phys.185 (1984) 1761-1766.

[18] H. Saito, D. Tsutsumi, T. Inoue, Temperature dependence of the Flory interaction parameter in a single-phase mixture of poly(hydroxy ether of bisphenol A) and poly(ether sulfone), Polym. J. 22 (1990) 128-134.

[19] L.M. Robeson, B. Furtek, Miscible blends of poly(butylene terephthalate) and the polyhydroxyether of bisphenol A, J. Appl. Polym. Sci. 23 (1979) 645-659.

[20] C.C. Su, S.C. Wang, W.J. Chen, L.T. Lee, Phase compatibilization through chemical exchange reactions in blends of copolyesters with poly(hydroxyether of bisphenol A) upon annealing, Ind. Eng. Chem. Res. 52 (2013) 12587-12595.

[21] I.M. Kalogeras, W. Brostow, Glass transition temperatures in binary polymer blends, J. Polym. Sci. Pol. Phys. 47 (2009) 80-95.

[22] G. Bélorgey, R.E. Prud´Homme, Miscibility of polycaprolactone/chlorinated polyethylene blends, J. Polym. Sci. Pol. Phys. 20 (1982) 191-203.

[23] J.I. Eguiazábal, J.J. Iruin, M. Cortazar, G.M. Guzmán, Ternary polymer mixtures: polyarylate/ phenoxy/ poly(butylene terephthalate), J. Appl. Polym. Sci. 32 (1986) 5945-5955.

[24] C.C. Huang, F.C. Chang, Reactive compatibilization of polymer blends of poly(butylene terephthalate) (PBT) and polyamide-6,6 (PA66): 1. Rheological and thermal properties, Polymer 38 (1997) 2135-2141.

[25] M.S. Nikolic, J. Djonlagic, Synthesis and characterization of biodegradable poly(butylene succinate-*co*-butylene adipate)s, Polym. Degrad. Stab. 74 (2001) 263-270.

[26] G. Pompe, L. Häubler, W. Winter, Investigations of the equilibrium melting temperature in PBT and PC/PBT Blends, J. Polym. Sci. Pol. Phys. 34 (1996) 211-219.

[27] R. Herrera, L. Franco, A. Rodríguez-Galán, J. Puiggalí, Characterization and degradation behavior of poly(butylene adipate-*co*-terephthalate)s, J. Polym. Sci. Pol. Chem. 40 (2002) 4141-4157.

[28] Z. Qiu, C. Yan, J. Lu, W. Yang, Miscible crystalline/crystalline polymer blends of poly(vinylidene fluoride) and poly(butylene succinate-*co*-butylene adipate): spherulitic morphologies and crystallization kinetics, Macromolecules 40 (2007) 5047-5053.

[29] M.M. Coleman, P.C. Painter, J.F. Graf, Specific Interactions and the Miscibility of Polymer Blends, CRC Press, Lancaster, 1995.

[30] E. Espi, J.J. Iruin, An attempt to predict phenoxy resin miscibility using a group contribution method, Macromolecules 24 (1991) 6458-6463.

[31] A. Sangroniz, A. Chaos, Y.M. Garcia, J. Fernández, M. Iriarte, A. Etxeberria, Improving the barrier character of polylactide/phenoxy immiscible blend using poly(lactide-*co*-ε-caprolactone) block copolymer as a compatibilizer, J. Appl. Polym. Sci. 134 (2017) 45396.

[32] N.A. Ibrahim, N.M. Rahim, W.Z. Wan Yunus, J. Sharif, A study of poly vinyl chloride / poly(butylene adipate-*co*-terephthalate) blends, J. Polym. Res. 18 (2010) 891-896.

[33] B. Hexig, Y. He, N. Asakawa, Y. Inoue, Diphenol miscibility effect on the immiscible polyester/polyether binary blends through intermolecular hydrogen-bonding interaction, J. Polym. Sci. Pol. Phys. 42 (2004) 2971-2982.

[34] J. Fernández, A. Larrañaga, A. Etxeberria, J.R. Sarasua, Effects of chain microstructures and derived crystallization capability on hydrolytic degradation of poly(l-lactide/ε-caprolactone) copolymers, Polym. Degrad. Stab. 98 (2013) 481-489.

[35] H. Tsuji, A. Mizuno, Y. Ikada, Properties and morphology of poly(L-lactide). III. Effects of initial crystallinity on long-term in vitro hydrolysis of high molecular weight poly(L-lactide) film in phosphate buffered solution, J. Appl. Polym. Sci. 77 (2000) 1452-1464.

[36] I.R. Herbert, Statistical analysis of copolymer sequence distribution, in: R.N. Ibbet (Ed.), NMR spectroscopy of polymers, Blackie Academic & Professional, London, 1993, pp. 50-79.

[37] A. Gleadall, J. Pan, M.A. Kruft, M. Kellomaki, Degradation mechanisms of bioresorbable polyesters. Part 1. Effects of random scission, end scission and autocatalysis, Acta Biomater. 10 (2014) 2223-32.

[38] J. Fernández, A. Etxeberria, J.R. Sarasua, In vitro degradation of poly(lactide/δ-valerolactone) copolymers, Polym. Degrad. Stab. 112 (2015) 104-116.

[39] A. Larrañaga, P. Aldazabal, F.J. Martin, J.R. Sarasua, Hydrolytic degradation and bioactivity of lactide and caprolactone based sponge-like scaffolds loaded with bioactive glass particles, Polym. Degrad. Stab. 110 (2014) 121-128.