Improving the barrier properties of a biodegradable polyester for packaging applications

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Abstract

Miscible and thermally stable blends of biodegradable poly(butylene adipate-co-terephthalate) (PBAT) with poly(hydroxy ether of bisphenol A) (PH) are investigated to obtain membranes for packaging applications. Previously the miscibility and adequate degradability of these blends was proven, therefore this system is a good candidate for packaging applications. The crystallinity degree and the free volume, both of crucial importance in transport properties, are analysed as a function of blend composition. The transport properties to different gases and vapours are greatly reduced with the addition of PH. The blends show high elongational viscosity values, which allows expecting good film processability. Overall, this work sheds light on the factors involved in the reduction of permeability which would allow to broaden this strategy to other promising biodegradable materials.

Keywords: Biodegradable polymer; free volume; permeability; packaging

1. Introduction

The growing concern about the environment, together with stricter policies have led to an increase on the interest of biodegradable polymers. Biodegradable polymers offer a potential solution for the problems associated with the disposed waste since they degrade releasing methane, water, CO_2 and biomass. Polylactide and poly(caprolactone) are among the most relevant biodegradable polymers and have been widely studied in literature [1, 2]. However, they usually present poor performance regarding their mechanical and transport properties. Consequently, different strategies have been employed to overcome these problems. One option is

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blending the biodegradable polymer with another polymer which has better properties. However, usually polymer blends are immiscible due to the high molecular weight and weak interactions between monomers. Accordingly, specific interactions are needed to guarantee the miscibility of the blend [3].

Biodegradable polymer blends can replace commodity polymers in packaging applications. In order to assess the suitability of the materials for packaging the study of the transport properties to different gases and vapours is of paramount importance. As it is well known water vapour and oxygen can cause chemical and physical changes deteriorating the food packaged and allowing the growth of microorganism. Furthermore, the loss of aroma compounds in packed food is an issue that has to be considered. Within this context, the permeability to limonene has been measured, since this substance is used as a model compound to characterize the behaviour of the materials to aromas. Another gas that has to be measured is carbon dioxide since it is widely employed in modified atmosphere packaging due to its ability to inhibit the growth of microorganisms [4].

In a previous work [5] we characterized poly(butylene adipate-co-terephthalate) (PBAT)/ poly(hydroxy ether of bisphenol A) (Phenoxy, PH) blends concluding that they were fully miscible when prepared by melt processing. Furthermore, the hydrolytic degradation of the blends was deeply analysed concluding that for blends rich in PBAT the degradation rate was similar or even higher than for other polymers such as polylactide and poly(caprolactone). Taking into account that these blends could have a potential application in packaging their performance in terms of transport properties and processing have been analysed. The free volume has been studied to understand how the addition of phenoxy affects these properties. The permeability and sorption of different gases and vapours has been analysed allowing a better understanding of how the permeability of biodegradable polymers can be improved.

2. Experimental part

2.1. Materials

Poly(butylene adipate-co-terephthalate) (Ecoflex, PBAT) was supplied by Basf (M_w = 75000 g/mol) and poly(hydroxy ether of bisphenol A) (Phenoxy, PH) supplied by Union Carbide (M_w = 50700 g/mol).

2.2. Sample preparation

PBAT/PH blends were prepared in the molten state employing a Model CS-183 MMX mixer operating at 40 rpm and 190 °C. The films were prepared by hot-pressing in a Graseby Specac device at 190 °C. The thickness of the films is between 50-200 μm. For PALS and rheological measurements sheets of 1 mm thickness were prepared.

2.3. Apparatus

2.3.1. 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. 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. The glass transition temperature was measured in the second scan of the thermogram.

2.3.2. Thermogravimetric analysis

Thermal degradation was analysed by thermal gravimetric analysis employing a TGA Q 500 (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.

2.3.3. Positron annihilation lifetime spectroscopy

Positron annihilation lifetime spectra were recorded employing a conventional fast-fast nuclear spectrometer with a time resolution of 230 ps. Measurements were performed in the blends using a positron source that was prepared by depositing [22]NaCl onto a Kapton foil. The procedure has been described in more detail elsewhere [6].

The positron annihilation lifetime in the free-volume holes can be correlated to the hole dimension. From the lifetime the hole radius, R, can be estimated by means of the Eldrup model following this equation [7],

$$\tau_3 = 0.5 \left(1 - \frac{R}{R_0} + \frac{\sin 2\pi \frac{R}{R_0}}{2\pi} \right)^{-1} \tag{1}$$

where $R_0 = R + \Delta R$ and τ is given in nanoseconds. ΔR is an empirical parameter, whose value is 1.656 Å [8]. The mean free volume hole size, V_H, can be calculated by the following equation assuming that the holes are spherical,

$$V_H = \frac{4\pi R^3}{3} \tag{2}$$

The relative intensity corresponding to the lifetime I_3 is related to the number of the free-volume elements. Free volume fraction is obtained combining the size and number of free volume holes by means of this equation [9],

$$f = c \, V_H I_3 \tag{3}$$

where c is a constant characteristic of each material. Due to the difficulty to know the value of the constant for many polymers it has been defined another parameter: the apparent fractional free volume,

$$f_{app} = V_H I_3 \tag{4}$$

Although some authors state in literature that I_3 depends on the positron source activity, the thermal history of the samples and the composition of the polymer, the apparent fractional free volume is widely accepted in literature [10].

2.3.4. Density measurements

Density measurements were carried out in a gradient density column, employing NaBr aqueous solution at 23 °C. The values reported are the average of three samples.

2.3.5. Transport properties measurements

Oxygen transmission rate (OTR) was measured using a Mocon Ox-Tran 2/21 MH model equipment. The oxygen transmission rate is related to the permeability coefficient by the following expression,

$$OTR \left(cc \, mil \middle/ m^2 day \right) \times \frac{2.405 \times 10^{-3}}{p(mmHg)} = P \text{ (Barrer)} \tag{5}$$

The measurements were carried out at 23 °C, 1 atm and 0 % and 45 % relative humidity [11]. The surface area exposed to oxygen is 5 cm².

Water and limonene vapour transmission rate were obtained by a permeation gravimetric cell. The cell, which is made of polytetrafluoroethylene, is a small

container partially filled with the penetrant and the top is sealed with the membrane. The solvent inside the cell, in this case water or limonene, permeates through the membrane and evaporates into the air. The cell is placed in a Sartorius analytical balance with a readability of 10^{-5} g and the weight loss is measured and recorded in a computer for further data treatment [12, 13]. The measurements were repeated five times to obtain the average values shown in this paper.

Carbon dioxide sorption measurements have been performed in the IGA-2 Hiden electromagnetic balance at 25 °C and in the range of 1-20 bar. More details about the equipment and method have been described elsewhere [14].

2.3.6. Rheological measurements

The dynamic viscoelastic functions were analysed in the linear regime using Small Amplitude Oscillatory Shear, SAOS, measurements. The measurements were performed under nitrogen in an ARG2 (TA) rheometer with parallel plates (diameter of 25 mm) at 150 °C. Frequency sweeps were carried out from 628 rad/s to 0.05 rad/s.

The extensional viscosity of the samples was studied at 150 °C using the Extensional Viscosity Fixture (EVF) of an ARES (TA) rheometer.

3. Results and discussion

3.1. Thermal analysis

In our previous work [5] the miscibility of the system was analysed concluding that poly(butylene adipate-co-terephthalate)/phenoxy blends are miscible in the entire composition range. Since in the previous work samples were obtained in extrudate form and in this case membranes are analysed, and taking into account that thermal properties would be different, these measurements have been repeated with the membranes, which are reported in Table 1. Melting temperature, T_m, and crystallinity level, X_c, are determined in the first heating scan whereas the glass transition temperature, T_g, is determined in the second heating scan.

As can be observed neat PBAT shows the glass transition temperature at -28 °C, whereas the glass transition temperature of neat PH is 99 °C. For the blends a single glass transition temperature is obtained indicating that the polymers are miscible, as it was reported before by some of us [5]. As the content of PH increases the T_g rises gradually. Considering the results of Table 1, we remark that at room temperature 75

PBAT/25 PH blend is in the rubbery state, 50 PBAT/50 PH is in the glass to rubber transition zone and 25 PBAT/75 PH is in the glassy state. This is a relevant clarification, because the sorption and diffusion processes are different in rubbery and glassy polymers [15]. As it can be observed there are slight differences between these results and the previous ones [5], although the trends in both series are similar. Anyway, as mentioned previously, the repetition of the measurements is appropriate when the preparation of the samples is not identical.

Table 1. Thermal properties of PBAT/PH blends obtained by differential scanning calorimetry.

Sample	T_g (°C)	T_m (°C)	X_c (%)	$X_{c\ PBAT}$ (%)
PBAT	-28	48, 89, 121	18	18
75 PBAT/25 PH	-6	50, 86, 118	12	16
50 PBAT/50 PH	27	90, 114	6	11
25 PBAT/75 PH	59	97	2	8
PH	99	-	-	-

In agreement with literature results [5, 16] poly(butylene adipate-co-terephthalate) shows three melting peaks located at 48 °C, attributed to the melting of butylene adipate sequences, and at 89 °C and 121 °C, respectively attributed to the melting and recrystallization of butylene terephthalate sequences.

Neat PBAT presents a crystallinity level of 18 %, which is reduced with the addition of phenoxy leading to a crystallinity of only 2 % for 25 PBAT/75 PH blend. This confirms our previous results [5] about the hindering effect of PH on the crystallization of PBAT. Needless to say, the crystallinity level is key factor for transport properties since the crystallites are considered impermeable [17].

3.2. Thermogravimetric analysis

Figure 1 shows the thermodegradation curves of PBAT/PH system, the $T_{5\%}$ data for all the samples is shown in Table S1 in Supporting Information. As can be seen

neat phenoxy exhibits the highest thermal stability among the investigated samples, with a degradation temperature above 400 °C. On the other hand, PBAT shows the lower thermal stability and as the blends become richer in PH the stability increases. All the blends show a lower thermal stability than expected. The thermodegradation curve obtained for 75 PBAT/25 PH is identical to that of PBAT whereas the thermodegradation curves corresponding to 50 PBAT/50 PH and 25 PBAT/75 PH are between those of the pure components.
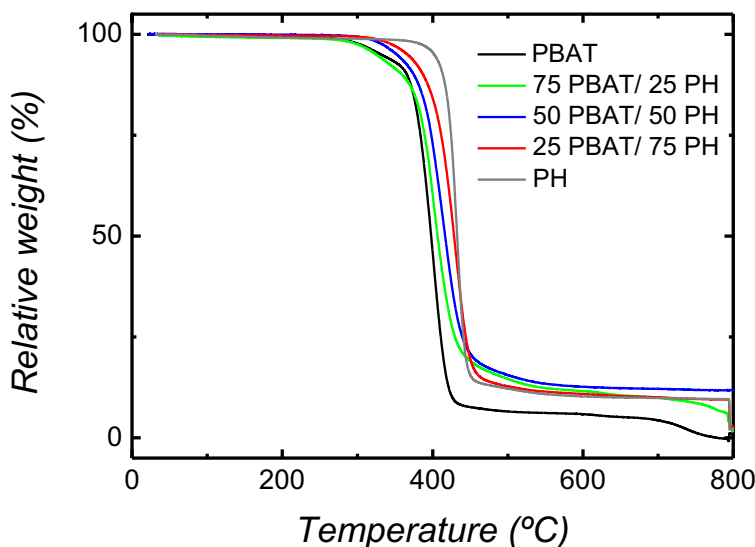

Figure 1. Thermogravimetric traces of PBAT/PH blends.

3.3. Density measurements

The density values obtained for PBAT/PH blends and neat polymers are shown in Figure 2 (for the values see Table S2 in Supporting Information). The black dots correspond to the experimentally measured density values, being the average standard deviation equal to $6.25 \ 10^{-4}$. For the blends a densification (positive deviation from the additive rule) is observed, indicating that the free volume is diminished, implying a decrease of the permeability coefficient, which is interesting for transport properties. This behaviour will be analysed more deeply taking into account the free volume fraction results obtained from PALS, exposed in the next section.

In literature it has been reported that the increase in density indicates the existence of intermolecular interactions that allow a better packing of the chains [18].
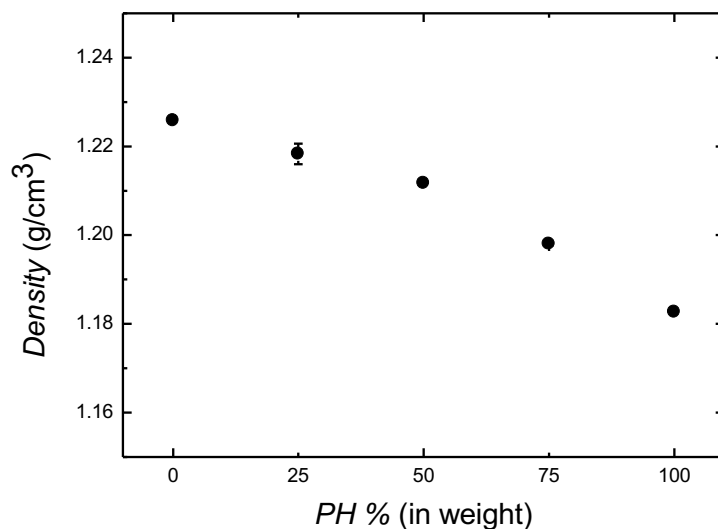
Figure 2. Density of PBAT/PH blends for the studied compositions.

3.5. Free volume characterization

The free volume of the system was characterized by positron annihilation lifetime spectroscopy (PALS). Employing this technique, the free volume hole size, V_3, and the free volume hole intensity, I_3, are obtained. From these parameters the fractional free volume can be estimated.

The free volume hole size and the free volume hole intensity are shown in Figure 3 (for the obtained values see Table S3 in Supporting Information). Poly(butylene adipate-co-terephthalate) presents a free volume hole size of 113.4 $Å^3$, this value being higher than that of phenoxy which shows a value of 73.1 $Å^3$. In the case of the blends the addition of phenoxy decreases considerably the free volume hole size deviating negatively from additive rule. The decrease is very meaningful for 50 PBAT/50 PH blend.

Poly(butylene adipate-co-terephthalate) shows the lowest free volume hole intensity, which is related to the free volume hole number, with a value of 19.8 % whereas in the case of phenoxy the value is 24.2 %. Therefore, PBAT presents less free volume holes, but these are bigger than in the case of PH. For the blends the addition of PH leads to an increase of the free volume hole intensity, however for 50 PBAT/50 PH and 25 PBAT/75 PH the increase is lower than expected.
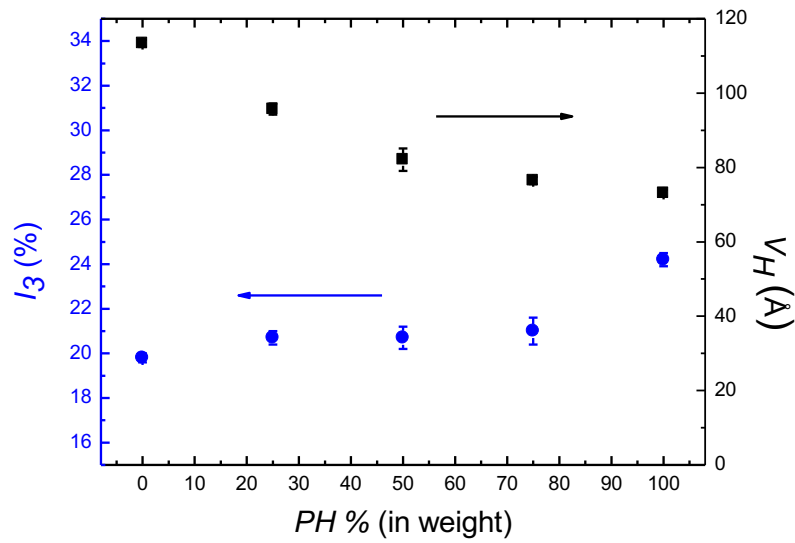
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Figure 3. Free volume hole volume (V_H) and relative intensity (I_3) of PBAT/PH blends.

The apparent fractional free volume, that encompasses the free volume hole size and the free volume hole intensity is shown in Figure 4. As can be seen PBAT shows a value of 2245 (a.u.) and phenoxy shows a value of 1769 (a.u.). Therefore this result shows that PBAT has a higher free volume than PH.

Regarding PBAT/PH blends the addition of phenoxy decreases considerably the free volume fraction leading to a synergetic behaviour since both 50 PBAT/50 PH and 25 PBAT/75 PH blends present a free volume fraction that is below the respective values of the neat components. The obtained results are in good agreement with the density values (Figure 2), where a densification of the blends is observed. The free volume reduction would lead to the barrier character improvement, at least with less interacting penetrants, which is the aim of this work.
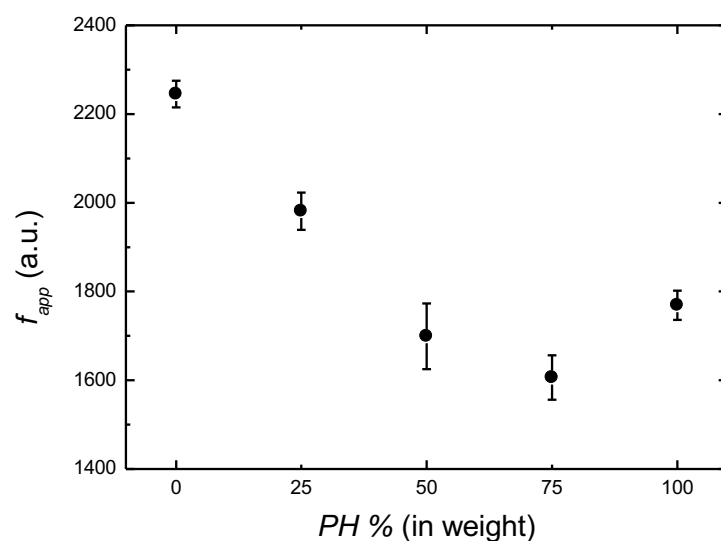
Figure 4. Apparent fractional free volume (f_{app}) of PBAT/PH blends.

3.6. Water vapour permeability

Water vapour permeability is of great importance in packaging since water can cause chemical or physical changes deteriorating food. For example for fresh foods, such as vegetables and fruits, dehydration must be avoided because moisture loss or uptake causes wilting, shrinkage and microbial growth. On the other hand for bakery products water entrance must be depleted to avoid caking, loss of crispness and microbial growth, among others [4].

Analysing the data obtained for water vapour permeability, shown in Figure 5 (values reported in Table S4 in Supporting Information), it can be observed that pure PBAT shows poor barrier properties with a WVTR value of 12.8 g mm/m^2 day. This permeability value is higher than that of other biodegradable polymers, such as poly(lactide) [19], poly(ε-caprolactone) [20] and poly(3-hydroxybutyrate) [12].

Figure 5 highlights that the addition of phenoxy reduces significantly the permeability to water vapour, showing a negative deviation from the additive rule. We found a decrease by 56 %, respect neat PBAT, with the addition of just 25 % phenoxy. The decrease of water permeability with PH content is in accordance with the results obtained from PALS in which a considerable decrease in the apparent free volume is observed with the addition of PH.

Another factor that leads to this result is the glass transition temperature since for

75 PBAT/25 PH blend the T_g is below room temperature, the blend with 50 % PH has a T_g of 27 °C and with more PH the blend is above the measuring temperature. This is of great importance since the sorption mode changes from predominantly Henry type sorption in the rubbery or elastomeric state, to another sorption mode, in the glassy state, in which Langmuir type sorption is also present. Furthermore, the diffusion also changes, being the mobility of the chains more difficult in the glassy blend with respect to the elastomeric blends.
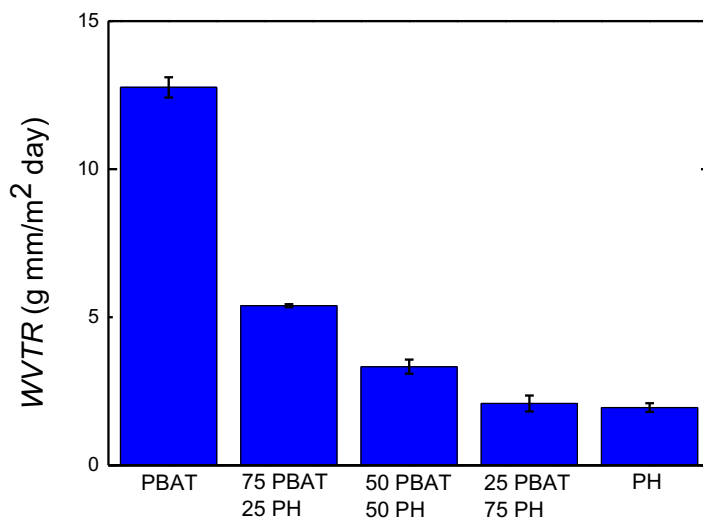
Figure 5. Water vapour transmission rate values for PBAT/PH blends.

3.7. Oxygen permeability

The oxygen permeability is also of great importance in packaging applications since it plays a fundamental role in goods preservation. The main concerns are oxidative reactions, such as lipid oxidations that cause rancid flavours, and colour and nutritive changes. The oxygen also enables the growth of aerobic microorganisms. On the other hand fruits and vegetables require respiration of oxygen and in absence of it undesirable changes happen such as those due to anaerobic microbial deterioration [2, 4]. Furthermore, the presence of water can change the permeability to oxygen, therefore the oxygen permeability in dry and humid conditions have been measured.
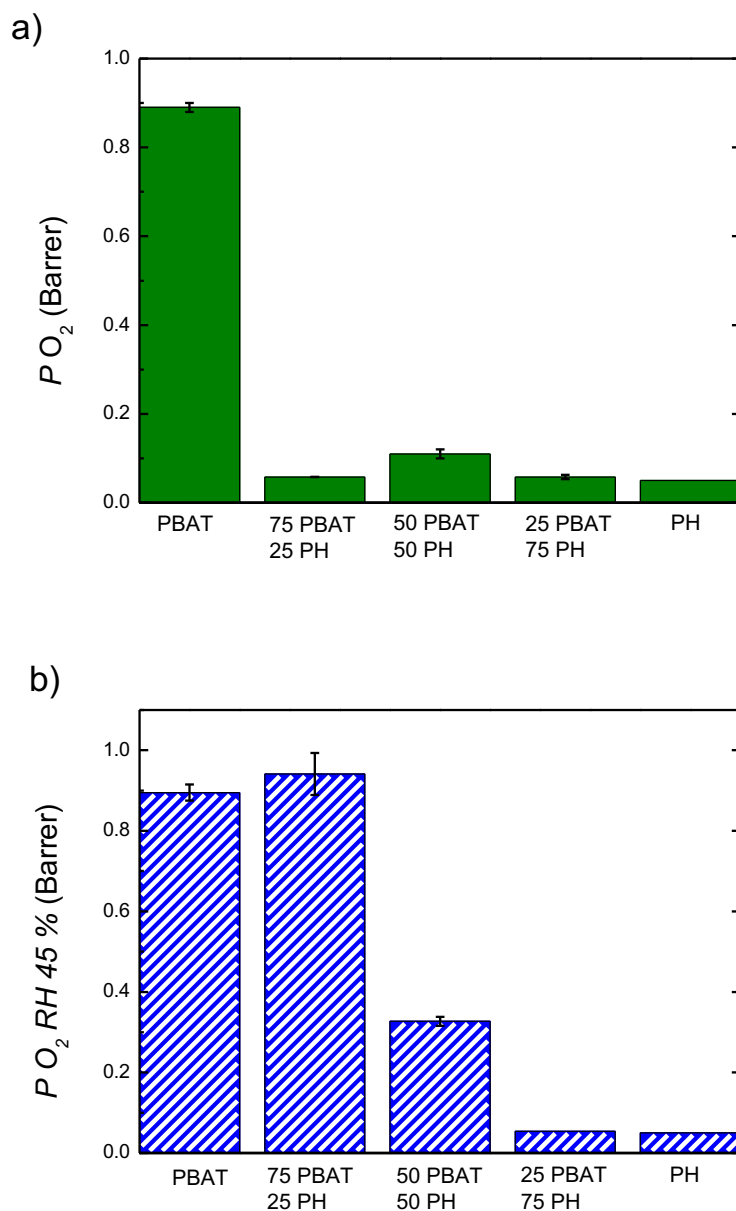
a)

b)

Figure 6. Oxygen permeability for PBAT/PH blends a) in dry conditions and b) 45 % relative humidity.

The obtained oxygen permeability in dry conditions for PBAT and PBAT/PH blends are shown in Figure 6 a (values shown in Table S5 in Supporting Information). The measured oxygen permeability coefficient for PBAT is 0.89 Barrer, comparing to other biodegradable polyesters is actually very similar to that of poly(caprolactone) PCL (0.88 Barrer, measured on our laboratory), which is also in the rubbery state at room temperature. However, the permeability of PBAT is much higher than that reported for PLLA [19] (0.6 Barrer), since the latter is in the glassy state at room temperature.

Regarding phenoxy a value of 0.05 Barrer has been measured at room temperature, which is explained considering that polymers which have a high cohesive energy and are packed efficiently show low permeability, because the free volume available for permeation is reduced. The high barrier to oxygen is related to the ability of the pendant functional groups to act as a hydrogen bond donor and acceptor.

In the case of PBAT/PH blends, the addition of phenoxy sharply decreases permeability (up to 90%) even for 75 PBAT/25 PH blend. The obtained values suggest that the free volume and glass transition temperature changes, as well as strong polymer-polymer interactions, hinder both, solubility and diffusion of the penetrant diminishing strongly permeability.

Taking into account that the relation between permeability and composition deviates from linearity, it can be suggested that the interactions between penetrants and polymers are playing a major role. In miscible blends the penetrant has more difficulties to form interactions with polymer, due to polymer-polymer interactions. This leads to a decreased sorption and the diffusion of the penetrant is also hindered. Similar behaviour is observed for carbon dioxide permeability of poly(hydroxy amino ether)/polyamide [21] blends.

Oxygen permeability is significantly lower than water permeability; in fact due to its chemical nature oxygen interacts with the polymer forming only weak van der Waals bonds, whereas water can interact strongly through dipole-dipole interactions or hydrogen bonds. In addition oxygen is a linear molecule and has a low condensation capacity.

Keeping in mind that the presence of water can influence considerably the transport properties the permeability of oxygen under humid conditions has been also studied. Regarding the data obtained for oxygen at 45 % relative humidity, Figure 6 b, it can be observed that for neat PBAT the permeability does not change considerably with the presence of water. For all the blends a huge increase in oxygen permeability is found whereas for neat PH the permeability does not change as compared to that obtained in dry condition. It is worthy to note that high barrier materials to oxygen such as poly(vinyl alcohol) and poly(amide 6) loss their barrier character in presence of water. However, in the case of phenoxy it presents a similar value compared to dry oxygen. In literature it has been reported that for poly(hydroxyaminoethers), which

have a similar structure compared to phenoxy, even a decrease on oxygen permeability is found under wet conditions. This effect has been related to the competition between water and oxygen molecules to fill the free volume holes [22, 23].

There are several factors that affect the permeability of oxygen in the presence of water. For instance, water molecules can plasticize the polymer blend increasing the permeability to oxygen since the sorption and diffusion of the penetrant is enhanced. The water molecules can also interact with the polymer and break the hydrogen bonds between PBAT and PH leading to an increased permeability. On the other hand, the water and oxygen molecules have to compete for the available free volume holes, which decreases the permeability [24]. Therefore, the results indicate that for ~~neat PBAT and~~ PBAT/PH blends the permeability increases drastically pointing out that the plasticization and interactions are playing a major role. In the case of phenoxy the counterbalance of the aforementioned effects provokes no changes in the permeability.

3.8 Limonene permeability

Given the potential application of these materials in food packaging sector, the permeability to limonene is studied. In fact, the permeability to this penetrant has been widely studied since it is considered as a model compound to determine the barrier character to aroma compounds.

In Figure 7 limonene vapour transmission rate (data shown in Table S6 in Supporting Information) for PBAT/PH blends is shown. As can be seen neat PBAT shows a value of 4.3 g mm/m^2 day, which is a much lower value than that obtained for water vapour. This result arises from the non-polar character of limonene that can interact with the polymer only by weak Van der Waals interactions. On the other hand water can form strong interactions through hydrogen bonds and dipole-dipole interactions. Phenoxy shows a value of 0.04 g mm/m^2 day, denoting an outstanding barrier character also to this penetrant.

The blends show also an excellent barrier character, with values that do not correlate linearly with the blend composition and that are far below from the additive rule values. As mentioned previously, the changes on the glass transition temperature and free volume, together with the interactions between the polymer blends and the

penetrant lead to this outstanding result. It can be suggested that for 75 PBAT/25 PH and 25 PBAT/75 PH blends the functional groups that interact with the penetrant are available enhancing the permeation of the penetrant. However, for 50 PBAT/50 PH the majority of the functional groups could be involved in interactions between both polymers therefore there would be less groups available to interact with the penetrant leading to a larger reduction of the permeability.
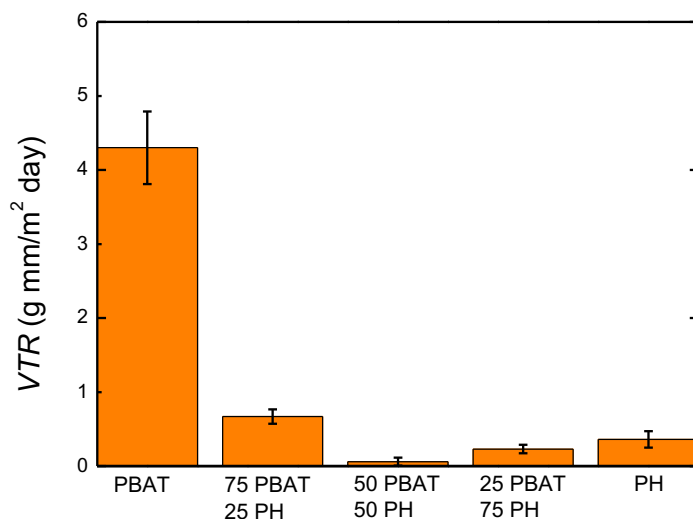

Figure 7. Limonene vapour transmission rate for PBAT/PH blends.

3.9 Carbon dioxide sorption

Carbon dioxide sorption isotherms for PBAT/PH blends are shown in Figure 8. As can be seen neat PBAT shows the highest CO_2 sorption and as the phenoxy content increases the concentration of carbon dioxide is reduced.

According to Figure 8 the carbon dioxide sorption isotherms for PBAT, 75 PBAT/25 PH and 50 PBAT/50 PH show a linear type relationship with the pressure whereas 25 PBAT/75 PH and neat PH show an anomalous behaviour.
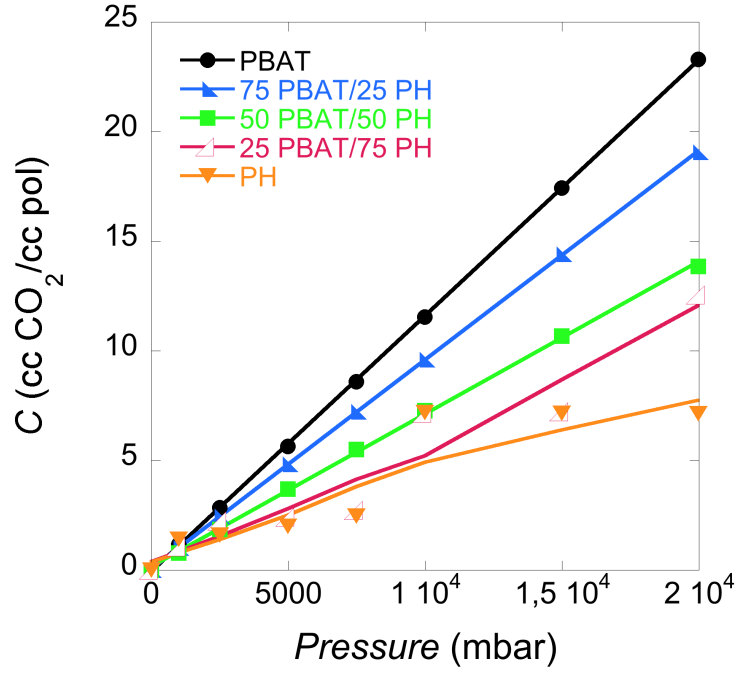
Figure 8. Carbon dioxide sorption isotherms for PBAT/PH blends.

For those polymers for which a linear relation is found the isotherm is well fitted to Henry type sorption that is given by the following equation,

$$C = K_D p \tag{6}$$

where C is the concentration, K_D is the Henry´s law constant and p is the pressure.

In the case of glassy polymers the data is usually well fitted to the dual mode sorption, which encompasses Henry and Langmuir type sorption:

$$C = K'_D + \frac{C'_H + b'p}{1 + b'p} \tag{7}$$

where C'_H and b' are the Langmuir capacity constant and the Langmuir affinity constant, respectively. K'_D is the Henry type sorption contribution. C'_H has been often used to measure the non-equilibrium excess free volume in the glassy state [15].

In Table 2 the Henry and dual mode sorption parameters obtained for PBAT/PH blends are shown. As can be seen the Henry´s mode sorption contribution decreases with the addition of phenoxy.

In the case of 25 PBAT/75 PH and PH samples that show an anomalous sorption, the isotherm until 10 bar can be fitted to the dual mode sorption. In Table 2 it can be observed that the Henry type sorption contribution is quite small. The C'_H

has been used to measure the non-equilibrium excess free volume, in this case a larger value is obtained for 25 PBAT/75 PH blend than for PH which is not in accordance with the data obtained from PALS. The b' parameter has been related to the interactions between the polymer and the penetrant: the higher value obtained for PH could suggest that the penetrant interacts more favourably with PH which leads to a decrease on the permeability. The anomalous behaviour observed could be related to plasticization or relaxation phenomena but it is not clear if these are the only factors that lead to this behaviour. The measurements have been performed at least 3 times obtaining very similar results.

Table 2. Henry (Equation 6) and dual (Equation 7) parameters obtained from carbon dioxide sorption isotherms.

Sample	Henry	Dual		
	K_D (10^3 cm^3 STP/cm^3 pol mbar)	K'_D (10^3 cm^3 STP/cm^3 pol mbar)	C'_H (cm^3 STP/cm^3 pol)	b' (mbar^{-1})
PBAT	1.17	-	-	-
75 PBAT/ 25 PH	0.95	-	-	-
50 PBAT/ 50 PH	0.70	-	-	-
25 PBAT/ 75 PH	-	0.10	2.43	0.001
PH	-	0.14	1.37	0.032

In Figure 9 the amorphous solubility of PBAT/PH blends at different pressures is shown (see Table S7 in Supporting Information). At atmospheric pressure neat phenoxy presents the highest solubility, followed by neat PBAT. For the blends the solubility decreases obtaining the lowest value for 50 PBAT/50 PH blend, probably this result arises from the interaction between both components that hinders the solubility of carbon dioxide. For higher pressures, 5000 and 15000 mbar, the trend changes: the solubility decreases with phenoxy content obtaining the lowest solubility for neat phenoxy. Only 25 PBAT/75 PH and neat PH samples are significantly

affected by pressure, showing both a drastic decrease for 5000 and 15000 mbar. This result arises from the sorption type: these samples follow dual mode sorption, therefore the concentration, C, at high pressures rises slowly comparing to Henry type sorption.
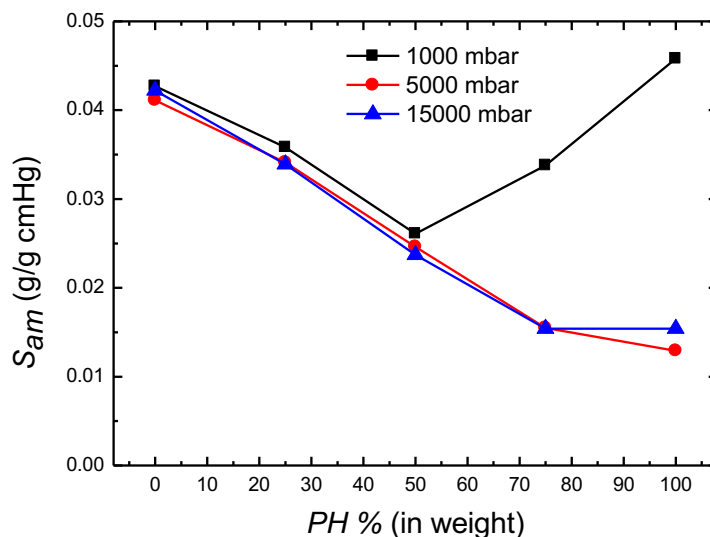

Figure 9. Amorphous solubility of PBAT/PH blends at different pressures.

Diffusion coefficients of PBAT/PH blends at different pressures are shown in Figure 10 (see Table S8 in Supporting Information). The addition of phenoxy decreases considerably the diffusion coefficient even with the addition of only 25 % PH. Furthermore, all the obtained values are below the additive rule. This can be attributed to the higher T_g, the lower free volume and also to the interactions between PBAT and PH that hinder the diffusion of the penetrant. At atmospheric pressure, both PH and 25 PBAT/75 PH blend, show the lowest diffusion coefficients which is in agreement with the results of the free volume fraction (Figure 4).

As in the case of solubility, the behaviour of the diffusion coefficient also changes considerably for higher pressures. For pressures higher than 1 bar the behaviour of the diffusion coefficient changes considerably and 25 PBAT/75 PH and PH samples present values comparable or higher than PBAT. It has to be considered that the free volume has been measured at 1 bar and the pressure can influence considerably the free volume fraction [25]. Carbon dioxide can plasticize the polymer at higher pressures influencing the obtained diffusion coefficients [26]. Furthermore, at higher pressures the driving force is higher and therefore the diffusion is increased.

It has to be considered also that at atmospheric pressure the small or isolated free volume holes could not be available. However at higher pressures these free volume holes would be available.
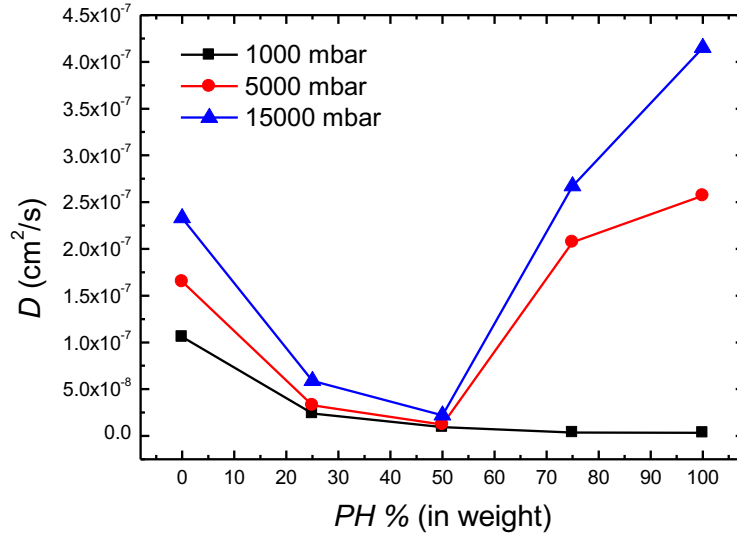

Figure 10. Diffusion coefficient of PBAT/PH blends at different pressures.

In order to calculate the permeability the following expression has been employed: $P = D \cdot S$. As it is well known this equation can be employed only under certain conditions such as when Henry type sorption occurs and the diffusion coefficient does not change with the penetrant concentration. Therefore the data obtained by this expression is more reliable for the permeability values obtained at 1 bar. The permeability values obtained for different blends are shown in Figure 11 (see Table S9). As can be seen for the values obtained at 1 bar the permeability of PBAT is decreased with the addition of PH, even with the addition of just 25 % of PH a significant reduction in permeability is found.

As the pressure increases the permeability rises which indicates that diffusion plays a major role than solubility. The obtained results follow the trend of the free volume hole size, although for 25 PBAT/75 PH a lower permeability could be expected *a priori*. Taking into account that this blend and neat PH are in the glassy state, contrary to the other blends that are in the rubbery state, it could be suggested that the plasticization could lead to a more significant change. Furthermore, as a consequence of the plasticization the T_g could be closer to measuring temperature, even becoming inferior. This would lead to relative important changes in the sorption

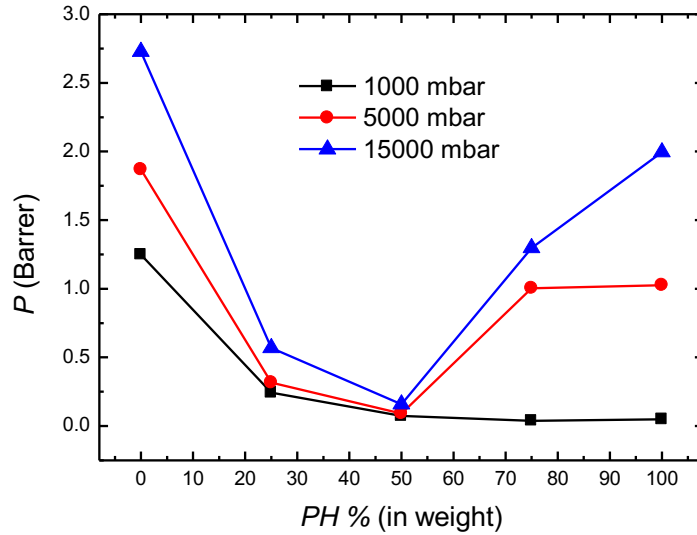mode increasing the Henry type sorption and it would also increase the diffusion coefficient.

Figure 11. Permeability of PBAT/PH blends at different pressures.

3.10. Parameters that affect permeability

The obtained permeability values for different penetrants show a completely different behaviour. Therefore, in order to elucidate the factors that lead to these results an attempt to correlate the permeability values with free volume and glass transition temperature has been carried out.

In Figure 12 a) the changes of the water vapour transmission rate and free volume fraction with respect to the additive rule are shown. The changes of the permeability to carbon dioxide and the glass transition temperature respect to additive rule are shown on the Figure 12 b) (for further details about the data and calculations see supporting information).
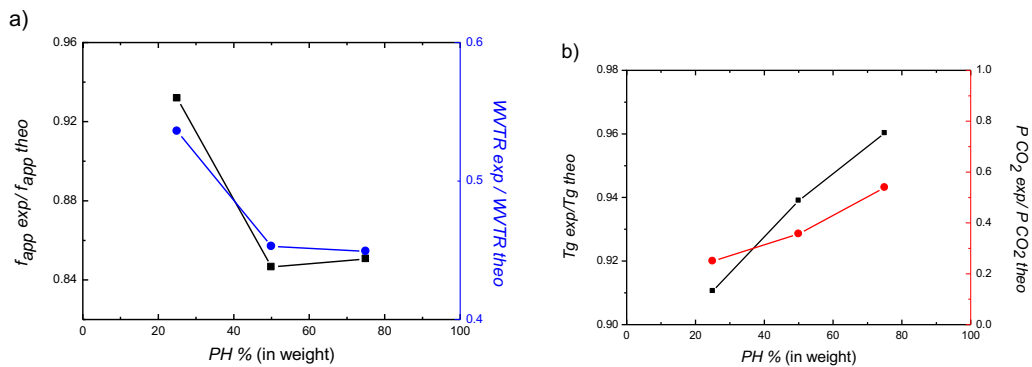
Figure 12. a) Apparent free volume fraction and WVTR experimental/theoretical ratio for PBAT/PH blends and b) glass transition temperature and carbon dioxide permeability experimental/theoretical ratio for PBAT/PH blends.

As can be seen the water vapour transmission rate is well correlated to the change found in the free volume fraction and similar results are obtained for oxygen permeability measured under humid conditions (not shown). On the other hand for carbon dioxide and oxygen the permeability is correlated to the glass transition temperature. In advance, the opposite behaviour could be expected since water can interact through hydrogen bonds and dipole-dipole interactions. However, the obtained results lead us to the conclusion that the bigger size of carbon dioxide and oxygen molecules lead to differences between free volume and permeability. In this case the obtained values follow the trend of the glass transition temperature.

3.11. Rheology

Considering the potential application of these blends in packaging, due to the improvement of barrier properties, the study of the properties under processing conditions is a necessary task. In order to ascertain the influence of adding PH to PBAT in terms of processability, the rheological properties under shear and extensional flow are studied.

Small Amplitude Oscillatory Shear, SAOS, measurements

Rheological measurements in the linear viscoelastic regime using small amplitude oscillatory shear measurements have been performed. Since small amplitude is employed, the microstructure of the sample is not destroyed, which allows determining the effect of secondary interactions on the viscosity.

In Figure 13 the complex viscosity against frequency for the homopolymers and blends is shown. At low frequencies all the systems show a Newtonian behavior, being the viscosity value constant. At a certain frequency the onset of the viscosity decrease is observed. The addition of PH to PBAT results in an increase of the viscosity, being the increase more prominent for the blend rich in PH. The high viscosity values observed for PH result from the presence of hydrogen bonds. As reported in literature, the secondary interactions, such as hydrogen bonds, ionic interactions or metal ligand coordination, restrict the diffusion of polymer chains. This hinders the flow of the polymer which results in an increase of the viscosity [27-

36]. Nevertheless, in our case it is difficult to analyze the effect of hydrogen bonding, since there is also an effect of the blend composition.

Addition of PH up to 50% does not increase viscosity very significantly and in the high frequencies zone, which is equivalent to high shear rates, the shear thinning effect leads to a reduction of the viscosity differences between pure PBAT and the blends. This is relevant from the processing point of view. It can be stated that the addition of PH, which improves the barrier properties of the system, does not indeed difficult the processing of the material.
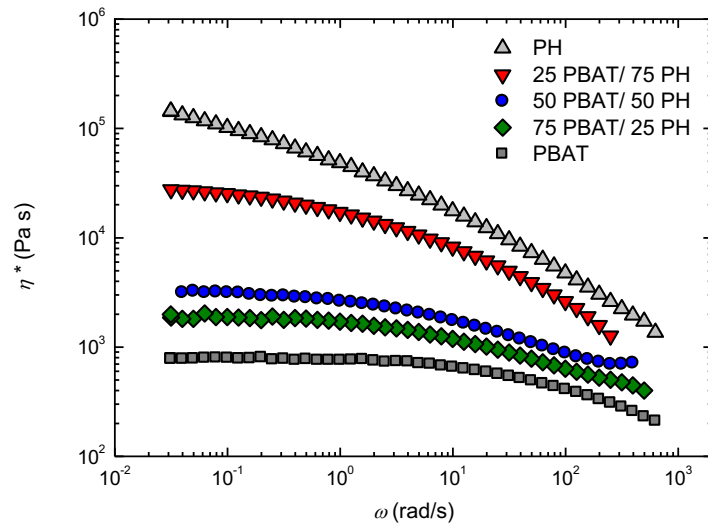

Figure 13. Complex viscosity obtained by SAOS 150 ℃ against frequency for the homopolymers and the blends.

Since hydrogen bonds are brought about in PH, this polymer is a suitable candidate to analyze the effect of these secondary interactions on the viscoelastic properties. Figure 14 shows the storage modulus, G', as a function of frequency for the investigated samples. PBAT shows the lowest G' values with a slope near 2 in the terminal zone (lower frequencies), a result which is practically in agreement with the linear viscoelastic model [37]. On the other hand, PH shows high G' values in log G'-logω plots, with a slope considerably smaller than 2 at low frequencies, which is due to the presence of hydrogen bonds. In the case of the blends the addition of PH to PBAT results in an increase of the storage modulus, as could be expected considering that the blends are miscible.

In literature it has been reported that for poly(butadiene) and poly(butyl

acrylate) the slope of G' in the terminal zone is near 2, whereas the modified polymers show lower slope values owed to the presence of hydrogen bonds [33-35]. Han et al. also observed that for miscible blends constituted by poly(vinylphenol) (PVPh) and different second polymers, the slope of log G'-logω plots was smaller than 2 and was reduced increasing the content of PVPh, which is the responsible of hydrogen bonds [38].
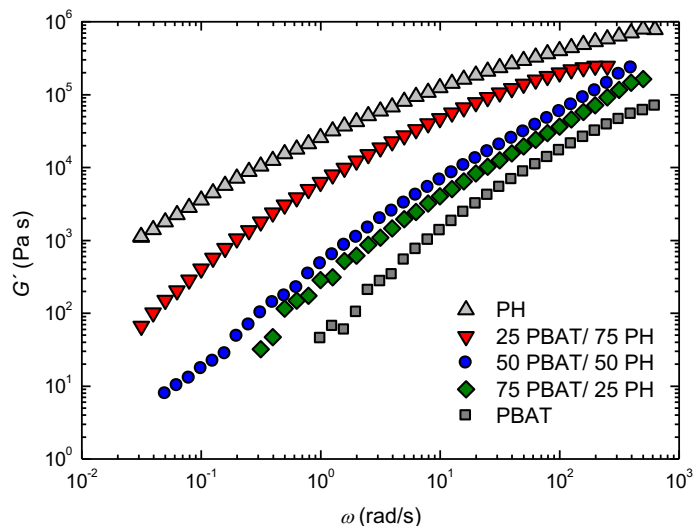

Figure 14. Storage modulus obtained by SAOS against frequency for the homopolymers and the different blends at 150 °C.

Figure 15 shows the Newtonian viscosity as a function of the blend composition. The presence of PH results in an increase of the viscosity. This increase arises from the nature of PH and the formation of hydrogen bonds.
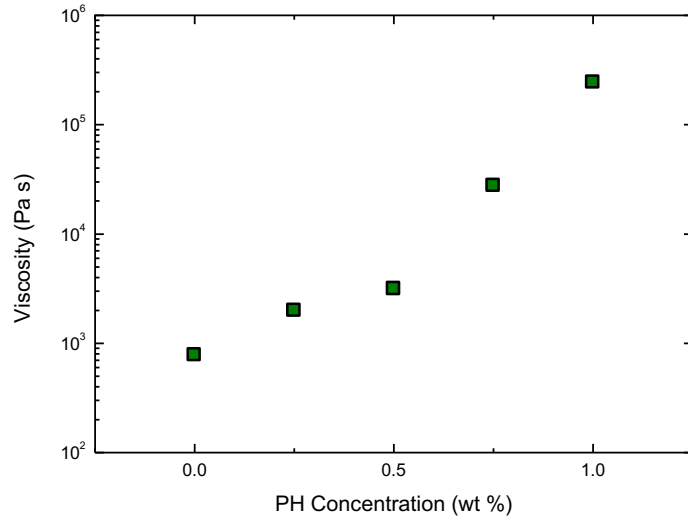
Figure 15. Viscosity of the samples against the concentration of PH.

Although in associative polymers the presence of secondary interactions alter both the storage modulus and the viscosity plots, for these blends the analysis of these parameters is restricted, since in addition to secondary interactions there is also a variation of the blend composition. Within this framework, the relaxation spectra of the different samples are analyzed. The spectra are calculated using the following equations [39, 40]:

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} \, d \ln\lambda \quad (8)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} \, d \ln\lambda \quad (9)$$

where $H(\lambda)$ represents the relaxation spectrum and λ the relaxation time.

In Figure 16 the relaxation spectra of the different polymers and blends are shown. PBAT shows the shortest relaxation times, with the peak centered at 0.02 s, which is a short time as compared to the values reported in literature [41, 42] for this polymer, i.e. 0.8 and 0.5 s. On the other hand, PH shows the longest relaxation times, with the maximum located at 4 s. This long time results from the presence of hydrogen bonds, which restrict the diffusion of the chains hindering the relaxation process. In the case of the blends, the presence of PH shifts the relaxation processes to longer times, being the shift quite significant for the blend rich in PH.

The results of the relaxation spectra are compatible with those of IR spectra,

analyzing the carbonyl stretching band [5]. In fact, an additional peak was observed for the blends rich in PH, due to the association of hydrogen bonds. This explains why the blend rich in PH shows higher elastic modulus and viscosity values, as well as longer relaxation times, whereas for the other blends the effect of the presence of PH is quite limited.
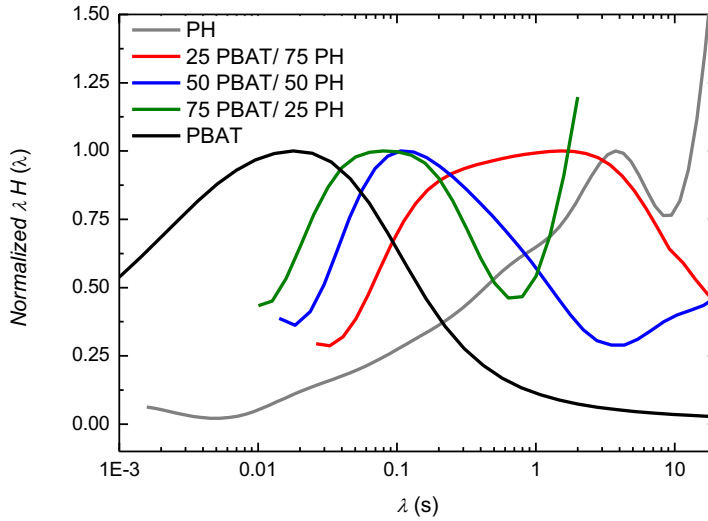

Figure 16. Normalized time weighted spectra for the homopolymers and the blends at 150 ºC.

In addition to linear measurements under shear flow, the non linear rheology has been studied, applying extensional flow. This is interesting, given the potential application of these blends in packaging and that usually films or bags are obtained by extrusion blow film process, where extensional flow plays a relevant role.

As it has been reported in literature [13, 43, 44], the extensional behavior can be related to the relaxation time spectrum. PBAT shows a strain softening behavior (see Figure 17), which is in agreement with the short relaxation times observed in the relaxation spectrum, as it has been reported in literature. On the other hand, PH shows an outstanding strain hardening, which is congruous with the observed long relaxation times (Figure 17). In the case of the blends, only the blend rich in PH shows strain hardening at this condition, since it shows relatively long relaxation times.

Actually, because of above mentioned physical reasons blends rich in PBAT are more suitable for packaging, but do not show strain hardening, which is not, in principle, a favorable rheological feature for extrusion blow process. But, we remark that for 75 PBAT/25 PH blend the extensional viscosity is approximately four times

higher than that of pure PBAT, a result that allows expecting a better extrusion blowing performance for the PBAT rich blend.
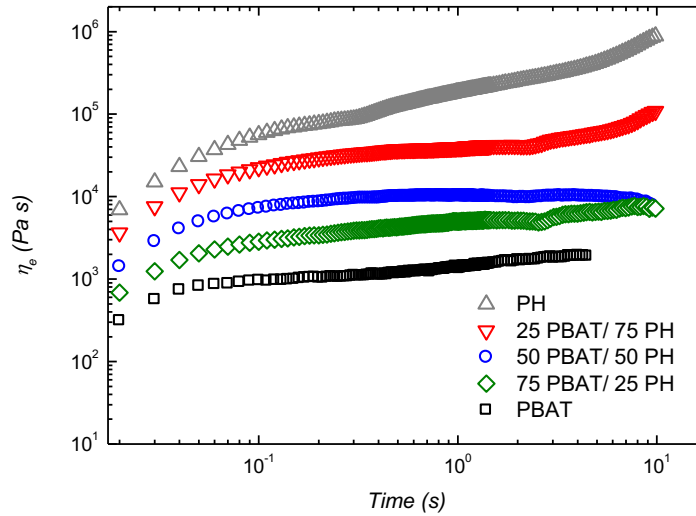

Figure 17. Extensional viscosity for the different blends obtained at 150 ºC and extension rate 0.3 1/s.

Conclusions

The suitability of miscible and hydrolytically degradable poly(butylene adipate-co-terephthalate)/phenoxy blends for packaging applications is assessed. For that purpose the thermal properties, free volume and permeability to different gases and vapours is investigated. The degree of crystallinity of the obtained PBAT/PH membranes decreases with the addition of PH. Density results and positron annihilation lifetime spectroscopy (PALS) measurements reveal that the free volume of the membranes decreases as the concentration of PH increases. The lowest value of the free volume is observed for 25 PBAT/75 PH blend, unveiling a synergetic behaviour.

Transport properties of neat PBAT are greatly improved with the incorporation of PH. Both water vapour and limonene transmission rate are considerably reduced in the case of PBAT/PH membranes, with respect to neat PBAT, which indicates that adding PH is a good option to tune the permeability required for food packaging. Oxygen permeability is also decreased as PH increased, although the relation with the composition is not linear. When the oxygen permeability is measured at a relative

humidity of 45 % a different behaviour is observed: the permeability decreases gradually with PH content, bringing about a similar behaviour to that noticed for water vapour permeability. Finally, the sorption measurements carried out with carbon dioxide show that the estimated permeability also decreases significantly with the addition of PH. Shear and elongational flow measurements have been also carried out to inquiry on the suitability of the blends for the manufacture of films by extrusion blow process. The considerable high elongational viscosity of 75 PBAT/25 PH, with respect to pure PBAT, opens good processing expectations.

Taking into account that the addition of small amount of PH improves the transport properties of PBAT, there is a wide window for adequate blend compositions that present an optimum hydrolytic degradation rate together with good barrier properties. Overall, the obtained results indicate that adding PH to PBAT is a good option to tune the permeability required for food packaging.

Acknowledgements

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References

[1] R.A. Gross, B. Kalra, Biodegradable polymers for the environment, Green Chem. 297 (2002) 803-807.

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

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

[4] W.J. Koros, Barrier polymers and structures, American Chemical Society, Washington, 1990.

[5] A. Sangroniz, A. Gonzalez, L. Martin, L. Irusta, M. Iriarte, A. Etxeberria, Miscibility and degradation of polymer blends based on biodegradable poly(butylene adipate- co -terephthalate), Polym. Degrad. Stabil. 151 (2018) 25-35.

[6] J. del Río, A. Etxeberria, N. López-Rodríguez, E. Lizundia, J.R. Sarasua, A PALS contribution to the Supramolecular Structure of Poly(L-lactide), Macromolecules 43 (2010) 4698-4707.

[7] M. Eldrup, D. Lightbody, S. J.N., he Temperature Dependence of Positron Lifetimes in Solid Pivalic Acid, Chem. Phys. 63 (1981) 51-58.

[8] H. Nakanishi, S.J. Wang, Y.C. Jean, in: C. Sharma (Ed.), Positron annihilation studies of fluids, World Scientific, Singapore, 1988, pp. 285-291.

[9] Y.Y. Wang, H. Nakanishi, Y.C. Jean, T.C. Sandreczki, Positronium formation at free-volume sites in the amorphous regions of semicrystalline PEEK, J. Polym. Sci. B: Polym. Phys. 27 (1990) 1419-1424.

[10] C.L. Wang, T. Hirade, F.H.J. Maurer, M. Eldrup, N.J. Pedersen, Free-volume distributionand positronium formation in amorphous polymers: temperature and positron-irradiation-time dependence, J. Chem. Phys. 108 (1998) 4654-4661.

[11] E. Lizundia, J.L. Vilas, A. Sangroniz, A. Etxeberria, Light and gas barrier properties of PLLA/metallic nanoparticles composite films, Eur. Polym. J. 91 (2017) 10-20.

[12] O. Miguel, J.J. Iruin, M.J. Fernandez-Berridi, Survey on Transport Properties of Liquids, Vapors, and Gases in Biodegradable Poly(3-hydroxybutyrate) (PHB) J. Appl. Polym. Sci. 64 (1997) 1849-1859.

[13] A. Sangroniz, L. Sangroniz, N. Aranburu, M. Fernández, A. Santamaria, M. Iriarte, A. Etxeberria, Blends of biodegradable poly(butylene adipate-co-terephthalate) with poly(hydroxi amino ether) for packaging applications: Miscibility, rheology and transport properties, Eur. Polym. J. 105 (2018) 348-358.

[14] A. Etxeberria, A. Garcia, M. Iriarte, J.J. Iruin, C. Uriarte, Transport properties of trogamid: Comparison of different experimental techniques, J. Appl. Polym. Sci. 102 (2006) 2034-2042.

[15] Y. Yampolskii, I. Pinnau, B.D. Freeman, Materials Science of Membranes, John Wiley & Sons Ltd., London, 2006.

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

[17] M.H. Klopffer, B. Flaconnèche, Transport properties of gases in polymers: bibliogreaphic review, Oil Gas Sci. Technol. 56 (2001) 223-244.

[18] D.R. Paul, S. Newman, Polymer Blends, Academic Press Inc., New York, 2012.

[19] A. Sangroniz, A. Chaos, M. Iriarte, J. del Río, J.-R. Sarasua, A. Etxeberria, Influence of the Rigid Amorphous Fraction and Crystallinity on Polylactide Transport Properties, Macromolecules 51 (2018) 3923-3931.

[20] R. Shogren, Water Vapor Permeability of Biodegradable Polymers, J. Environ. Polym. Degrad. 5 (1997) 91-95.

[21] S. Eceolaza, M. Iriarte, C. Uriarte, A. Etxeberria, Barrier property enhancement of polyamide 6 by blending with a polyhydroxyamino-ether resin, J. Polym. Sci. B: Polym. Phys. 47 (2009) 1625-1634.

[22] J.E. White, H.C. Silvis, M.S. Winkler, T.W. Glass, E. Kirkpatrick, Poly(hydroxyaminoethers): a new family of epoxy-based thermoplastics, Adv. Mater. 12 (2000) 1791-1800.

[23] D.J. Brennan, J.E. White, A.P. Haag, S.L. Kram, M.N. Mang, S. Pikulin, C.N. Brown, Poly(hydroxy amide ethers): New High-Barrier Thermoplastics, Macromolecules 29 (1996) 3707-3716.

[24] A. García, S. Eceolaza, M. Iriarte, C. Uriarte, A. Etxeberria, Barrier character improvement of an amorphous polyamide (Trogamid) by the addition of a nanoclay, J. Membrane Sci. 301 (2007) 190-199.

[25] X. Hong, Y.C. Jean, H. Yang, S.S. Jordan, W.J. Koros, Free-Volume Hole Properties of Gas-Exposed Polycarbonate Studied by Positron Annihilation Lifetime Spectroscopy, Macromoelcules 29 (1996) 7859-7864.

[26] S. Kanehashi, T. Nakagawa, K. Nagai, X. Duthie, S. Kentish, G. Stevens, Effects of carbon dioxide-induced plasticization on the gas transport properties of glassy polyimide membranes, J. Membrane Sci. 298 (2007) 147-155.

[27] R.J. Boyce, W.H. Bauer, E.A. Collins, Flow behavior of low molecular weight polybutadiene, carboxyl-polybutadiene, and butadiene-acrylonitrile copolymers, T. Soc. Rheol. 10 (1966) 545-570.

[28] L.L. Blyler, T.W. Haas, The influence of intermolecular hydrogen bonding on the flow behavior of polymer melts, J. Appl. Polym. Sci. 13 (1969) 2721-2733.

[29] E.A. Collins, T. Mass, W.H. Bauer, Influence of chemical nature on flow behavior of polymers. I. Shear rate and temperature dependence, Rubb. Chem. Technol. 43 (1970) 1109-1115.

[30] M. Jacovic, M. Yamada, W.J. Macknight, R.S. Porter, Rheological properties of partially hydrolyzed ethylene-vinyl acetate copolymers, J. Appl. Polym. Sci. 20 (1976) 1321-1330.

[31] T.R. Earnest, W.J. Macknight, Effect of hydrogen bonding and ionic aggregation on the melt rheology of an ethylene-methacrylic acid copolymer and its sodium salt, J. Polym. Sci. B: Polym. Phys. 16 (1978) 143-157.

[32] R.A. Weiss, P.K. Agarwal, Influence of intermolecular interactions on the melt rheology of a propylene-acrylic acid copolymer and its salts, J. Appl. Polym. Sci. 26 (1981) 449-462.

[33] R. Stadler, L. de Lucca Freitas, Thermoplastic elastomers by hydrogen bonding 1. Rheological properties of modified polybutadiene, Colloid Polym. Sci. 264 (1986) 773-778.

[34] L. de Lucca Freitas, R. Stadler, Thermoplastic elastomers by hydrogen bonding 3. Interrelations between molecular parameters and rheological properties, Macromolecules 20 (1987) 2478-2485.

[35] C.L. Lewis, K. Stewart, M. Anthamatten, The influence of hydrogen bonding sidegroups on viscoelastic behavior of linear and network polymers, Macromolecules 47 (2014) 729-7740.

[36] Z. Zhang, Q. Chen, R.H. Colby, Dynamics of associative polymers, Soft Matter 14 (2018) 2961-2977.

[37] R.B. Bird, R.C. Armstrong, O. Hassager, Dynamics of Polymeric liquids: Fluid Mechanics, Wiley and sons, New York, 1987.

[38] Z. Yang, C.D. Han, Rheology of Miscible Polymer Blends with Hydrogen Bonding, Macromolecules 41 (2008) 2104-2118.

[39] C. Elster, J. Honerkamp, J. Weese, Using regularization methods for the determination of relaxation and retardation spectra of polymeric liquids, Rheol. Acta 30 (1991) 161-174.

[40] J. Honerkamp, J. Weese, A nonlinear regularization method for the calculation of relaxation spectra, Rheol. Acta 32 (1993) 65-73.

[41] M. Nofar, A. Maani, H. Sojoudi, M.C. Heuzey, P.J. Carreau, Interfacial and rheological properties of PLA/PBAT and PLA/PBSA blends and their morphological stability under shear flow, J. Rheol. 59 (2015) 317-333.

[42] R. Al-Itry, K. Lamnawar, A. Maazouz, Biopolymer Blends Based on Poly (lactic acid): Shear and Elongation Rheology/Structure/Blowing Process Relationships, Polymers 7(12) (2015) 939-962.

[43] L.J. Kasehagen, C.W. Macosko, Nonlinear shear and extensional rheology of long-chain randomly branched polybutadiene, J. Rheol. 42 (1998) 1303-1327.

[44] L. Sangroniz, A. Sangroniz, A. Alegría, M. Fernández, L. Irusta, A.J. Müller, A. Etxeberria, A. Santamaria, Effect of hydrogen bonding on the physicochemical and rhelogical features of chemically modified phenoxy, Polymer 159 (2018) 12-22.