Tributyl citrate as an effective plasticizer for biodegradable polymers: effect of the plasticizer on the free volume, transport and mechanical properties

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Abstract

The effectiveness of tributyl citrate (TbC) as plasticizer for polylactide (PLLA) and poly(hydroxybutyrate) (PHB) was analyzed in order to improve the ductility of these polymers and make them good candidates for food packaging applications. Although the thermal and mechanical properties have been widely studied in literature the effect of the plasticizer on free volume and transport properties have not been deeply analyzed. The free volume was characterized by

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positron annihilation lifetime spectroscopy observing its linear increase with the TbC content. The permeability to water vapor, oxygen and carbon dioxide was determined and the obtained results were related to the changes on glass transition temperature, the crystallinity level of the samples and free volume. This work would allow a better understanding of the effect of the plasticizer on the barrier and mechanical properties of polymers allowing the development of competitive materials for packaging applications.

Keywords: Biodegradable polymer; plasticizer; free volume; transport properties; packaging

Introduction

The growing awareness about the environment and Government regulations have led to the development of new materials that are more respectful with the environment. On the search of more sustainable materials, biodegradable and bio-based polymers have attracted a great attention.[1]

In literature great efforts have been made to tune the properties of biodegradable polymers specially in the case of PLLA and PHB, since they usually show low ductility and flexibility. In order to obtain suitable materials for packaging applications different approaches have been carried out; such as the addition of plasticizers, which is a cheap and simple method. For food packaging applications the selection of the plasticizer is limited by the Government regulations and only additives agreed for food contact can be employed.

Among biodegradable polymers polylactide has been widely studied specially for biomedical applications since it shows good biocompatibility. The improvements carried out the last years have allowed a more economic production of this polymer broadening its applications.[2] Therefore, it is an interesting material for packaging, since it presents adequate properties such as strength, stiffness and optical properties. However, PLLA has poor ductility, therefore several approaches have been carried out to overcome this disadvantage. In order to improve the low ductility and low toughness of polylactide, plasticizers such as different citrates and glycols have been used: triethyl citrate, trybutyl citrate, acetyl triethyl citrate, acetyl tributyl citrate[3], poly(ethylene glycol), poly(propylene glycol) etc.[4] However, the use of plasticizers could compromise the barrier properties so a study on the relation between free volume, glass transition temperature and permeability is necessary.

Another polymer that has attracted great interest in the last years is poly(hydroxybutyrate), a biodegradable polymer of the family of poly(hydroxyl alkanoates). It presents excellent barrier properties[5,6] however it has high crystallinity degree, is brittle and stiff. Several plasticizers have been studied in order to increase the ductility: triethyl citrate, tributyl citrate[7], Lapol 108[8], glycerol, poly(ethylene glycol), tri(ethylene glycol) bis(2-ethylhexanoate)[9], triacetyl glycerol, dioctyl phthalate and dioctyl adipate, among others.[10] However no extensive works have been performed to analyze the relation between the free volume and transport properties in plasticized polymers.

The aim of this work is to determine the effect of the addition of a plasticizer in the free volume and consequently, in the transport and mechanical properties. Although there is a huge amount of works that deal with the thermal and mechanical properties of PLA/TbC and PHB/TbC systems, to our knowledge, there is not sound work regarding the free volume and transport properties. The addition of the plasticizer would lead to the increase of permeability, however the mechanical properties must be improved to broaden the applications of these polymers, especially in the PHB case. Tributil citrate has been selected as plasticizer since it is biocompatible and non-toxic.[11] The plasticizing effect of TbC has been analyzed by means of changes in glass transition temperature, crystallinity degree, mechanical properties and free volume. Furthermore, the relation between the free volume and permeability to oxygen, carbon dioxide and water vapor is studied.

Experimental part

Poly(L-lactide) (weight-average molecular weight M_w = 150000 g/mol and a polydispersity index of 1.2) with a L:D isomer ratio 98:2, was purchased from Natureworks. Poly(hydroxybutyrate) (M_w = 437 000 g/mol and a polydispersity index of 1.7) and Tributyl citrate were obtained from Aldrich and Fluka, respectively.

Polylactide samples were prepared by solution/evaporation process using chloroform as a solvent. Blends with 2.5, 5 and 10 % of TbC (in weight) were prepared and the membranes obtained were dried in vacuum and at room temperature for at least one weak. The thickness of the membranes is between 50-130 μm, 300-400 μm and 1 mm for permeability, tensile and PALS measurements, respectively.

Poly(hydroxybutyrate) blends were obtained heating the solution under reflux. Blends containing 2.5, 5, 10 and 20 % TbC (in weight) were prepared. The membranes were annealed at 80 °C for one week and dried at vacuum at room temperature for another week to ensure crystallization until completion. The thickness of the membranes for water permeability is between 8-12 μm and for oxygen and carbon dioxide between 45-55 μm. Mechanical properties were characterized for films with 300-400 µm thickness and 1 mm for PALS measurements.

Differential Scanning Calorimetry

Samples of approximately 5 mg were encapsulated in aluminum pans and measurements were performed in a TA Instrument Q2000 V24 calorimeter. The thermal program employed was as follows: first a heating ramp was carried out from -80 °C for PHB and from -50 °C for PLLA to 200 °C at 10 °C/min. Then a cooling scan is performed down to -80 °C and -50 °C for PHB and PLLA, respectively, at 80 °C/min and a second heating scan up to 200 °C at 10 °C/min.

The crystallinity of the samples has been calculated employing the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100 \qquad (1)$$

where ΔH_m^0 is 93 J/g for PLLA[12] and 146 J/g for PHB[13]. The crystallinity of PLLA and PHB has been normalized taken into account the plasticizer content.

Positron annihilation lifetime spectroscopy

Positron lifetime spectra were recorded using a fast-fast nuclear spectrometer with a time resolution (full width at half maximum) 230 ps. Measurements were performed using a positron source that was prepared by depositing ^{22}NaCl onto a Kapton foil. The procedure has been described in more detail elsewhere.[14] Lifetime spectra were registered and analyzed using the program PATFIT-88.

According to the theory developed by Eldrup[15] the lifetime of the ortho-positronium, τ_3, and the free volume hole radius, *R,* are related by the following equation,

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

where R_0 is $R_0 = R + \Delta R$ and ΔR is an empirical parameter with value 1.66 Å. Assuming that the shape of the free volume hole is spherical we can calculate the mean free volume hole size using the following equation,

$$V_H = \left(\frac{4\pi R^3}{3}\right) \qquad (3)$$

The fractional free volume can be calculated combining the free volume hole size and the intensity of the free volume, I_3, that is related to the number of free volume holes.

$$f = cV_H I_3 \qquad (4)$$

c is a characteristic parameter for each material and is between 0.001-0.002. However, its determination is not easy and some authors chose arbitrarily an intermediate value (c = 0.0015) while other authors define the apparent free fractional volume,[14]

$$f_{app} = V_H I_3 \qquad (5)$$

Some authors state that I_3 depends on the positron source activity, the chemical composition of the polymer and the thermal history of the samples. However relative free volume values obtained from the equation 5 are widely accepted in the literature.[16]

Mechanical properties

Tensile measurements were conducted with an Instron 5565 testing machine at a crosshead displacement rate of 5 mm/min and 22 °C. Films with a thickness between 300-400 μm were employed and the specimens were cut according to ASTM D638 type V. At least 6 specimens were tested for each reported value.

Oxygen permeability

The measurements were performed in a MOCON OX-TRAN 2/21 MH Model in accordance with ASTM standard D3985. The permeability was measured at 1 atm, 23 °C and 0 % relative humidity.

Carbon dioxide permeability

Carbon dioxide permeability for PLLA was measured employing a laboratory made equipment that has been described elsewhere.[17,18] It consists of a stainless steel cell in which the polymeric membrane is placed separating the upstream and downstream chambers. The increase of the pressure at the downstream chamber is measured and the permeability is calculated from the slope of the pressure vs time plot.

The permeability to carbon dioxide for PHB and its blends has been determined in a Cahn D-200 electrobalance at 25 °C. The films have been degassed under vacuum in the electrobalance until constant weight was obtained. The measurements were performed at 1 atm until the equilibrium was reached. Further details about the equipment and method have been described elsewhere.[19]

Water vapor permeability and sorption

Water vapor permeability was measured using a permeation gravimetric cell at 25 °C according to ASTM E96-95 standard. The cell is a small container that is partially filled with water and is sealed by the polymeric membrane. The cell is placed on a Sartorius balance with 10^{-5} g readability and the weight loss is recorded on a computer.[5,20,21] Sorption experiments were performed in the IGA-2 Hiden electromagnetic balance at 25.5 °C and 0.24-0.92 water vapor activity. More details about the equipment and method have been described elsewhere.[22]

Results and discussion

Thermal properties

The characterization of the glass transition temperature is the most employed method to determine the miscibility of polymer blends. Blends that show a single glass transition temperature are miscible, whereas blends showing two transitions are immiscible.

Glass transition temperature (T_g), melting temperature (T_m) and crystallinity of PLLA/TbC and PHB/TbC blends ($X_{c\,PLLA}$ and $X_{c\,PHB}$, respectively) are shown in Table 1. Glass transition temperature has been determined from the second scan, whereas the melting temperature and crystallinity have been determined from the first scan. First DSC heating scans of PLLA/TbC and PHB/TbC are shown in Figure 1 and Figure 2, respectively.

Table 1

Table 1 shows that tributyl citrate decreases the glass transition temperature of polylactide and poly(hydroxybutyrate). The addition of TbC increases the molecular mobility reducing the glass transition temperature and confirming the plasticizing effect of the additive. The addition of the plasticizer is more effective at lower contents in the case of PLLA, at high TbC contents the reduction in the glass transition temperature is lower than expected.

Some theoretical models have been applied and it has been observed that the data deviates negatively from the mixture rule. This is a typical behavior in blends in which the interactions between the two components are weak.[23] Fox model has been applied (see Figure S1 and S2 in supporting information) observing that for PHB/TbC blends the model predicts quite well the glass transition temperature until a 20 % TbC content, when it deviates considerably from the prediction. For PLLA/TbC system the experimental values deviate positively from the glass transition temperature prediction indicating that phase separation occurs.[24]

Comparing the two systems the plasticization is more effective for PLLA since for all the compositions the reduction on the glass transition temperature is higher than for PHB. For example: at 5 % TbC a decrease of 9 °C is found for PLLA whereas for PHB the reduction is only of 6 °C. Although these differences could be consider not significant, glass transition of pure polymers must be taken into account: the T_g of PLLA is above the room temperature (55.5 ° C) while in the case of the PHB its T_g is below (-1.2 °C). In both cases, the plasticizer increases the chain mobility, but its greater effectiveness in the case of PLA could come from the fact that the greater proximity of the T_g of the PLLA-TbC mixtures to room temperature may imply a larger relative increase of mobility in comparison to the PHB-TbC samples. Later, we will return to this point.

In addition, the second aspect to be considered is the crystallinity of the sample, for the PHB the high crystallinity raises the glass transition temperature.[25] The results obtained for plasticized PLLA and PHB are very similar to that reported in literature for different citrates[3,7,26], glycols of low molecular weights[4] and esters.[8-10]

The melting temperature of PLLA is decreased with TbC, being the reduction proportional to the plasticizer content. The melting point depression is an indicator of polymer blends miscibility that arises from thermodynamic factors and morphological effects.[11]

Crystallinity of pure PLLA is about 26 %, similar to that obtained by other authors[27] and it shows cold crystallization, (ΔH_{cc} = 4 J/g and T_{cc} =159.6 °C). For the blends the crystallinity increases with TbC content since the plasticizer enhances the chain mobility promoting the crystallization of PLLA.

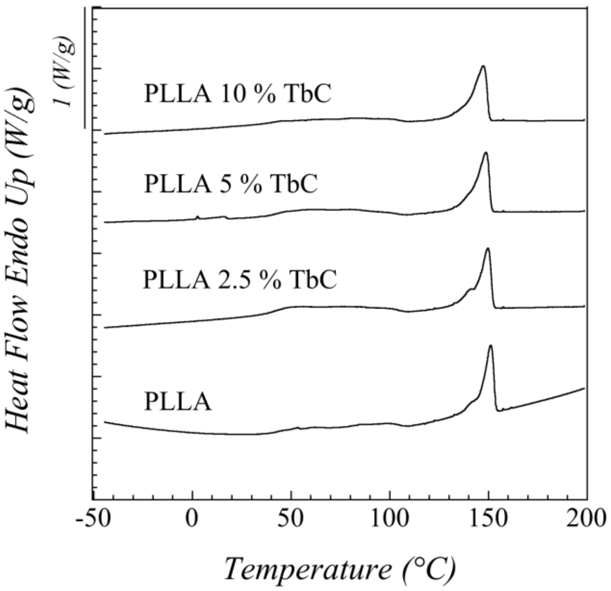

Figure 1. First DSC heating scans of PLLA/ TbC blends.

Poly(hydroxybutyrate) shows two melting peaks: one located at 170.3 °C and the other one at 155.4 °C that is attributed to the melting and rearranging process.[7] The latter has been also attributed to the bimodal crystal size distribution provoked by the reduction on the molecular weight due to random scission of polymer chains when the polymer is melt processed.[7,28] The addition of plasticizer decreases gradually both melting temperatures, being the change most noticeable in the peak located at lower temperatures.

It is worthy to note that the crystallinity of PHB is very high, 64 %, and it increases with plasticizer content. Therefore, the addition of the plasticizer facilitates the segmental mobility of the chains promoting further the crystallization of PHB.[29]

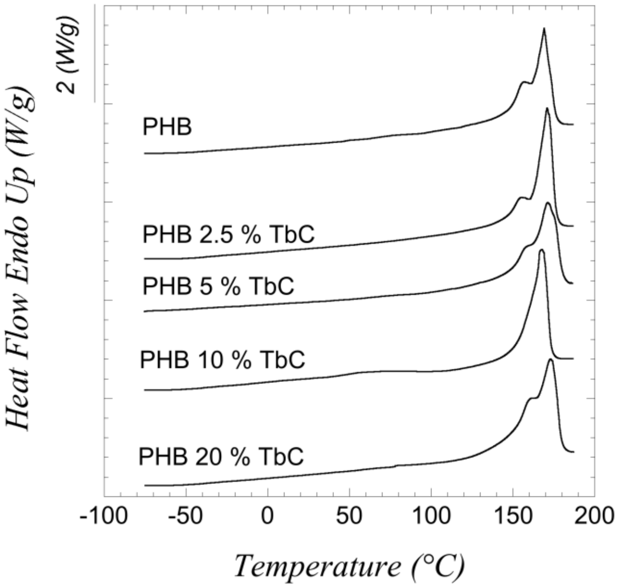

Figure 2. First DSC heating scans of PHB/TbC blends.

Free volume

Positron annihilation lifetime spectroscopy (PALS) has been carried out to gain insight into the effect of the plasticizer in the free volume. This technique provides both the free volume hole size, V_H, and the relative intensity, I_3, and the apparent fractional free volume can be estimated from Equation 5, playing all these magnitudes a fundamental role in the transport properties.

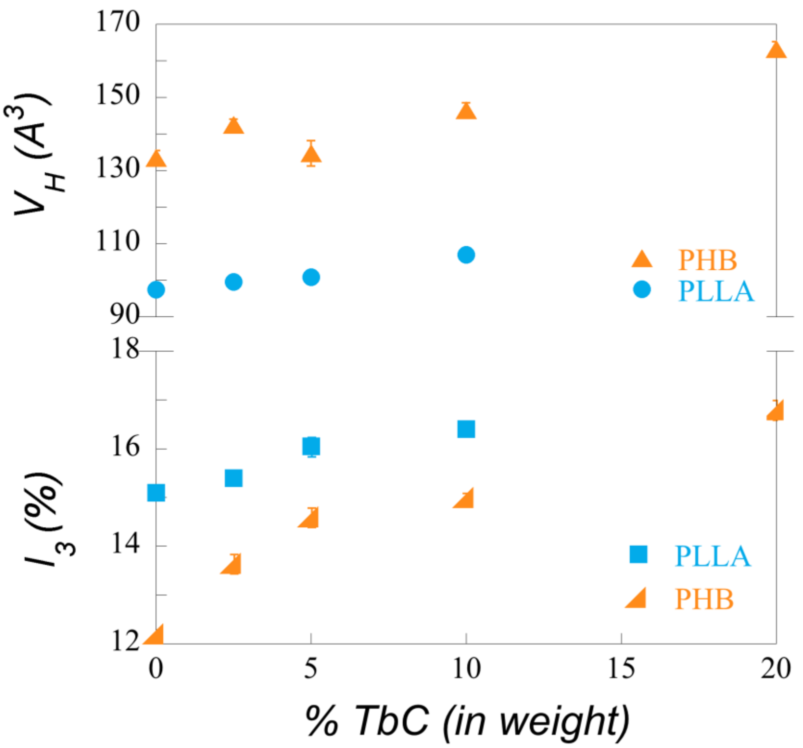

Figure 3. Relative intensity and mean free volume hole size for plasticized PLLA and PHB blends.

Analyzing the two polymers, see Figure 3, it is remarkable the increase of the intensity, related to the free volume hole number, with the addition of TbC, specially below 5 % TbC. PLLA shows higher free volume hole number than PHB, however the addition of TbC causes a major increase of the intensity on PHB, for example for 2.5 % of TbC the intensity increases a 2 % for PLLA, whereas for PHB an increase of 14 % is observed.

Concerning the free volume hole size it can be observed in Figure 3 that for PLLA and PHB the size increases gradually with plasticizer content. The increase is higher for PHB than for PLLA as occurs in I_3. It is worthy to note that poly(hydroxybutyrate) with 2.5 % TbC deviates from the observed trend.

Figure 4 shows the apparent fractional free volume that encompasses the two parameters analyzed previously. The fractional free volume increases linearly for the two polymers with the plasticizer content. The plasticizer molecules locate between polymer chains, interrupting the polymer-polymer interaction and increasing chain mobility, which leads to a higher free volume.[30] For PHB a greater increase in the free volume is found with the addition of the plasticizer. It has to been taken into account that the free volume is principally located in the amorphous regions and that the high crystallinity of PHB, 64 %, provokes that its amorphous region will contain more plasticizer comparing to that of PLLA. However, the plasticizer is more efficient lowering the glass transition of PLLA than that of PHB that can be attributed to the constraining effect of crystals taking into account the high crystallinity level of PHB. In literature it have been widely accepted that the addition of plasticizer increases the mobility of polymer chains decreasing T_g and generating more free volume. However, these results reveal that the effect of a plasticizer on the T_g and free volume of two polymers is not directly related, and this is an issue of great importance in order to analyze different properties, such as mechanical and transport properties that are analyzed in the following section.

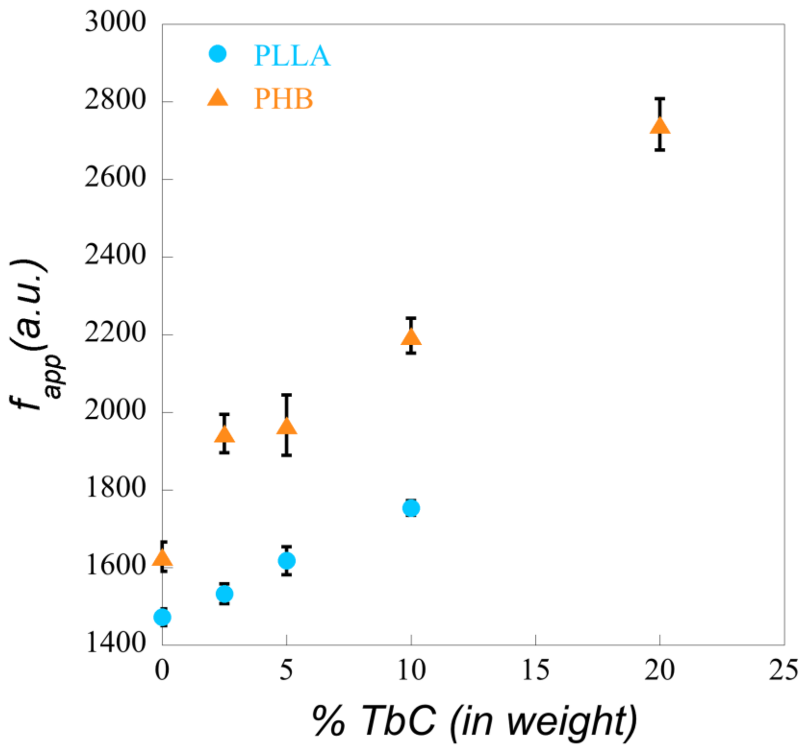

Figure 4. Apparent fractional free volume for plasticized PLLA and PHB.

Mechanical properties

The plasticizer is added to decrease the stiffness and the brittleness and to increase the ductility of the polymer. The addition of a low molecular weight plasticizer reduces the polymer-polymer interaction decreasing the chain cohesion.[31]

Table 2.

In Table 2 the mechanical properties of plasticized PLLA and PHB are shown, the figures of the mechanical properties are shown in supporting information Figure S3, S4 and S5. Polylactide shows a Young´s modulus of 2480 ± 270 MPa, tensile strength of 57 ± 6 MPa and elongation at break of 4.2 ± 0.6 %. The obtained results for polylactide are in great accordance with the data reported in literature except Young´s modulus, which is higher than expected.[31,32] With the addition of plasticizer a decrease in the Young´s modulus and tensile strength and an increase in the elongation at break are observed, as expected for polymer/plasticizer blends. The reduction of Young´s modulus and tensile strength is not directly related to plasticizer composition. For applications in which good tensile strength and stiffness are needed the blend with 5 % TbC shows interesting characteristics.

The tensile strength values obtained are similar to that reported by Harte et al.[26] for the same system. It is worthy to note that citrate plasticizers[26] seem to be more effective than other plasticizers like poly(propylene glycol) and poly(ethylene glycol).[4,33] However, these results need to be interpreted with caution since the polymers and preparation methods influence the results obtained.

Poly(hydroxybutyrate) exhibits a Young´s modulus of 5460 ± 340 MPa, and an ultimate stress (tensile strength) of 37 ± 5 MPa, being the Young´s modulus very high comparing to the data reported in literature.[10,34] The elongation at break is only 0.7 ± 0.0 %, much lower than that of PLLA although both get to break in brittle mode before yielding. This explains also the low value of ultimate stress obtained for PHB and is attributed to the high crystalline fraction obtained in regard to PLLA. PHB/TbC blends show also a decrease in Young´s modulus and tensile strength although no direct relation with the plasticizer amount is found.

Reviewing the data reported in literature for plasticized PHB the reduction found in the tensile strength is similar to that provoked by triacetyl glycerol (TAG) and dioctyl adipate (DOA)[10] being the plasticizers that most reduce the tensile strength of PHB. For Young´s modulus the highest decrease is obtained with TbC, being similar to TAG.[10]

Comparing the two systems it can be concluded that the addition of TbC provokes a greater decrease on Young´s modulus in PHB than in PLLA, on the other hand for the tensile strength there are not great differences.

The elongation at break for PLLA increases with the addition of TbC, being this rise directly related with the plasticizer content. The obtained elongation at break for plasticized polylactide is much lower than the data reported in literature with other plasticizers like citrates and glycols.

Concerning PHB a great increase in the elongation at break is found respect to other plasticizers studied in literature for PHB.[7,8,10] However, careful attention must be paid since the polymer and preparation methods are different and this could affect significantly the final properties including thermal and mechanical properties.

Comparing to PLLA blends higher increments of elongation at break are obtained for the plasticized PHB blends, which is consistent with the free volume changes observed in both cases. In any case the improvement of the elongation at break for both polymers is very small. The crystallization of the polymer provokes the phase separation of the plasticizer increasing its content in the amorphous phase that leads to premature failure.[35] In order to obtain better results higher amount of plasticizer must be added.[3] However, in this case low plasticizer content is added to minimize the migration of the plasticizer. In this way the composition of the blend is well established and it can be related to PALS and transport properties.

Transport properties

Oxygen permeability

Oxygen provokes oxidation reactions, such as fat rancidity, vitamin oxidation and the growth of aerobic microorganisms. This provokes deterioration of color, changes in flavor and the creation of toxic compounds. Therefore, the characterization of the oxygen permeability is of great importance since it plays a major role in the shelf life of food.

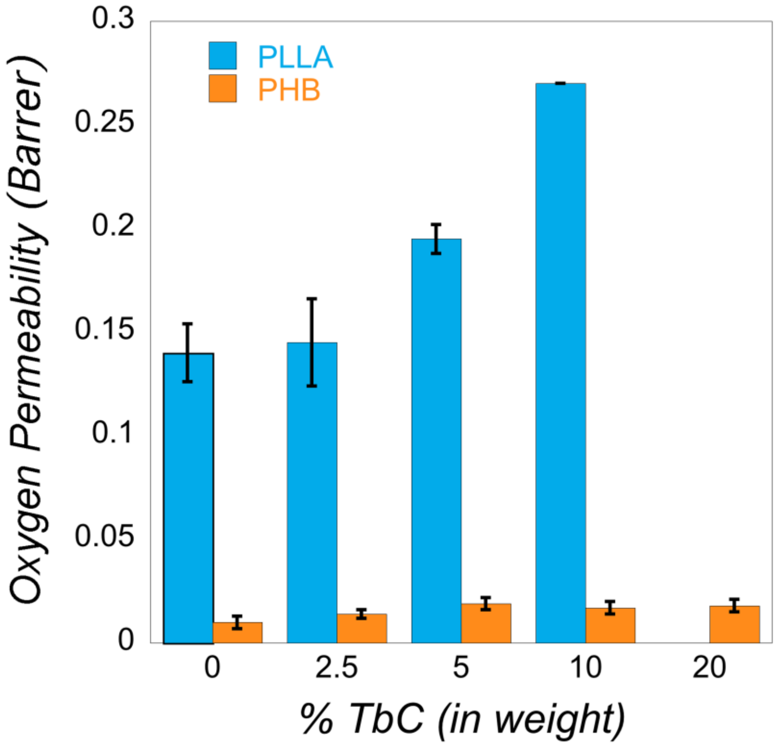

Figure 5. Oxygen permeability for PLLA and PHB with tributyl citrate.

Figure 5 shows the oxygen permeability values for PLLA and PHB blends, see Table S1 in supporting information for permeability coefficients. Polylactide presents a value of 0.14 Barrer that is the same value reported by Bao et al.[36] and slightly lower than that reported by others authors that are about 0.26 Barrer.[37] The permeability results obtained for plasticized polylactide blends increase gradually with the addition of tributyl citrate.

Poly(hydroxybutyrate) presents a permeability to oxygen of 0.01 Barrer, which makes PHB a quite good barrier material comparable to intermediate and high oxygen barrier materials like poly(ethylene terephthalate),[38] polyamide 6[39] and poly(ethylen vinyl alcohol).[40] For plasticized blends, see Figure 3, the permeability to oxygen increases significantly with the amount of the plasticizer, despite this great increase all the blends show a low permeability to oxygen.

PLLA and all PLLA/TbC blends show permeability values ten times higher than those of poly(hydroxybutyrate) revealing the good barrier properties of PHB. These results are analyzed at the end of this section.

Carbon dioxide permeability

Another penetrant of great interest is carbon dioxide, in spite of its limited presence on the air, it plays a major role in modified atmosphere packaging since it can stimulate or inhibit the growth of microorganisms.

Permeability values of polylactide and poly(hydroxybutyrate) plasticized blends measured by a direct and indirect permeation method respectively, are shown in Figure 6, see Table S2 in supporting information for permeability coefficients. The permeability value obtained for neat polylactide, 0.5 Barrer, is lower than that reported by others authors[41,42] that can be attributed to the different preparation methods employed. For the blends containing TbC carbon dioxide permeability rises with the addition of the plasticizer. It is worth highlighting that with the addition of 10 % TbC the permeability is three times higher than in pure PLLA.

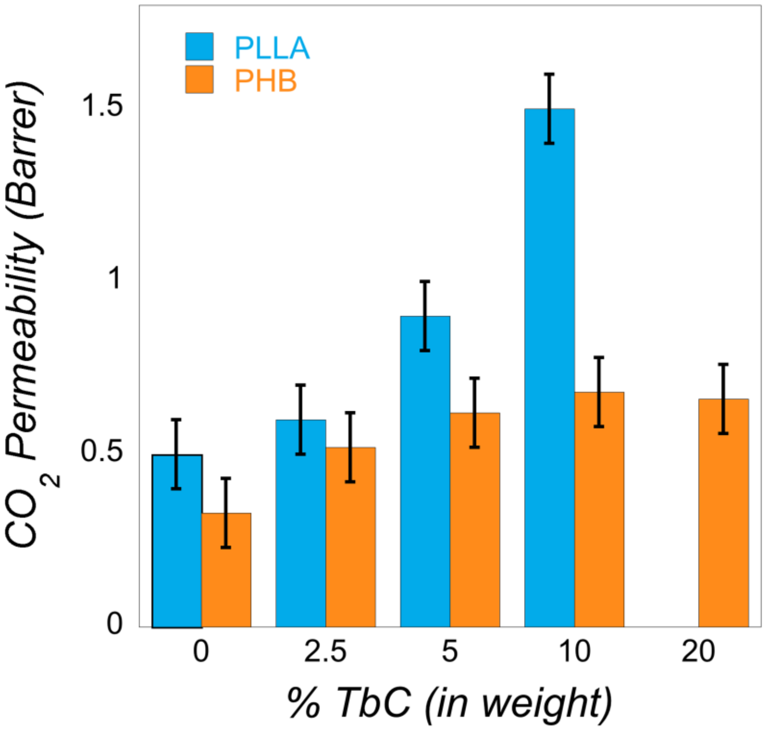

Figure 6. Carbon dioxide permeability for plasticized polylactide and poly(hydroxybutyrate), obtained by direct and indirect method respectively.

Permeability for PHB and its blends have been obtained by indirect permeation method, employing the following expression $P = D \times S$, the data is shown in Figure 6. Poly(hydroxybutyrate) has a value of 0.33 Barrer, which is in accordance with the data reported in literature[43], a value lower than that obtained for PLLA, that is the trend observed for all the penetrants. Plasticized PHB blends exhibit higher permeability values: with TbC content in the range of 5-20 % the permeability is almost two times higher. It can be seen that a plateau is reached which lead us to the conclusion that for the samples richer in TbC the higher crystallinity level counteracts the effect of the plasticizer.

Table 3

The amorphous solubility of plasticized poly(hydroxybutyrate) blends are reported in Table 3. No clear trend in the solubility parameter with the addition of the plasticizer is found although the changes are slight.

Diffusion increases slightly with plasticizer content and the variation is directly related to the changes in the free volume hole size and especially free volume intensity, being the tendency of the last one the same as the diffusion. PHB containing 5 % TbC shows a diffusion coefficient larger than expected due to the lower crystallinity level of the sample. It is considered that crystals are impermeable and they increase the tortuosity decreasing the diffusion coefficient.

Water vapor transmission rate

The characterization of water vapor permeability is of great interest since it can affect the food quality and safety. For bakery products low permeability to water vapor is desired since the water can provoke the loss of crispness and the growth of yeasts and molds, however for fresh vegetables and fruits permeability to water is necessary to maintain the product hydrated.[44]

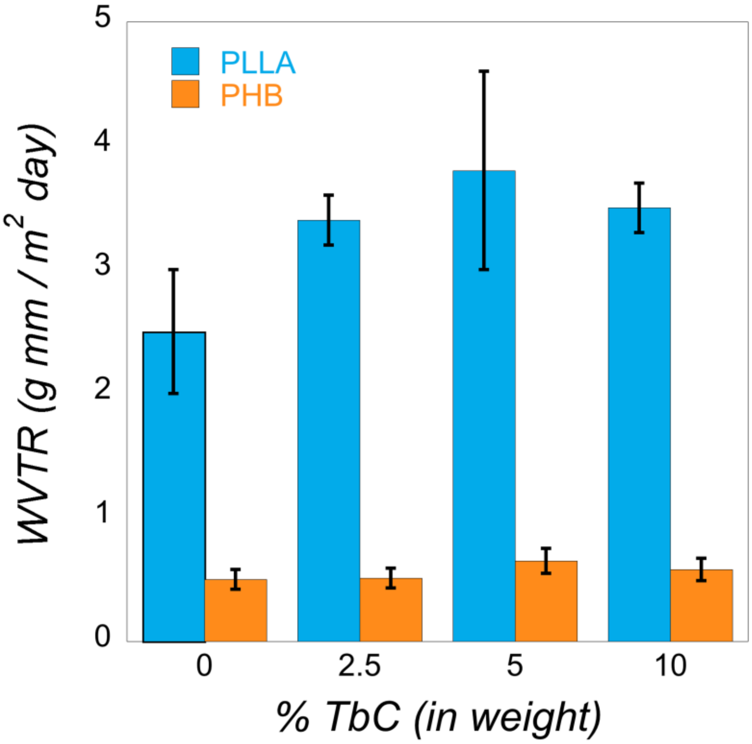

Figure 7. Water vapor transmission rate of plasticized PLLA and PHB.

Figure 7 shows the water vapor transmission rate for PLLA and PHB blends, the permeability coefficients are reported in Table S3 in supporting information. As can be seen in Figure 7 PLLA shows a water vapor transmission rate of 2.5 g mm/m^2 day, which is in accordance with the data reported in literature.[45,46,47] The plasticized blends exhibit a higher water vapor transmission rate: for all the blends the addition of the plasticizer increases WVTR more than 30 % but not clear relation between the composition and the permeability is found. For 10 % of TbC a value lower than expected is found but there is no correlation with sample crystallinity. Therefore, further studies have been carried out analyzing the sorption process of water vapor in PLLA/TbC system, that are shown in the next section, which could allow us to gain insight into the role of solubility and diffusion in the obtained results.

Poly(hydroxybutyrate) has a water vapor transmission rate of 0.50 g mm/m^2 day, which is a low value and comparable to poly(ethylene terephthalate) and polyamide 6,6 and similar to that reported previously in literature.[48] The high crystallinity level, that reduces the permeability, makes PHB a good barrier material. The addition of TbC increases gradually the water vapor permeability with plasticizer composition except for 5 % TbC, which exhibits a higher permeability value than expected due to the lower crystallinity of the blend.

Water vapor transmission rate for different PHB/plasticizer blends have been analyzed in literature.[49] Among different citrates studied, such as tributyl citrate, triethyl citrate and acetyl tributyl citrate, the blends containing TbC show the lowest permeability. Rapa et al. found that the addition of plasticizer increases significantly the permeability. Curiously in our case the changes are not so significant, probably the differences in preparation method, crystallinity level, film thickness and measurement technique provoke these dissimilarities in the obtained values.[49]

For both polymers the relationship between tributyl citrate content and water vapor transmission rate is not lineal witch leads us to the conclusion that clustering process or plasticizing by water occurs.

Overall, the transport properties values obtained indicate that the increase in the permeability with the addition of TbC can be attributed to two effects: the apparent fractional free volume that increases with TbC content and the decrease in the glass transition temperature. Both effects, in general, tend to increase the solubility and diffusion coefficients.[50] The addition of plasticizer decreases the T_g of the blend and this can lead to changes in the sorption mode:

the sorption of glassy polymers is usually described by the dual-model in which two types of sorption occur: Langmuir and Henry. On the other hand the solubility of rubbery polymers obeys Henry´s law. Therefore the decrease on the glass transition temperature may provoke an increase in the Henry-site contribution.[50]

Taking into account the data of the free volume, crystallinity and glass transition temperature reduction it can be deduced that in the case of PHB the crystallization overbalances, even overcomes, the other two effects.

Returning to the discussion about the effectiveness of TbC as a plasticizer, from the point of view of a barrier material we have observed for the three studied penetrants that the permeability increase in the PLLA-TbC system is significantly higher than in the PHB-TbC system, with similar decreases in T_g in both cases and even larger increase in the crystallinity for the PLLA samples. In our opinion, as mentioned above, these results are due to the fact that in the case of PLLA the T_g is above the room temperature (55.5 ° C) while in the case of the PHB its T_g is below (-1.2 °C). In both cases, the plasticizer increases the chain mobility, but its greater effectiveness in the case of PLLA could be due to the reduction in the T_g which approximates to room temperature, i.e. at temperatures used in permeation measurements, leading to larger relative increase of chain mobility for PLLA samples in comparison to PHB ones.

Water vapor sorption

Equilibrium sorption isotherms for PLLA are shown in Figure 8, see Table S4 in supporting information for water vapor concentration values. The addition of TbC decreases the overall water sorption. This decrease can come from two factors. One; the high crystallinity level compared to neat PLLA and two; water molecules must compete with the interaction between the TbC and PLLA. For all the samples an upward curvature is observed at high activities that is associated to plasticization or clustering phenomena. In plasticization process water molecules weaken polymer-polymer interactions, the glass transition temperature is reduced and the free volume increased. Therefore more water molecules are dissolved and the diffusion coefficient increases.[51] On the other hand, in clustering process water has a tendency to self-interact and water molecules form clusters hindering diffusion.[52,53]

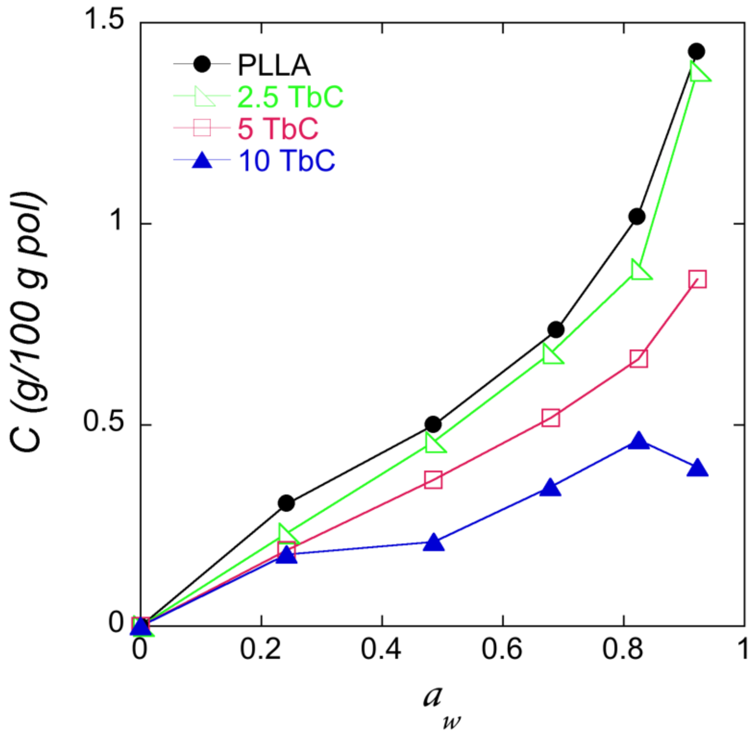

Figure 8. Water vapor sorption isotherms in PLLA/TbC blends.

Oliveira et al.[54] studied the water vapor sorption on PLLA obtaining lower values probably due to the applied thermal treatment that provokes differences in crystallinity and in the free volume and also the different technique employed: they employed a quartz crystal microbalance. Furthermore, they observed Henry type sorption whereas in this case an upturn in the isotherm is observed.

The addition of the plasticizer reduces the glass transition temperature and increases the free volume, which leads to a major chain mobility and higher Henry type sorption. However from the data obtained it can be stated that the plasticizer interacts unfavorably with the water molecules decreasing water sorption.

Table 4

Diffusion coefficients for PLLA/TbC system are reported in Table 4. Diffusion coefficients show a constant value or a slight increase until $a_w = 0.7$ in which a remarkable decrease is observed. This decrease in diffusion and the upturn in the isotherm mentioned previously, indicate that clustering of water molecules occur due to the higher interaction between water molecules than between water and polymer. Zimm and Lundberg provide a function to calculate the cluster size[55],

$$\frac{G_{WW}}{V_W} = -\left(1-\phi_W\right)\left[\frac{\partial\left(a_W/\phi_W\right)}{\partial a_W}\right]_{P,T} - 1 \qquad (6)$$

where G_{ww} is the clustering integral, V_w is the partial molar volume of water, ϕ_w is the water fraction in volume and a_w is the water activity.

Figure 9 shows the average number of water molecules per cluster, as can be observed at low activities monomers are predicted by the model and increasing the water activity higher clusters are formed. The addition of plasticizer decreases the cluster size indicating the presence of favorable interactions between water and plasticizer.

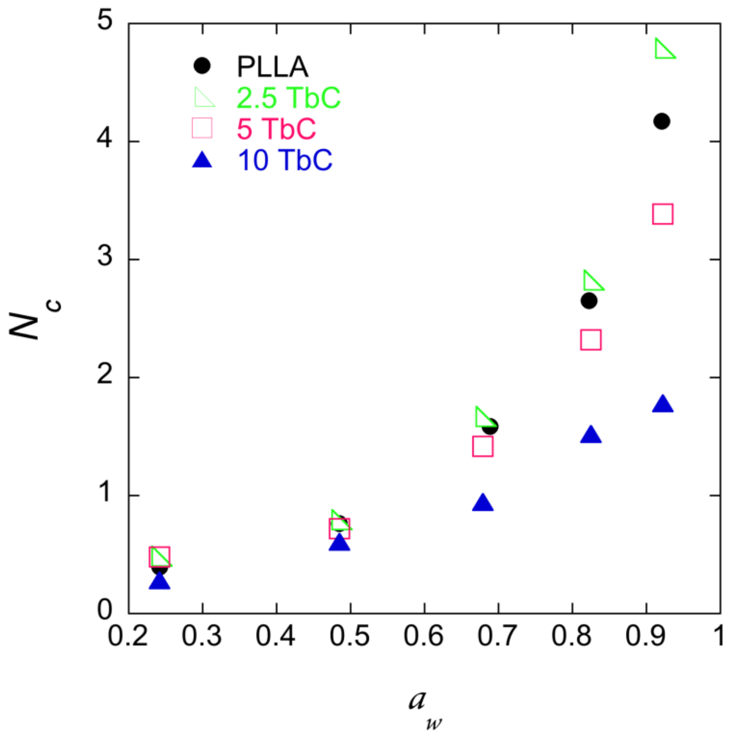

Figure 9. Average cluster size on PLLA/TbC blends over activity.

Conclusions

This work aims at analyzing the effect of the addition of trybutyl citrate plasticizer in the glass transition temperature and free volume and its correlation with transport properties of PLLA and PHB. From the thermal characterization a reduction in the glass transition temperature is observed with plasticizer content, whereas positron annihilation lifetime spectroscopy shows that the apparent free volume fraction increases. The results obtained for both polymers reveal also that the changes provoked by the plasticizer in the glass transition temperature are not directly related to the increase found in the free volume, therefore the effect of the crystalline fraction in both polymer systems has to be considered.

Taking into account the changes induced by the plasticizer in the T_g and free volume of both polymers it can be stated that several factors affect the obtained results: for mechanical properties the increase of the free volume plays a major role, being the effect of the plasticizer more relevant on PHB. However in the transport properties the high crystallinity of PHB is the predominant factor and the permeability increase for PHB/TbC system is less pronounced than for PLLA/TbC system. Furthermore PHB shows outstanding barrier properties despite the addition of plasticizer. Therefore, depending on the application a material with better mechanical performance can be chosen, PLLA/TbC, or a material with a higher barrier character, PHB/TbC. In conclusion, the study carried out provides a better understanding of the plasticization effect which would allow the development of packaging materials with adequate barrier and mechanical properties.

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Tables

Table 1. Thermal properties of plasticized PLLA and PHB blends.

Sample	T_g (°C)	T_m(°C)	$\Delta H_m (J/g)$	$X_{c\ PLLA}$(%)/ $X_{c\ PHB}$(%)
PLLA	55.5	176.7	24	26
PLLA 2.5 % TbC	50.0	178.2	26	29
PLLA 5 % TbC	46.6	175.8	26	30
PLLA 10 % TbC	38.8	173.6	26	31
PHB	-1.2	155.4, 170.3	93	64
PHB 2.5 % TbC	-3.4	155.6, 169.2	90	63

PHB 5 % TbC	-7.1	153.5, 168.3	87	63
PHB 10 % TbC	-14.2	153.7, 169.0	88	67
PHB 20 % TbC	-17.1	151.6, 169.0	84	72

Table 2. Mechanical properties of plasticized PLLA and PHB blends.

Sample	Young Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PHB	5460 ± 340	37 ± 5	0.7 ± 0.0
PHB 2.5% TbC	4320 ± 220	30 ± 5	0.8 ± 0.0
PHB 5% TbC	3680 ± 670	33 ± 5	1.3 ± 0.3
PHB 10% TbC	2210 ± 520	24 ± 1	2.5 ± 0.3
PHB 20% TbC	1640 ± 260	17 ± 1	5.1 ± 0.7
PLLA	2480 ± 270	57 ± 6	4.2 ± 0.6
PLLA 2.5% TbC	1720 ± 210	32 ± 3	3.7 ± 0.2
PLLA 5% TbC	1840 ± 200	31 ± 2	3.0 ± 0.3
PLLA 10% TbC	1460 ± 110	29 ± 7	9.1 ± 3.4

Table 3. Sorption and diffusion coefficients of plasticized poly(hydroxybutyrate).

% TbC	$S_{amorphous}$ (cm^3 STP/ cm^3 cm Hg)	10^{-9} D (cm^2/s)
0	0.030	1.10
2.5	0.031	1.68
5	0.025	2.46
10	0.032	2.15
20	0.027	2.45

Table 4. Diffusion coefficients for PLLA and PLLA/TbC blends.

Sample	a_w	10^8 D (cm^2/s)
PLLA	0.69	2.7
	0.82	2.3
	0.92	2.0
2.5 % TbC	0.24	1.8
	0.48	1.9
	0.68	2.4
	0.82	2.3
	0.92	1.4

5 % TbC	0.24	2.3
	0.48	2.3
	0.68	2.3
	0.83	2.3
	0.92	1.6
10 % TbC	0.24	2.6
	0.48	3.0
	0.68	3.9
	0.83	2.3
	0.92	2.2