

Addition of α -Tocopherol on Poly(lactic acid): Thermal, Mechanical, and Sorption Properties

Carla M. B. Gonçalves,¹ Liliana C. Tomé,¹ João A. P. Coutinho,¹ Isabel M. Marrucho^{1,2}

¹CICECO, Departamento de Química, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

²Instituto de Tecnologia Química e Biológica, ITQB2, Universidade Nova de Lisboa, Av. República, Apartado 127, 2780-901 Oeiras, Portugal

Received 26 February 2010; accepted 11 June 2010

DOI 10.1002/app.32952

Published online 1 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This work investigates the effect of the addition of a well-known antioxidant, α -tocopherol in poly(lactic acid) flexural and barrier properties. For that purpose, films of poly(lactic acid) enriched with 0, 2.2, and 4.4% of α -tocopherol were prepared. Differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis were used to characterize the changes in the mechanical and thermal properties. The sorption of oxygen and carbon dioxide in the prepared enriched films of poly(lactic acid) was measured at different temperatures between 283 and 313 K and pressures up to atmospheric

pressure using a Quartz Crystal Microbalance. Although no significant changes were found in the mechanical and thermal properties, the addition of α -tocopherol promotes an increasing in the oxygen sorption and the convex shape of the isotherms indicate a strong interaction gas-polymer. Regarding the sorption of carbon dioxide, no pronounced effect was found. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2468–2475, 2011

Key words: biorefinary polymers; poly(lactic acid); α -tocopherol; sorption

INTRODUCTION

In recent years, many efforts have been devoted to the development, formulation, and characterization of new ecologically friendly and sustainable plastic materials that can overcome the major environmental problems created by the extensive use of petrochemical-based plastics. It is expected that these new materials will perform equally well when applied in many important industries such as construction, automotive, appliances, and medical, to mention a few. Poly(lactic acid) (PLA) is a biodegradable thermoplastic polyester, made from annually renewable resources, that has been the subject of intensive research because of its intrinsic characteristics. It has been shown that PLA can replace hydrocarbon-based polymers such as polystyrene in certain packaging applications.^{1,2} It has also been successfully used as a textile material and found an unquestionable place in the biomedical field. The expansion of PLA's application to the packaging industry passes essentially through the ability to tailor its gas

barrier properties and flexural properties such as rigidity and brittleness, which are an expression of its low deformation at break. Considerable efforts have been made to overcome these limitations by blending PLA with low-molecular weight plasticizers or with other polymers. Blends of PLA with other aliphatic polyesters such as poly(ϵ -caprolactone),^{3,4} poly(hydroxybutyrate),^{5,6} and other petroleum-based polymers have been reported in the literature. Some of these blends were found to phase separate, resulting in materials with fairly poor mechanical properties. Other works include preparation of nanocomposites by using inorganic clays such as montmorillonite,^{7,8} hydroxyapatite,⁹ carbon nanotubes,¹⁰ or compounding with natural fibers, mainly lignocellulosics¹¹ and derivatives, that are renewable, biodegradable, sustainable, and cheap. In many cases, the use of these fibers in polymer composites can lead to materials with improved performances in comparison with traditional glass-fiber-reinforced composites. However, the incompatibility of natural fibers with the polymer matrices, the tendency to form aggregates during processing, and their poor resistance to moisture represent some important drawbacks that limit the use of these materials.

Examples of plasticizers used in PLA include citrate ester, glucose monoesters, partial fatty acid esters,^{12–15} and more recently glycols.¹⁶ The efficiency of these plasticizers is usually evaluated in terms of the glass transition or melting temperature

Additional Supporting Information may be found in the online version of this article.

Correspondence to: I. M. Marrucho (imarrucho@itqb.unl.pt).

shift for amorphous or semi crystalline polymers, respectively, and mechanical properties improvement. The obtained results indicate that although the low-molecular weight plasticizers seem to be quite efficient, the use of glycols need particular attention because it can lead to phase separating mixtures depending not only on the mixture composition but also on the glycol molecular weight.

The main objective of this work is to investigate the effect of the addition of α -tocopherol in the thermal and mechanical properties of PLA films and also barrier properties, namely the sorption of gases, in the active packaging context. Antioxidants are widely used as food additives to improve the stability of lipids to oxidation and to prolong shelf-life of dried products and oxygen sensitive foods. They have also been incorporated in small concentrations in films to obtain additional stability under processing conditions.^{17–21} The impregnation of Food and Drug Administration approved antioxidants, such as butylated hydroxytoluene in polymeric films has also been subject of research.²² α -tocopherol (the component of Vitamin E that has the highest free radical scavenging activity) is a natural antioxidant that has already been studied as a polymer film stabilizer and an antioxidant.²³ Recognized as safe and worldwide approved for use in food applications, α -tocopherol has been used to improve the biostability and biocompatibility of different biomaterials.^{24–27} Reno et al.²⁷ studied the effect of α -tocopherol added to poly((D,L)lactic acid) for medical applications and they verified that it alters the surface wettability. Wessling et al.¹⁹ observed that incorporation of high levels (3600 ppm) of α -tocopherol into LDPE films inhibits the oxidation of organic acids stored in contact with the film. More recently, Byun et al.²⁸ clearly showed the high antioxidant activity of α -tocopherol, by the incorporation of 1% of α -tocopherol PLA films, which increased the radical scavenging activity from 0.84 to 90.43%.

In this work, we describe the effect of the addition of the different amounts of α -tocopherol to PLA films. The changes in the mechanical and thermal properties of the obtained materials will be addressed using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). Carbon dioxide and oxygen sorption results in the prepared films will be analyzed in the active packaging context.

EXPERIMENTAL

Materials

Biodegradable polymer, PLA with (L:D) ratio of 98 : 2 with molecular weight of 87,131 Da and density

of 1.26 g cm^{-3} was provided by Cargill-Dow Polymers.²⁹ (\pm)- α -Tocopherol, with assay $\geq 97\%$, density of 0.950 g cm^{-3} , was purchased from Fluka. Dichloromethane was obtained from Riedel-de-Haan with analytical reagent grade. Oxygen with 99.995% and carbon dioxide with 99.999% are from Air Liquid. Solvents and gases were used with no further purification. Quartz crystals of 9 MHz base frequency with silver electrodes have been supplied by Dimofel, Lisbon, Portugal.

Sample preparation

Solutions with $\sim 25 \text{ mg/mL}$ of PLA in dichloromethane were prepared. Different amounts of α -tocopherol were added to obtain solutions with concentrations of 2.2 and 4.4% of α -tocopherol (w/w) to PLA. The solutions were stirred during 30 min in the dark to avoid α -tocopherol degradation. Thin films were prepared by the casting method. The solvent was allowed to evaporate at room temperature for ~ 3 days and dried in oven at 30°C for at least 2 days.

The study of the crystallite growth was achieved using films that were melted at 200°C for 3 min and then crystallized at the annealing temperature of 140°C for 60 min. The films used in dynamic mechanical analysis were used as cast and the ones used in the sorption studies were melted at 200°C for 10 min followed of subsequent quenching at 0°C .

QCM crystals of 9 MHz AT-cut quartz were thoroughly washed with dichloromethane to remove undesired compounds adsorbed. They were considered clean when the base frequency becomes constant ($\pm 2 \text{ Hz}$). Crystals with active area of 0.25 cm^2 were then coated with a drop of thin polymer film on both sides using solutions with 0, 2.2, and 4.4% α -tocopherol. The frequency change due to the polymer layer was of 99,391 Hz for PLA and 70,404 Hz and 105,907 Hz for PLA with 2.2 and 4.4% α -tocopherol, respectively.

Characterization methods

Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectrophotometer, FT Bruker IFS 55, was used to obtain spectra of thin films co-adding 256 scans at a resolution of 8 cm^{-1} . Spectra were collected from 4000 to 400 cm^{-1} .

Thermal analysis and dynamic degradation measurements were carried out in a differential scanning calorimeter Shimadzu, DSC-50/DTA-50. All experiments were done under nitrogen conditions. Both temperature and heat flow were calibrated with In and Pb standards. Roughly 4.5 mg of each film was weighed and sealed in an aluminium pan. The DSC experiments were carried out with an heating rate of 10°C/min . The crystallinity index of samples was

calculated considering that the enthalpy of melting of 100% crystalline PLA, 93.6 J/g.³⁰

A thermogravimetric analyzer Shimadzu TGA-50 was used to study the dynamic degradation. The dynamic tests were run at an heating rate of 10°C/min from room temperature up to 500°C and in nitrogen environment (flow rate 20 mL/min) to guarantee the constancy of atmosphere during the whole test. Samples weighting between 7 and 8 mg were used without any previous treatment.

Microscope Olympus BX51 with polarized light was used to observe the effect of α -tocopherol on the growth and morphology of spherulites when a sample is subjected to thermal treatment by melting and subsequent annealing at temperature above T_g or quenched at temperature 0°C.

Rectangular specimens of the films prepared were tested in a dynamic mechanical analyzer Tritec 2000 DMA, Triton Technology Ltd. Displacement and force amplitudes were adjusted according to samples for a single cantiliver bending deformation mode. The experiments were done at 1 Hz of frequency in temperature range from 30°C to 100°C with heating rate of 2°C/min. The storage modulus or Young's modulus with temperature was monitored.

Gas solubility measurements

QCM sensors have been successfully used in a variety of applications using standard oscillator techniques and frequency counting. One of them is its applicability in sorption of gases in solid thin films.^{31–41} In this work, the sorption of oxygen and carbon dioxide in PLA and PLA enriched with α -tocopherol films was obtained by QCM technique, described in detail in a previous work³⁶ along with its basic operating principle. Special care was taken so that the Sauerbray equation⁴² is valid, meaning that the added mass was evenly distributed over the electrodes and is much smaller than the weight of the quartz disk, $\Delta f/f \ll 1$.⁴³

Among the methods used to prepare thin film samples for the QCM, the drop coating method has proved to be successful in our previous studies.^{34,35,44} Assuming that the layer which traps a material is thin, uniform, and rigidly attached to the electrodes and vibrates synchronously with the crystal, the data obtained can be interpreted based on Sauerbrey equation. The effect of viscoelastic environment for oxygen and carbon dioxide at low pressures is negligible, and thus no corrections were applied.

MODELS

The sorption of a gas in polymer films can display a variety of behaviors. Depending on the specific char-

acteristics of the system, different models have been proposed to describe and to analyze the results obtained. The interpretation of the sorption phenomena based on these models may lead to interesting conclusions since the coefficients are usually linked to properties that have a role in the sorption mechanism. In particular, the dual-mode sorption model (DMSM) has been widely used to correlate the solubility of gases in glassy polymers films. This model assumes that two types of mechanisms occur during the sorption, one follows the Henry's law and the other a Langmuir adsorption isotherm.^{45–48} Although DMSM has encountered an enormous success in the description of gas or vapor sorption isotherms concave toward the activity axis, only the engaged species induced clustering (ENSIC) model is able to describe isotherms convex to the activity or pressure axis.⁴⁹ Feng⁵⁰ recently reported the modeling of vapor sorption in glassy polymers using a new dual mode sorption model. Besides describing the two mechanisms previously referred, the new model can simultaneously describe sigmoidal isotherms, which could only be addressed by Guggenheim-Anderson-de Boer (GAB) model. The underlying sorption mechanism can be explained as a contribution of two sorption phenomena, one of which occurs in the matrix region and the other in the microvoids. The sorbate concentration in the polymer is also a sum of both mechanisms given by eq. (1)

$$c = \bar{C}_p \frac{k'p}{1 - k'p} + \bar{C}_p \frac{(A' - 1)k'p}{1 + (A' - 1)k'p} \quad (1)$$

The new dual mode sorption has three parameters, \bar{C}_p , k' , and A' , as many as the conventional dual mode sorption, where the penetrant concentration is given by eq. (2):

$$c = k_D p + C'_H \frac{bp}{1 + bp} \quad (2)$$

where k_D , C'_H , and b are the correspondent parameters. \bar{C}_p is the weight value of the sorption capacity of the polymer to the sorbate, gas, or vapor and it mainly depends on the structure and physical state of the polymer and on the volume of the sorbate; k' is the difference between the interaction of vapor molecules among themselves and the interaction between the vapor and the polymer molecule segment; large k' values indicate strong interaction between the sorbate and the polymer; A' is a measure of interaction between the sorbate molecule and the microvoid. Indeed, eq. (2) is a special case of eq. (1) for $k' \ll 1$. The $k_D p$ parameter represents the penetrant dissolved in the polymer matrix at equilibrium and b characterizes the sorption affinity for a

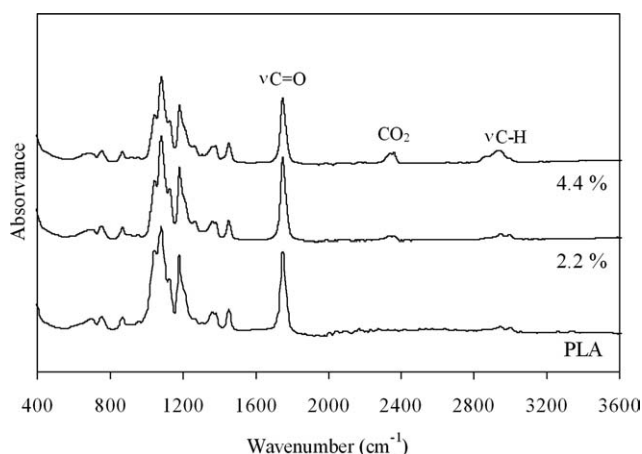


Figure 1 ATR-FTIR spectra of PLA and enriched PLA with α -tocopherol.

particular gas-polymer system. Finally, C'_H gives the amount of the nonequilibrium excess free volume in the glassy state.

RESULTS

Film characterization

The infrared spectra of PLA and PLA enriched with various concentrations of α -tocopherol films were recorded in the spectral region of 3500 to 1500 cm^{-1} and are presented in Figure 1. The increase in the band at 3000 cm^{-1} with the increase in the amount of α -tocopherol in films confirms that the addition procedure was successful. The control of PLA structure is done using the band at 1748 cm^{-1} , corresponding to C=O stretching.

The thermal stability of the films was monitored by thermogravimetric analysis. No significant differences were noticed in thermal degradation temperature. The DSC thermogram obtained during

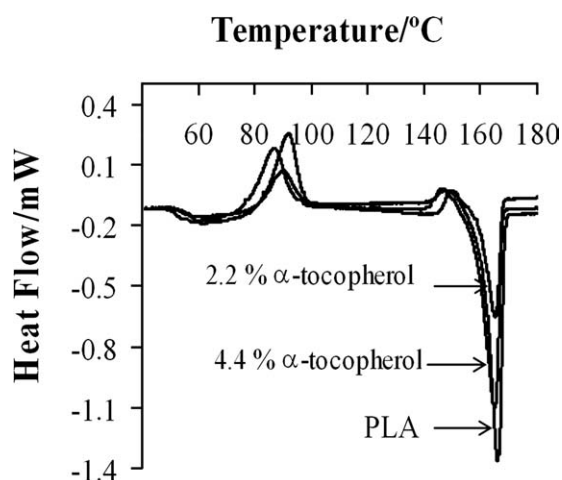


Figure 2 DSC thermogram obtained during the heating of samples and the glass transition region around 50°C.

the heating of samples and presented in Figure 2 shows that the glass transition region starts around 50°C and the cold crystallization ends at about 100°C; at $\sim 160^\circ\text{C}$, a premelting crystallization followed by the melting can be found in Figure 2. The DSC results show that no significant changes were found in the glass transition temperature, only slightly decrease with the increase in α -tocopherol was found. The effect of the addition of the α -tocopherol in crystallinity is also small and has the opposite behavior, as depicted in Figure 3. These results indicate that α -tocopherol behaves as a plasticizant, i.e., increasing the mobility of PLA chains in the amorphous regions, thus allowing more rearrangements of polymer chains and consequently higher crystallinity. Piorkowska et al.⁵¹ have obtained a similar result when PLA was plasticized with poly(propylene glycol), PPG.

The effect of α -tocopherol in the number density of spherulites when the films are melted followed by annealing at a crystallization temperature (T_c) above the T_g can be evaluated from the polarized light micrographs presented in Figure 4. An increase in the number of spherulites with the increase in α -tocopherol content can be observed. From both Figures 3 and 4, it can be concluded that the amount of spherulites in the PLA enriched with 2.2% (w/w) α -tocopherol film is smaller than what would be expected from the 4.4% enriched films results. No spherulites are observed when films are melted and quenched at 0°C. Therefore, the overall crystallization of PLA enriched with α -tocopherol can be controlled by thermal treatment and the final films should always be characterized.

Dynamic mechanical spectra of the as-cast PLA films with 0, 2.2, and 4.4% of α -tocopherol are shown in Figure 5. Lower modulus values were found in films for higher concentrations of α -tocopherol, decreasing from about 900 MPa for nonenriched films to about 500 MPa for both

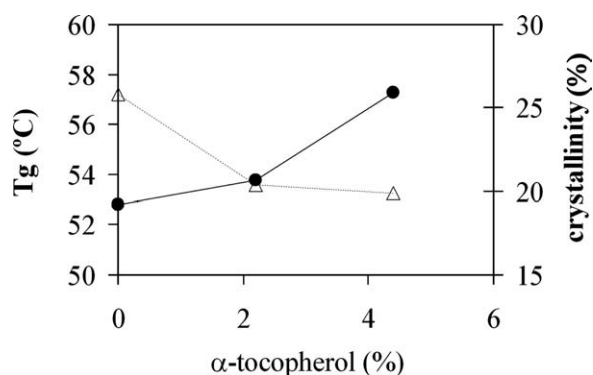


Figure 3 T_g (Δ) and crystallinity (\bullet) change of PLA films as a function of α -tocopherol content.

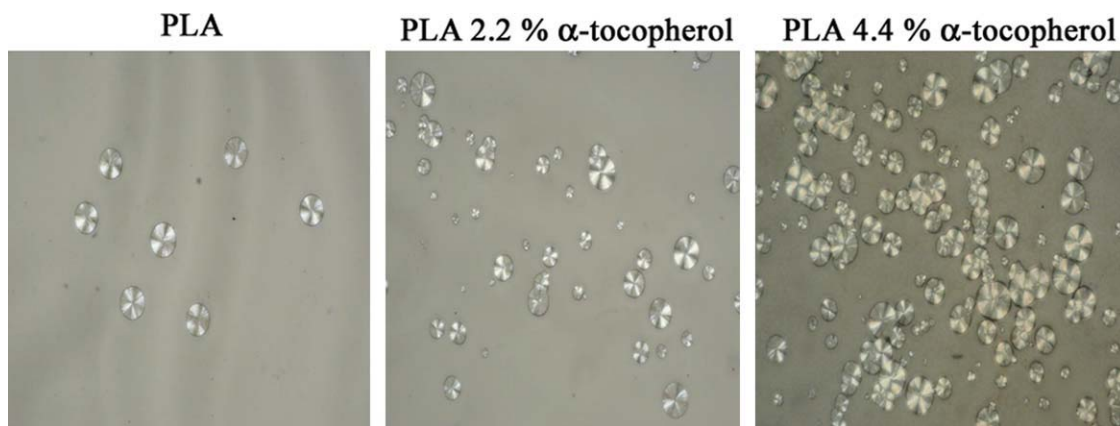


Figure 4 Photomicrographs of the films annealed at 140°C from the melt for PLA enriched with 0, 2.2, and 4.4% (w/w) of α -tocopherol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

enriched PLA. This behavior is similar to the one found in plasticized films with glycerol, poly(ethylene glycol) or oligomeric lactic acid by Martin et al.² and suggests that α -tocopherol does not significantly improve the performance of the material in terms of flexural properties.

Sorption results

The sorption results obtained by QCM and their relative standard deviation are presented in Supporting Information (Table S1 for the oxygen and in Table S2 for carbon dioxide in PLA and enriched PLA films with α -tocopherol). The relative standard deviation (δC) of the gas concentration, C , was obtained by differentiating with respect to ΔF_C and ΔF_S the following expression:

$$C = \frac{\Delta F_S}{\Delta F_C} \times \frac{V_m(PTN)}{M_{\text{gas}}} \quad (3)$$

where ΔF_C represents the total mass of polymer coated on the quartz crystal and is determined by the difference in the oscillation frequency measured

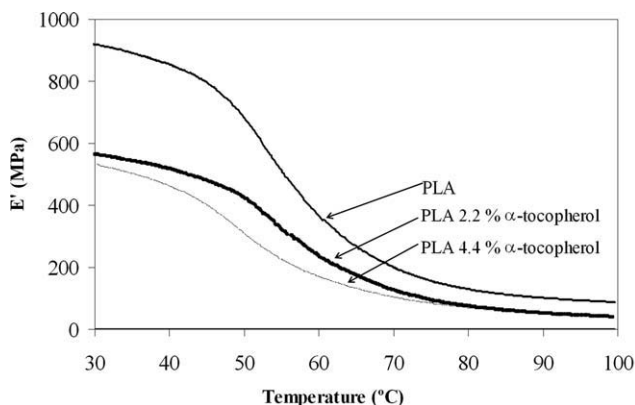


Figure 5 Young's modulus of PLA and enriched α -tocopherol PLA.

before coating and after the thermal treatment of the crystal with the coating. ΔF_S is calculated from the frequency change due to gas sorption between the reference crystal (uncoated) and the measuring

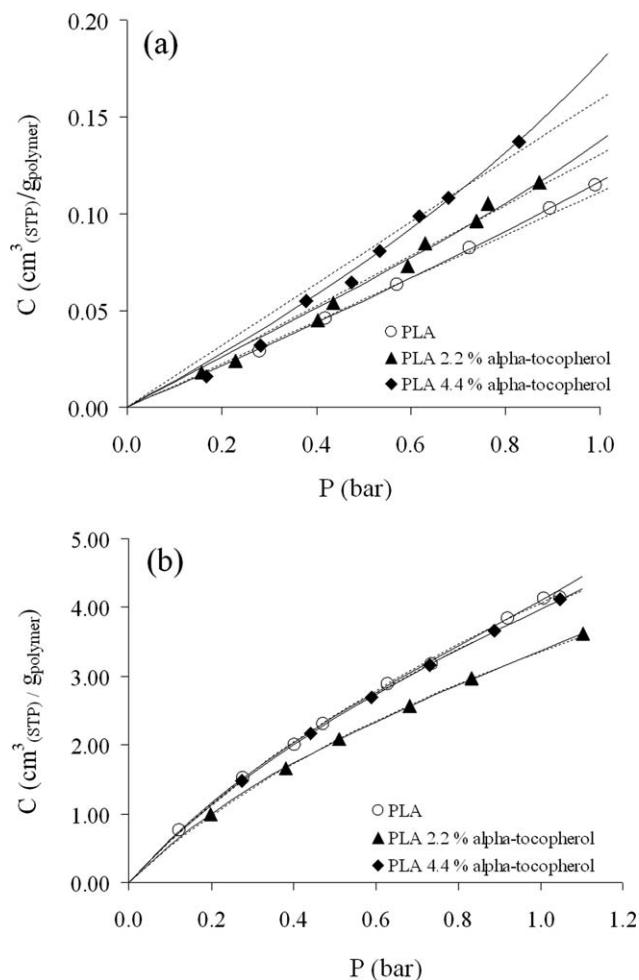


Figure 6 Sorption isotherms at 282 K of (a) oxygen and (b) carbon dioxide in PLA and enriched α -tocopherol PLA. The solid and the dashed lines are the new DMSM and the DMSM, respectively.

TABLE I
Estimated Values of the Parameters of the New DMSM for O₂ in PLA and PLA Enriched With α -Tocopherol

New DMSM				
T (K)	C_p (cm ³ _(STP) g ⁻¹)	K'	A'	AAD (%)
PLA				
282.9	0.30	0.27	1.22	2.8
292.7	0.31	0.26	1.14	2.7
302.8	0.49	0.13	1.12	1.4
312.7	0.58	0.10	1.12	8.6
PLA 2.2 (w/w)% α -tocopherol				
282.9	0.25	0.28	1.66	2.1
292.7	0.28	0.23	1.65	2.8
302.8	0.30	0.22	1.50	6.9
312.7	0.55	0.10	1.50	7.0
PLA 4.4 (w/w)% α -tocopherol				
282.9	0.30	0.32	1.35	2.4
292.7	0.36	0.24	1.34	2.1
302.8	0.36	0.24	1.33	9.7
312.7	0.60	0.15	1.31	4.2

crystal coated with polymer. M_{gas} and V_m are the molecular weight and the molar volume of the gas.

An example of the equilibrium sorption isotherms behavior at 282 K is depicted in Figure 6. For both gases, the sorption increases over the entire pressure range for all three films. The CO₂ sorption in the three films exhibits the dual mode sorption nature for the three films as typically observed for glassy polymers. The O₂ sorption follows a predominant Henry behavior for the PLA, whereas the α -tocopherol enriched films present a convex behavior toward the pressure axis, which is generally found for vapor sorption in polymers.⁵²⁻⁵⁴ This different behavior has led to the choice of an alternative model to describe the sorption isotherms: the new DMSM, described by eq. (1) was used to correlate the O₂ sorption results, whereas for the CO₂

isotherms, the performance of both models, the classical DMSM represented by eq. (2) and the new DMSM, was evaluated in terms of the average absolute deviation (AAD). The estimated model parameters are reported in Tables I and II for oxygen and carbon dioxide, respectively.

Although both models can provide an adequate representation of the CO₂ sorption data, the correct representation of the O₂ sorption isotherms can only be achieved when the new DMSM is used. As it was mentioned before, the model parameters can be used for interpretation of the sorption phenomena and provide relevant information about the system under study. Comparing Tables I and II, it can be observed that the C_p values for O₂ and CO₂ are very different from each other indicating, as expected, that the volume of these gases plays a significant role in the sorption process. The A' values are also 3-5 times higher for CO₂ revealing that this gas has more affinity to the microvoids than O₂, and most probably the CO₂ sorption occurs to a large extent in microvoids. Surprisingly, the K' parameter has very similar values for the two gases, leading to the conclusion that the magnitude of the interaction polymer-sorbate is similar in both cases. Nevertheless, the convex behavior of the oxygen isotherms indicates that there is a strong specific interaction between the molecules and the glassy PLA, the fact that does not happen for CO₂.

Another form to evaluate the underlying sorption mechanism is through the use the infinite-dilution solubility, S_0 , expressed by

$$S_0 = \lim_{p \rightarrow 0} \left(\frac{c}{p} \right) \quad (4)$$

TABLE II
Estimated Values of the Parameters of the New DMSM and DMSM for CO₂ in PLA and PLA Enriched With α -Tocopherol

New DMSM					DMSM			
T (K)	C_p (cm ³ _(STP) g ⁻¹)	K'	A'	AAD (%)	K_D	C'_H	b	AAD (%)
PLA								
282.9	4.29	0.28	5.80	0.3	1.90	4.02	1.16	0.8
292.7	5.48	0.14	5.67	0.7	1.41	3.79	0.80	0.7
302.8	5.76	0.11	4.79	0.3	1.27	2.89	0.57	0.3
312.7	6.66	0.08	3.63	0.2	1.09	2.78	0.32	0.2
PLA 2.2 (w/w)% α -tocopherol								
282.9	3.98	0.22	6.84	0.3	1.17	4.30	1.04	0.8
292.7	3.90	0.18	5.64	0.4	1.17	3.03	0.88	0.6
302.8	4.41	0.10	5.50	0.5	0.88	2.79	0.59	0.5
312.7	5.09	0.07	5.22	0.4	0.71	2.67	0.39	0.4
PLA 4.4 (w/w)% α -tocopherol								
282.9	5.42	0.19	6.46	0.03	1.61	4.64	1.04	0.2
292.7	5.46	0.13	5.85	0.5	1.15	4.44	0.70	0.5
302.8	5.89	0.10	4.44	0.2	1.000	4.40	0.38	0.2
312.7	6.40	0.10	3.08	0.9	0.999	4.01	0.17	0.8

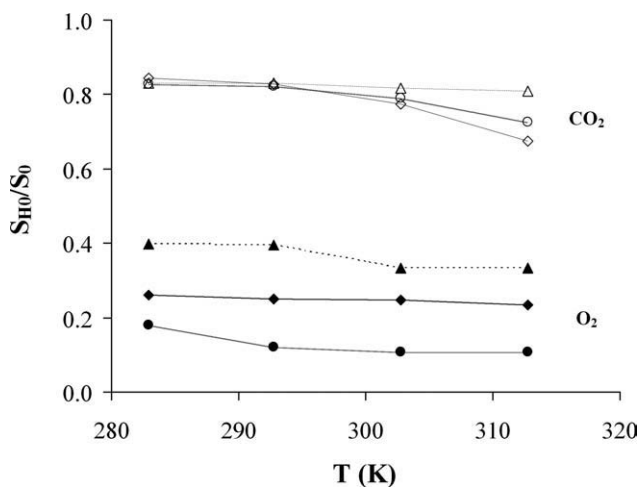


Figure 7 Effect of α -tocopherol on Langmuir capacity of O_2 and CO_2 sorption in PLA (\circ) and enriched PLA 2.2% (\triangle) and 4.4% (\diamond) of α -tocopherol.

S_0 gives an indication of whether a gas molecule prefers to dissolve in the polymer matrix or sorbs into microvoids and can help to understand the effect of α -tocopherol on the gas access to microvoids. In Figure 7, the weight of Langmuir capacity, $S_{H0} = C_p(A' - 1)k'$, on total solubility for O_2 and CO_2 is reported. The most important conclusion is that the sorption mechanism of both gases in PLA is not affected by the presence of α -tocopherol: the sorption of CO_2 occurs essentially in microvoids while the O_2 solubilizes mostly in the polymer matrix. For CO_2 , the Langmuir capacity is roughly the same ($\sim 80\%$) for the three films in the studied temperature interval. The O_2 sorption presents an almost constant Langmuir capacity of $\sim 20\%$ for PLA and 4% enriched PLA films in the all temperature range, whereas values around 40% are observed for the 2% enriched film.

The product C_pK' can also yield valuable information regarding the sorption mechanism because

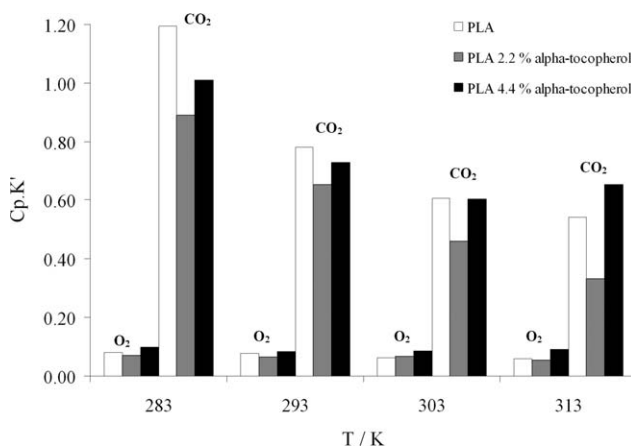


Figure 8 C_pK' values for O_2 and CO_2 in PLA and enriched PLA films.

it is related to the sorption sites and the properties of the penetrant. This product is presented for each isotherm for both gases in Figure 8. The difference in magnitude of C_pK' between the two studied gases reflects the CO_2 higher polarity and condensability relatively to O_2 . It is also interesting to observe the change in relative magnitude of C_pK' for PLA and PLA 4.4% enriched films below, at and above the CO_2 critical temperature (304.1 K).⁵⁵ Note that this type of data do not allow us to infer about what happens at the molecular level about the role of α -tocopherol in the sorption of the two studied gases. For CO_2 , the unexpected behavior for the 2.2% (w/w) enriched films is captured by the model parameters, where C_pK' is consistently lower than what would be expected from the values for the 4.4% (w/w) enriched films for each gas. As shown previously in Figure 6, the presence of α -tocopherol in PLA films only influences the O_2 solubility, which displays an increasing sorption with the α -tocopherol content. The CO_2 solubility in PLA and PLA enriched films with 4.4% of α -tocopherol is roughly the same, whereas the CO_2 solubility in enriched films with 2.2% of α -tocopherol is always lower. As the sorption of CO_2 takes place predominantly in the microvoids, the α -tocopherol content seems to somehow affect their size and distribution in 2.2% (w/w) enriched PLA film.

Finally, the enthalpy change due the dissolution of the gas was analyzed. Figure 9 shows the sorption behavior with temperature at 1 bar for both CO_2 and O_2 . The enthalpy of sorption, ΔH_S , for both gases in PLA and enriched PLA films was obtained using the van't Hoff relationship. The sorption process is exothermic for both gases. The ΔH_S values obtained for CO_2 in PLA and PLA enriched films with 2.2 and 4.4% α -tocopherol are almost constant $-24.1 (\pm 0.1)$, $-23.2 (\pm 0.1)$, and

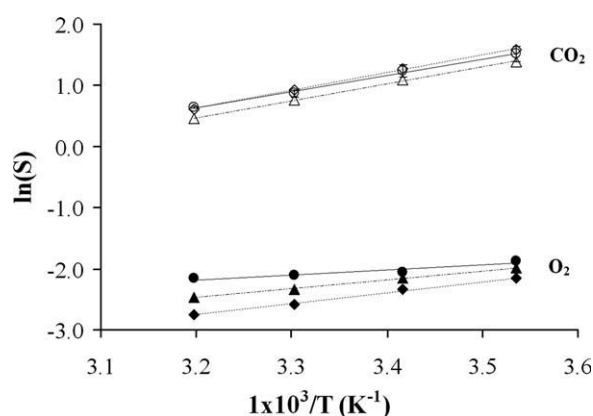


Figure 9 van't Hoff relationship for O_2 and CO_2 to PLA (\circ) and α -tocopherol enriched PLA 2.2% (\triangle) and 4.4% (\diamond).

$-21.9 (\pm 0.2)$ kJ mol $^{-1}$, respectively, indicating again that the presence of α -tocopherol does not affect the energetics of CO $_2$ sorption. Nevertheless, the ΔH_S values obtained for O $_2$ in PLA enriched films with 0, 2.2, and 4.4% α -tocopherol are $-15.1 (\pm 0.1)$, $-11.9 (\pm 0.1)$, and $-6.6 (\pm 0.2)$ kJ mol $^{-1}$, respectively, show that the sorption of oxygen is clearly affected by the increasing concentration of α -tocopherol, in agreement with the sorption results, rendering a less exothermic processes.

CONCLUSIONS

This work presents the characterization of PLA enriched films with α -tocopherol, regarding their material properties and oxygen and carbon dioxide sorption behavior, indicating the viability of their use. The obtained results show that (i) the presence of α -tocopherol does not affect in a significant way thermal and mechanical stability of the prepared films; (ii) the O $_2$ sorption increases with the α -tocopherol content and the convex shape of the isotherms indicates a strong interaction gas-polymer; (iii) the sorption mechanism for both gases remains unchanged with the addition of α -tocopherol: the sorption of O $_2$ occurs essentially in polymer matrix, whereas the CO $_2$ solubilizes mostly in the microvoids.

References

- Drumright, R. E.; Gruber, P.; Henton, D. E. *Adv Mater* 2000, 12, 1841.
- Martin, O.; Averous, L. *Polymer*, 2001, 42, 6209.
- Wang, L.; Ma, W.; Gross, R. A.; McCarthy, S. P. *Polym Degrad Stab* 1998, 59, 161.
- Tsuji, H.; Ikada, Y. *J Appl Polym Sci* 1996, 60, 2367.
- Koyama, Y.; Doi, Y. *Polymer* 1997, 38, 1589.
- Ohkoshi, I.; Abe, H.; Doi, Y. *Polymer* 2000, 41, 5985.
- Chang, J. H.; An, Y. U.; Cho, D. *Polymer* 2003, 44, 3715.
- Ray, S. S.; Yamada, K.; Okamoto, M.; Ogami, A.; Ueda, K. *Chem Mater* 2003, 15, 1456.
- Cui, W. U.; Li, X. H.; Zhou, S. B.; Weng, J. *J Biomed Mater Res A* 2007, 82, 831.
- Chiu, W. M.; Chang, Y. A.; Kuo, H. Y.; Lin, M. H.; Wen, H. C. *J Appl Polym Sci* 2008, 108, 3024.
- Bondeson, D.; Oksman, K. *Compos A* 2007, 38, 2486.
- Hu, Y.; Hu, Y. S.; Topolkaev, V.; Hiltner, A.; Baer, E. *Polymer* 2003, 44, 5681.
- Kulinski, Z.; Piorkowska, E. *Polymer* 2005, 46, 10290.
- Ljungberg, N.; Wesslen, B.; Andersson T. J. *J Appl Polym Sci* 2003, 88, 3239.
- Shibata, M.; Someya, Y.; Orihara, M.; Miyoshi, M. *J Appl Polym Sci* 2006, 99, 2594.
- Kulinski, Z.; Piorkowska, E.; Gadzinowska, K.; Stasiak, M. *Bio-macromolecules* 2006, 7, 2128.
- Wessling, C.; Nielsen, T.; Giacini, J. R. *J Sci Food Agric* 2001, 81, 194.
- Wessling, C.; Nielsen, T.; Leufven, A. *Food Addit Contam* 2000, 17, 713.
- Wessling, C.; Nielsen, T.; Leufven, A. *Packag Technol Sci* 2000, 13, 19.
- Wessling, C.; Nielsen, T.; Leufven, A.; Jagerstad, M. *Food Addit Contam* 1998, 15, 709.
- Wessling, C.; Nielsen, T.; Leufven, A.; Jagerstad, M. *J Sci Food Agric* 1999, 79, 1635.
- Ozdemir, M.; Floros, J. D. *Crit Rev Food Sci* 2004, 44, 185.
- Lopez-Rubio, A.; Almena, E.; Hernandez-Munoz, P.; Lagaron, J. M.; Catala, R.; Gavara, R. *Food Rev Int* 2004, 20, 357.
- Ernsting, M. J.; Labow, R. S.; Santerre, J. P. *J Biomater Sci Polym Ed* 2003, 14, 1411.
- Galli, F.; Canestrari, F.; Buoncristiani, U. *Blood Purif* 1999, 17, 79.
- Oral, E.; Rowell, S. L.; Muratoglu, O. K. *Biomaterials* 2006, 27, 5580.
- Reno, F.; Aina, V.; Gatti, S.; Canna, S. M. *Biomaterials* 2005, 26, 5594.
- Byun, Y.; Kim, Y. T.; Whiteside, S. J. *Food Eng* 2010, 100, 239.
- Oliveira, N. S. PhD Thesis, Universidade de Aveiro, Aveiro, Portugal, 2006.
- Schmack, G.; Tandler, B.; Vogel, R.; Beyreuther, R.; Jacobsen, S.; Fritz, H. G. *J Appl Polym Sci* 1999, 73, 2785.
- Aubert, J. H. *J Supercrit Fluids* 1998, 11, 163.
- Matsuguchi, M.; Maeda, N.; Sakai, Y. *J Appl Polym Sci* 2002, 83, 401.
- Mikkilineni, S. P. V. N.; Tree, D. A.; High, M. S. *J Chem Eng Data*, 1995, 40, 750.
- Oliveira, N. S.; Dorgan, J.; Coutinho, J. A. P.; Ferreira, A.; Daridon, J. L.; Marrucho, I. M. *J Polym Sci Part B: Polym Phys* 2007, 45, 616.
- Oliveira, N. S.; Goncalves, C. M.; Coutinho, J. A. P.; Ferreira, A.; Dorgan, J.; Marrucho, I. M. *Fluid Phase Equilib* 2006, 250, 116.
- Oliveira, N. S.; Oliveira, J.; Gomes, T.; Ferreira, A.; Dorgan, J.; Marrucho, I. M. *Fluid Phase Equilib* 2004, 222, 317.
- Pantoula, M.; Panayiotou, C. *J Supercritical Fluids* 2006, 37, 254.
- Pantoula, M.; von Schnitzler, J.; Eggers, R.; Panayiotou C. *J Supercritical Fluids* 2007, 39, 426.
- Smith, A. L.; Mulligan, R. B.; Shirazi, H. M. *J Polym Sci Part B: Polym Phys* 2004, 42, 3893.
- Smith, A. L.; Shirazi, H. M. *J Therm Anal Calorim* 2000, 59, 171.
- Zhang, C.; Cappleman, B. P.; Defibaugh-Chavez, M.; Weinkauff, D. H. *J Polym Sci Part B: Polym Phys* 2003, 41, 2109.
- Sauerbrey, G. *Zeitschrift Fur Physik* 1959, 155, 206.
- Rodahl, M.; Hook, F.; Krozer, A.; Brzezinski, P.; Kasemo, B. *Rev Sci Instrum* 1995, 66, 3924.
- Oliveira, N. S.; Dorgan, J.; Coutinho, J. A. P.; Ferreira, A.; Daridon, J. L.; Marrucho, I. M. *J Polym Sci Part B: Polym Phys* 2006, 44, 1010.
- Favre, E.; Schaetzel, P.; Nguyen, Q. T.; Neel, J. *J Macromol Theory Simul* 1994, 3, 379.
- Kanehashi, S.; Nagai, K. *J Membr Sci* 2005, 253, 117.
- Wang, J. S.; Kamiya, Y. *J Membr Sci* 1999, 154, 25.
- Wang, J. S.; Kamiya, Y. *J Polym Sci Part B: Polym Phys* 2000, 38, 883.
- Favre, E.; Nguyen, Q. T.; Clement, R.; Neel, J. *J Membr Sci* 1996, 117, 227.
- Feng, H. D. *Polymer* 2007, 48, 2988.
- Piorkowska, E.; Kulinski, Z.; Galeski, A.; Masirek, R. *Polymer* 2006, 47, 7178.
- Russell, S. P.; Weinkauff, D. H. *Polymer* 2001, 42, 2827.
- Zhang, C.; Wyatt, J.; Russell, S. P.; Weinkauff, D. H. *Polymer* 2004, 45, 7655.
- Serad, G. E.; Freeman, B. D.; Stewart, M. E.; Hill, A. J. *Polymer* 2001, 42, 6929.
- NIST Chemistry Webbook. Available at: <http://webbook.nist.gov/chemistry>.
- Miller, J. C.; Miller, J. N. *Statistics and Chemometrics for Analytical Chemistry*, 4th ed.; Prentice Hall: Harrow, UK, 2000.