

**Light olefins/paraffins sorption in Poly(lactic acid) films**

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Light olefins/paraffins sorption in Poly(lactic acid) films

C. M. B. Gonçalves, J. A. P. Coutinho, I. M. Marrucho*

CICECO, Chemical Department, University of Aveiro, 3810-193 Aveiro, PORTUGAL

For Peer Review

* To whom correspondence should be addressed: e-mail: imarrucho@ua.pt. Phone: +351 234 401 406. Fax: +351 234 370 084.

Abstract

The sorption behavior of small molecules like ethane and ethylene in Poly(lactic acid), PLA, was studied in the temperature interval from 283 to 313 K using a Quartz Crystal Microbalance (QCM). The effect of the polymer structure on the solubility selectivity of PLA films with respect to these two gases was studied using polymer with two different L:D ratios (98:2 and 80:20). Furthermore, the polymer films were submitted to different thermal treatments in order to address the influence of crystallinity and morphology of the non-crystalline fraction on the sorption behavior. The sorption results obtained indicate that ethylene solubility coefficient in annealed PLA 98:2 is about 26% higher than that of ethane and 41% higher in PLA 98:2 melted. The dual-mode sorption model describes well the sorption isotherms behavior, which is concave concerning the pressure axis. The fully amorphous PLA presents the better selectivity for the studied gases, since the crystallinity seems to produce a negative effect on the selectivity.

Keywords: sorption; solubility selectivity, quartz crystal microbalance; Poly(Lactic Acid) (PLA);

Introduction

In recent years, the separation of olefin and paraffin gases has received increased attention. The usual method using cryogenic distillation is very expensive and thus a large demand for alternative energy saving processes that respect the enforced environmental regulations has been verified. Among a number of alternative processes, membrane separation technologies would be the best option if it wasn't their low selectivity in terms of olefins relatively to parent paraffins [1]. Separation using facilitated transport membranes, which are composed of a polar polymer containing oxygen atoms with physically dissolved ion metals such as Cu^+ or Ag^+ , has been the subject of intensive research since high separation performances were obtained [2-4]. Recently, Kim H. *et al* [5] developed membranes based on zwitterionic compounds with an ester group that presented high performances for application in separation olefin-paraffin mixtures. However, this technique still has some problems to be overcome, being the most important the poor chemical stability due to carrier poisoning [6]. The olefin/paraffin separation through the use of polymeric membranes without carriers has also been studied in the literature. In particular, poly(imides) showed a higher permselectivity for propylene/propane when compared to other polymers [7-9].

In the present work, the solubility selectivity of poly(lactic acid)(PLA), a poly(ester) membrane towards ethane/ethylene is investigated. Polyesters are polar polymer with oxygen atoms and their applicability in gas separation has not yet been studied. Nevertheless, interesting results of solubility of condensable gases, namely ethylene, carbon dioxide and water vapour in PLA films with various L:D ratios and thermal treatments were reported in earlier works [10-13]. Gas sorption in polymers depends not only on the condensability of permeant gas but also on the polymer-penetrant gas interactions. In the present case of the ethane/ethylene, the carbon-carbon double bond in ethylene is responsible for the higher density of negative charge in the region of the π bond, susceptible to electron-seeking, and can interact favourably with the ester group of the polymer, thus promoting an increase in its solubility when compared to that of ethane. Ethylene can establish strong interactions with the PLA membrane that has hydrolytically labile aliphatic ester linkages in its backbone [11, 14]. Despite its high condensability, the weak interaction between ethane and poly(lactic acid) results in lower solubility relatively to ethylene.

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The polymer crystallization is also another parameter that has to be taken into account, since it determines the final properties of many technologically relevant systems based on semicrystalline polymers. The change of solubility, diffusivity and permeability coefficients with temperature and pressure can be explained in part by the “impermeability” of crystalline region. The effect of thermal treatment in the gas solubility of poly(lactic acid) films is well documented [10, 11] and has proved to be a valuable tool in tailoring polymer films to obtained specific values for sorption, diffusivity and permeability. If the presence of crystallites can reduce the available volume for penetrant sorption, they can also increase the microcavities or Langmuir sites and thus the second mode of sorption (Langmuir type) can play a more important role than Henry’s sites [15].

The improvement of permeability and permselectivity of new membranes for gas separation has been object of study by many authors [1, 16-19]. The first step in this type of work is to evaluate the solubility of the gas or gas mixture in the polymer film in order to evaluate the possible interactions between them. The second step would be to address the transport properties that are necessary for this purpose. In this work we only explore the first aspect. The study of the influence of the structure of the polymer PLA film on the sorption and consequently on the sorption selectivity of ethane and ethylene was performed using the QCM technique, which has already been successfully used for that purpose. This method is based on the piezoelectric effect of the Quartz Crystals and, presents high sensitivity and accuracy for studying the solubility of gases in polymers. Two AT-cut Quartz Crystals were used: the measuring crystal, coated with a thin layer of the polymer under study, and the reference crystal, used uncoated. If the polymer film is uniformly spread and vibrates synchronously with the quartz crystal, the frequency of the wave is a function of the coated mass. According to the Sauerbrey equation [20], the frequency change of the crystal, ΔF can be related to a mass change, Δm , by:

$$\Delta F = -k \Delta m \quad (1)$$

where k is a proportionality constant that includes physical and geometrical properties of the crystal. When gas, or solvent, is injected into the system, the frequencies of both

crystals change. This frequency change is a sum of three independent terms: hydrostatic, impedance and sorption. The first two terms are measured together using the reference crystal. For each temperature and pressure the frequencies of the coated and uncoated crystal were experimentally measured and their difference is proportional to the mass of the coating, polymer and gas, sorbed in it. Thus, the solubility of the gas in polymer, C , was calculated according to the following equation:

$$C = \frac{\Delta F_s \rho_{pol.} V_m}{\Delta F_C M} \quad (2)$$

where $\rho_{pol.}$ is the polymer density, ΔF_C is the difference between the frequencies of the coated and the uncoated crystals after the equilibrium was reached, M is the gas molecular weight and V_m is the gas molar volume at STP conditions ($22414 \text{ cm}^3 \text{ mol}^{-1}$). This equation assumes that the gas obeys ideal gas behavior and that the volume of the film remains constant.

Among the models generally used to describe the sorption behavior in semi crystalline polymers, the dual mode sorption model (DMSM) is the most used. This model admits that the gas solubility occurs by two different processes: one that takes place in the amorphous part and can be understood as a liquid-like solubility described by the Henry's law; and the other in the microcavities of the intercrystalline regions, a Langmuir type of sorption in porous materials. This model can be written as:

$$C = k_d p + C_h \frac{bp}{1+bp} \quad (3)$$

where C is the total concentration of the gas in the polymer film, the gas solubility, k_d is the Henry's law coefficient, b represents the hole affinity parameter, which is a measure of the affinity between the solute molecules and the Langmuir sites, C_h is the capacity parameter, characterizing the saturation of these cavities and p is the pressure.

Experimental

Materials and methods

The biodegradable polymer, poly(lactic acid) (PLA) with (L:D) ratio of 80:20 and 98:2 was provided by Cargill-Dow Polymers. Dichloromethane was obtained from Riedel-de Haan with analytical reagent grade. Ethane with 99.99% and Ethylene with 99.5 % of purity were purchased from Aldrich. Solvent and gases were used with no further purification. Quartz crystals of 9 MHz base frequency, with silver electrodes were supplied by Dimofel, Lisbon, Portugal.

Solutions of 25 mg/ml of PLA of different L:D ratios in dichloromethane were prepared. The QCM apparatus used in this work to measure gas solubility in PLA films has been thoroughly described by Oliveira et al [10, 13]. In this apparatus, the two 9 MHz quartz crystals used, were carefully cleaned with dichloromethane until the base frequency became constant (± 2 Hz). The measuring crystal was then coated with a thin polymer film, which was prepared by dropping this solution on both sides of the quartz crystal electrode surface. The quartz crystals coated with the polymer film were submitted to two distinct thermal treatments: the melting treatment and the annealed treatment. The first, consists in heating the coated crystal from ambient temperature up to 523 K, at 2 K/min, and cool it down to ambient temperature at 10 K/min. In the annealed treatment, the crystal is introduced into an oven at 336 K, slightly above the glassy transition temperature, for two days, cooled to room temperature for one day and introduced again into the oven at 336 K for one day more. The total mass of polymer coated on the quartz crystal is determined by difference in the oscillation frequency measured before coating and after the thermal treatment. The thickness of the three films annealed PLA 80:20, annealed PLA 98:2 and melted PLA 98:2, was measured in Tapping mode AFM, from the Digital Instruments and the results were 0.36, 0.75 and 0.71 μm , respectively. The coated crystal and the reference crystal connected to an oscillator have been placed inside a solubility cell, which is placed inside a thermostatic water bath. The sorption measurements start by evacuating the apparatus until the frequency of both crystals are constant at a desired temperature. The gas, previously thermostated is admitted into the solubility cell, promoting a change in the frequency of both crystals. The frequency change is monitored as a function of time until sorption equilibrium has been achieved, i.e. until a stable frequency is reached. Several pressures

of the gas up to 1 bar have been studied. The glassy transition temperature and the melting temperature of PLA were measured by a Differential Scanning Calorimeter, DSC-50/DTA-50 from Shimadzu. The crystallinity of the polymer films was estimated with X-Ray diffraction tests performed in a Philips X'Pert automatic X-ray diffractometer with 2θ between 5 and 30° .

Film Characterization

The PLA films were characterized with DSC and X-ray diffraction. All the measurements in DSC were performed up to 473.2 K at 2 K/min with 2 complete scans. The first scan is used to measure the crystallization percentage, considering 93.6 J/g for a 100 % crystalline L-PLA [21] and the second scan is used to calculate the glass transition temperature without polymer stress. The DSC results of the PLA 98:2 films with the two above described thermal treatments are presented in Table 1 and compared with literature results. It can be seen that the thermal treatment does not significantly change T_g and T_m but it strongly influences the percentage of crystallinity, which is reduced to half when the melted treatment is performed. There is a significant difference between these results and literature results reported by Auras *et al.*[22], but no conclusions can be drawn since this author does not specify the thermal treatment performed.

The results obtained for both films by X-ray diffraction were performed at ambient temperature with 2θ between 5 and 30° , 3 second per step and 0.05° step width. The crystalline peaks were observed at 16.6° and 18.7° . The results for PLA 98:2 films obtained by the X-ray diffraction confirm those obtained by DSC where the crystallization level is about 20% and 10% (v/v) for the annealed and the melted treatments, respectively.

Sorption Results and Discussion

In Table 2 the experimental sorption results obtained in this work for C_2H_6 in the 3 PLA films (annealed PLA 80:20, annealed PLA 98:2 and melted PLA 98:2) and for C_2H_4 in annealed PLA 80:20, between 283 and 313 K and up to the atmospheric

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pressure are presented. In Figures 1 and 2 the sorption of ethane at 283 and 313 K respectively are compared the results obtained in a previous work for C₂H₄ in annealed and melted PLA 98:2 [10]. The lines represent the correlation with de DMSM. The sorption results have a precision of ± 0.02 cm³ (STP) of gas/vapour per cm³ of polymer. These results were corrected for 100% amorphous polymer, taking into account that the crystalline regions do not accommodate any solute:

$$C_a = \frac{C}{\theta_a} \quad (4)$$

where C_a is the solubility in amorphous phase, C is the experimental solubility of semi-crystalline polymer and θ_a is the amorphous volume fraction of the polymer [10].

The first conclusion that can be drawn from the Figures is that the solubility of ethylene is always larger than the solubility of ethane, for the same experimental conditions. Unlike what is commonly observed the solubility of these gases does not follow their condensability order (T_c ethane= 305.3 K; T_c ethylene= 282.5 K) [23]., The higher solubility of ethylene relatively to ethane can be explained by the strong interaction between this gas and the polymer. PLA is a poly (α-hydroxy acid) and, as all poly (α-esters) with hydrolytically labile aliphatic ester linkages in its backbone, can interact with the weak hydrogen bond basicity of alkenes, such as ethylene. On the other hand, ethane has no such capacity. For the studied systems, the polymer–penetrant interaction plays a more important role than the condensability of gas. Also as the temperature increases, the difference in condensability between the two gases decreases and thus the solubility of ethane and ethylene should become similar, which is not observed confirming that the polymer-penetrant interaction of ethylene is the driving force in the solubility of this gas in PLA.

Analyzing the sorption results in terms of the thermal treatments of the PLA films, the ethylene sorption presents an opposite behavior to that observed for ethane. The sorption of ethylene in the annealed films (either PLA 80:20 or 98:2) is higher than in melted PLA 98:2. When the films are submitted to temperatures higher than T_g, the polymeric chain mobility is enhanced. The re-organization of linkages can promote a different positioning of the hydroxyl groups to the outer side of the chain and thus the interaction these linkages with the double bond of ethylene becomes more favorable. The lower solubility of PLA 98:2 annealed relatively at PLA 80:20 annealed should be

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5 due the presence of crystalline domains that difficult the molecular orientation and
6 inhibit the interaction. Note also that the annealing process was performed on films
7 which already contained many micro-crystallites, while in the melted PLA 98:2 film
8 they are formed from the molten polymer. This means that the crystallites present in
9 these two films are naturally different from each other and thus can influence in
10 different ways the gas solubility.
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15 At lower temperatures the results show yet a larger difference in solubility
16 between the PLA 80:20 and PLA 98:2 for both thermal treatments. This difference
17 decreases with increasing temperature and at 313 K they are similar. This behavior can
18 be explained by a decrease of the condensability of gases with the temperature.
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22 Ethane has a same behavior on overall range of temperature. The sorption is
23 higher in PLA 98:2 annealed than in the other two films. The parameters of the dual
24 mode sorption model for the studied systems are summarized in Table 3. In Figures 3
25 and 4, the parameters related to the first and second sorption modes for ethane are
26 depicted. For all the films the Henry's solubility constant decreases as the temperature
27 increases. The semi-crystalline polymers present higher values for the Langmuir
28 concentration, $C'_{H,b}$ when compared with the PLA 80:20 (100% amorphous). This
29 behaviour shows that there is a strong correlation between the crystallinity and the
30 microcavities, meaning that the crystallites might act as virtual cross-linkers enhancing
31 the available free volume and thus the Langmuir sites.
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40 The DMSM correlates very well the sorption results obtained for both ethane
41 and ethylene in the three polymer films in the temperature range from 293 to 313 K
42 with overall average absolute deviation (AAD) smaller than 3% for ethane and 5% for
43 ethylene.
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47 Since semi-crystalline polymers have an important role at industrial level due to
48 the fact that their properties can be manipulated to desired values, the change in the
49 overall solubility coefficient in PLA 98:2 with temperature and thermal treatment
50 performed is shown in Figure 5. It can be seen that as the temperature increases, the
51 solubility coefficient decreases for all the studied systems. On the other hand, for the
52 same temperature the solubility coefficient increases with the increase of crystallinity in
53 the film for both gases.
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Finally, the solubility selectivity of ethylene over ethane was calculated for the different PLA films prepared in the studied temperature range and is presented in Figure 6. Surprisingly, three different behaviours are observed: for the annealed PLA 80:20 film the solubility selectivity decrease with temperature, for melted PLA 98:2 film the solubility selectivity remains constant and for the annealed PLA 98:2 film the solubility selectivity increases with the temperature. These differences can be explained by the differences in solubility dependence with the temperature

From the results presented so far it is obvious that the control of polymer structure is very important in the production of a PLA films with an adequate selectivity for the studied gases. The difference in the interactions between ethane and polymer film and ethylene and the polymer film are due to a specific interaction of the latter with the polymer chains but this interaction is also due to the control of the polymer structure through the crystallinity, which results in different mechanisms of sorption. For the PLA 80:20, where there is no crystallinity, the solubility selectivity can be enhanced by lowering the working temperature. As for the other two semi crystalline films, it is interesting to observe that while for the melted film (10% crystallinity) the temperature does not have any effect on the solubility selectivity, for the annealed film (20% crystallinity) this parameter can be improved by increasing the temperature. Moreover, if the working temperature of separation is higher than 310 K, better solubility selectivity is obtained if PLA 98:2 annealed films are used. Among the membranes studied the PLA 80:20 presents the better performance, followed by the melted PLA 98:2 and the annealed PLA 98:2.

Conclusions

The use of PLA membranes for light olefin/paraffin separation process was here studied for the first time. The QCM technique was successfully used to measure the solubility of C_2H_6 and, C_2H_4 , in PLA with 80:20 and 98:2 (L:D) content, within the temperature range from 283 to 313 K and pressures up to 1 bar. The differences in sorption between ethane and ethylene can be attributed to a specific interaction between ethylene and the polymer chains. A difference in sorption behaviour between membranes with different thermal treatments was observed and was explained by the creation of extra free volume due to the presence of different percentage of crystallites. The performance of these membranes decreases with the increase of their crystallinity.

Acknowledgments

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FIGURE CAPTIONS:

Figure 1: Sorption isotherms of ethane and ethylene at 283 K. The lines represent the correlation with dual-mode sorption model.

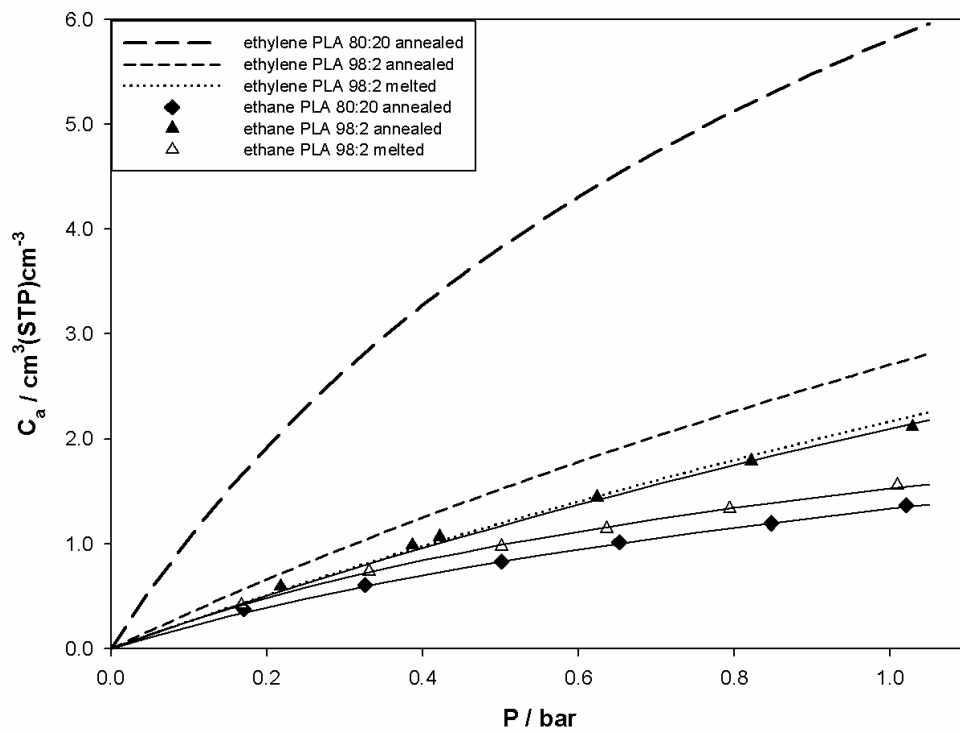
Figure 2: Sorption isotherms of ethane and ethylene at 313 K. The lines represent the correlation with dual-mode sorption model.

Figure 3: Henry's law coefficient for ethane in annealed PLA 80:20 and 98:2 and in melted PLA 98:2 from 283 to 313 K.

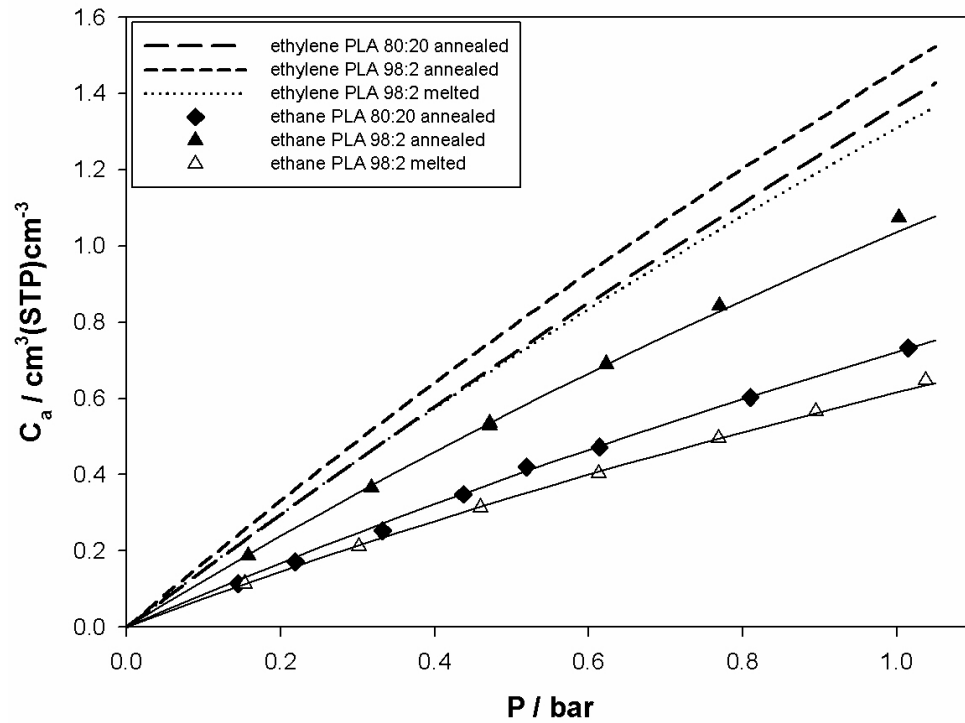
Figure 4: Langmuir concentration for ethane and affinity parameter between ethane and annealed PLA 80:20 and 98:2 and in melted PLA 98:2 from 283 to 313 K.

Figure 5: Temperature dependence of the solubility coefficients of ethane and ethylene for PLA 98:2.

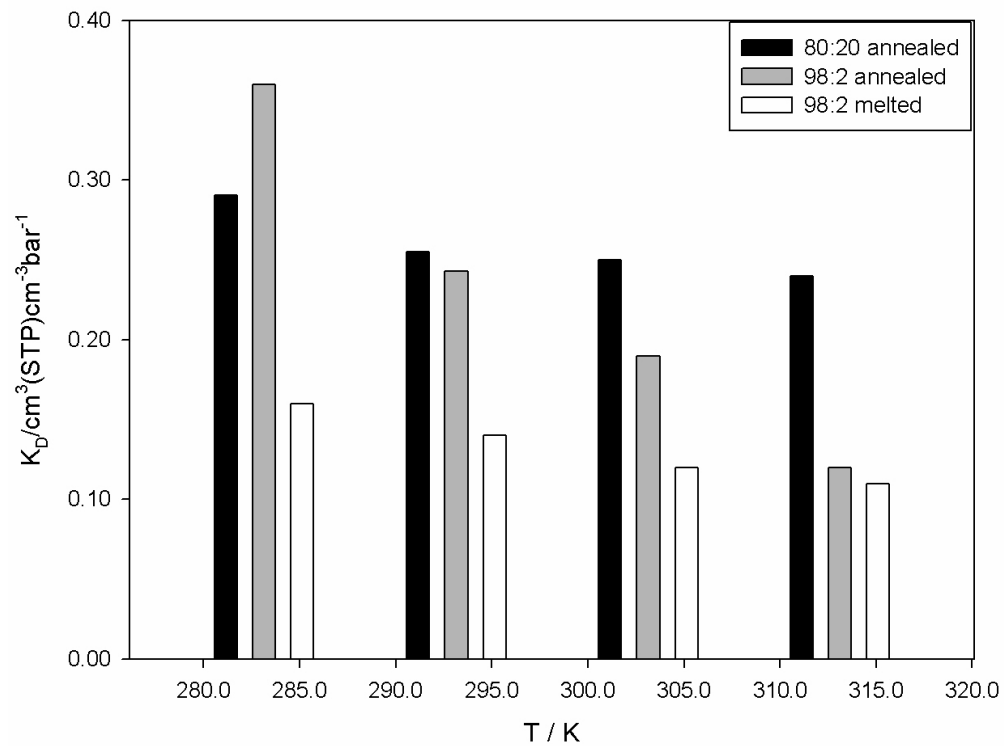
Figure 6: Temperature dependence of the solubility selectivity of ethylene over ethane for the three different PLA films.



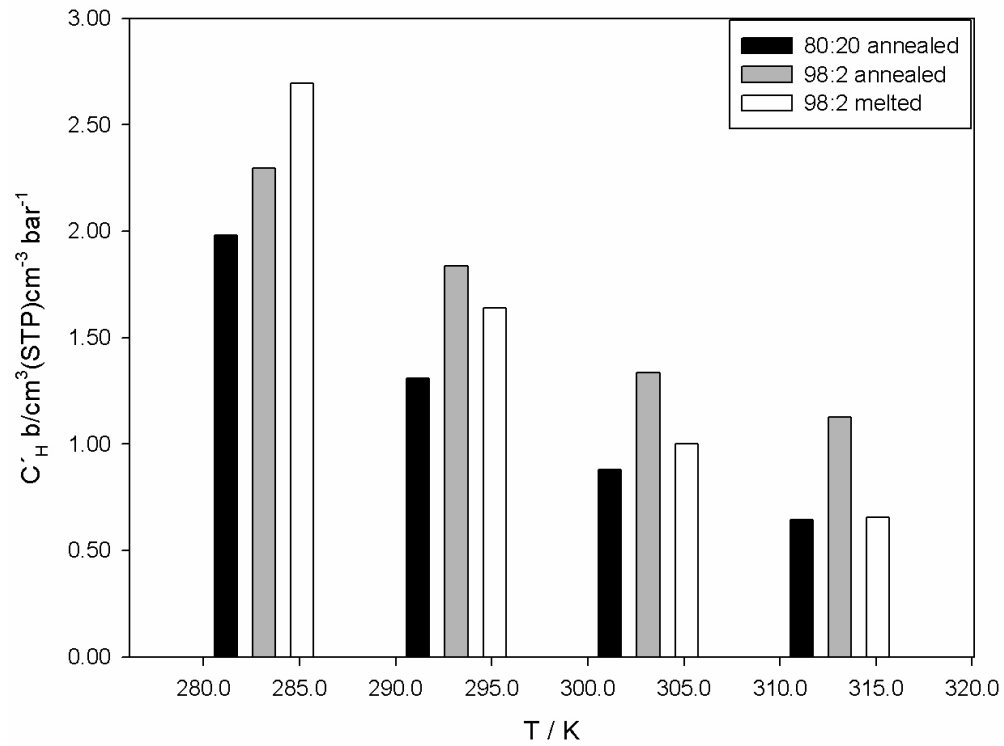
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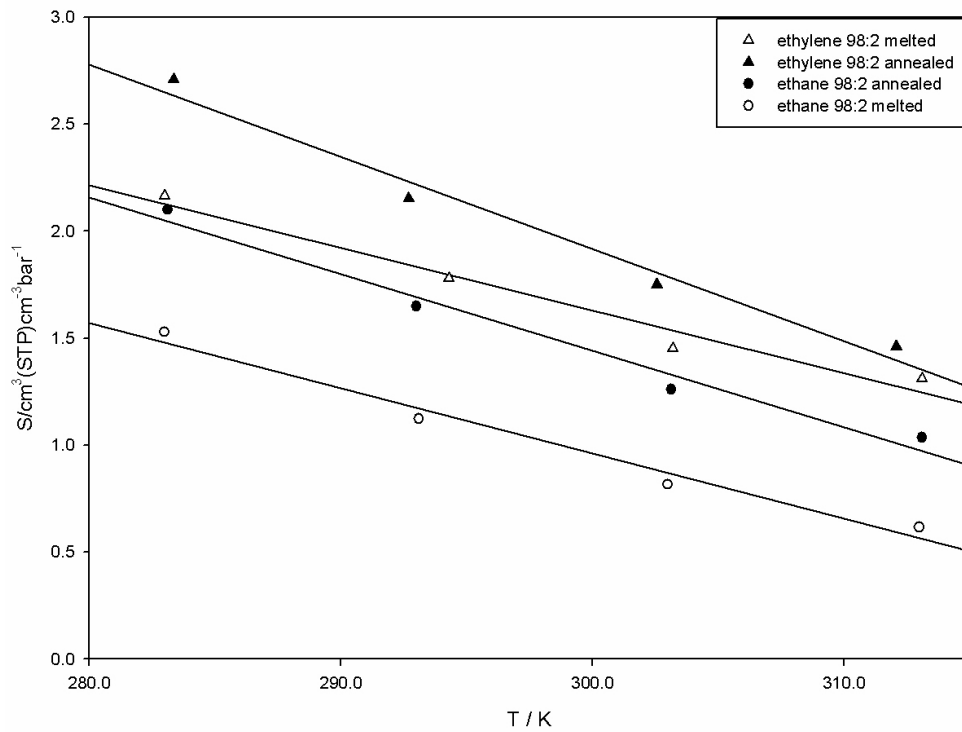
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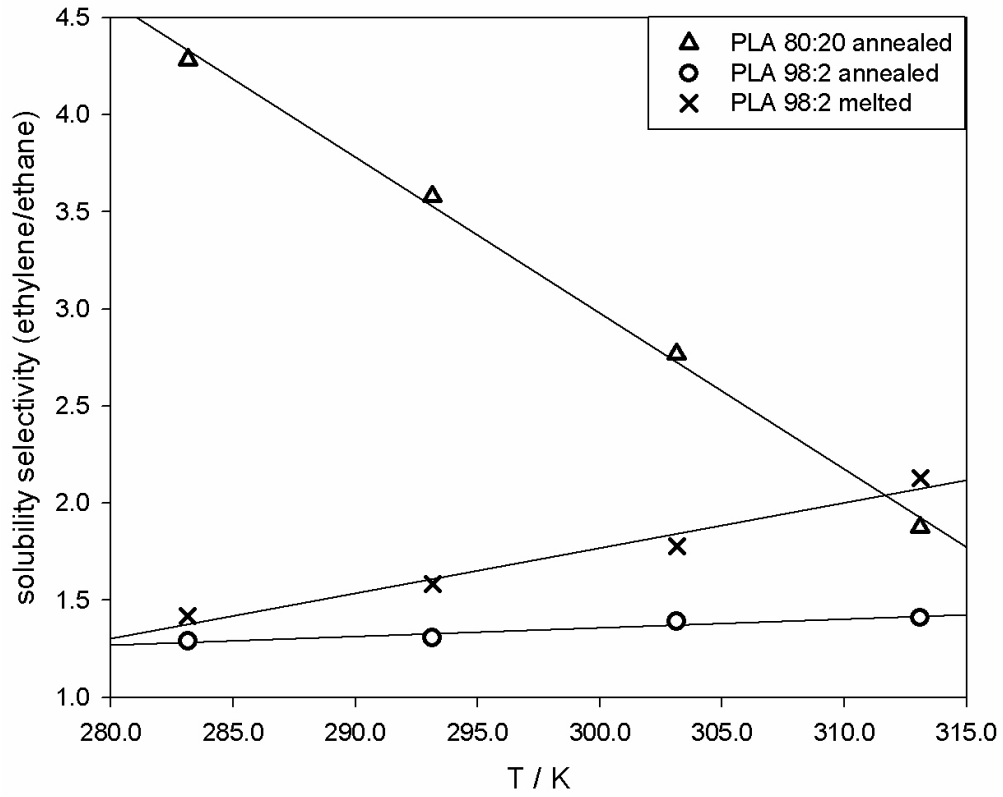
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Table 1: DSC Results for the annealed PLA 80:20 and 98:2 and melted PLA 98:2 films and literature comparisons. T_g – glass transition temperature, T_c – crystallization temperature, T_m – melting temperature, χ % - percentage of crystallinity.

L:D		T_g /K	T_c /K	T_m /K	χ %/(v/v)
98:2	annealed	328.3	375.4	439.4	20
	melted	326.0	372.3	439.5	10
Auras <i>et al.</i> , 2004	344.6			436.6	40
80:20	annealed	325.3	---	---	0

Table 2: Experimental results of sorption of ethane in PLA

PLA 80:20 annealed		PLA 98:2 annealed		PLA 98:2 melted	
283.1 K		283.1 K		283.0 K	
P/bar	$C_a/\text{cm}^3(\text{STP})\text{cm}^{-3}$	P/bar	$C_a/\text{cm}^3(\text{STP})\text{cm}^{-3}$	P/bar	$C_a/\text{cm}^3(\text{STP})\text{cm}^{-3}$
0.170	0.38	0.218	0.59	0.167	0.42
0.326	0.61	0.387	0.99	0.331	0.74
0.501	0.83	0.422	1.06	0.501	0.98
0.652	1.01	0.624	1.44	0.636	1.14
0.847	1.20	0.821	1.79	0.794	1.33
1.020	1.37	1.028	2.12	1.009	1.56
293.1 K		293.0 K		293.1 K	
0.167	0.20	0.166	0.32	0.171	0.27
0.325	0.42	0.322	0.62	0.325	0.48
0.497	0.65	0.489	0.91	0.469	0.64
0.665	0.79	0.676	1.23	0.717	0.89
0.868	0.99	0.874	1.48	0.867	1.03
1.014	1.08	1.027	1.68	1.030	1.14
303.1 K		303.1 K		303.0 K	
0.139	0.14	0.157	0.22	0.136	0.14
0.315	0.32	0.310	0.41	0.295	0.30
0.469	0.47	0.467	0.63	0.443	0.42
0.639	0.60	0.705	0.94	0.741	0.64
0.817	0.72	0.865	1.15	0.885	0.75
1.017	0.87	1.041	1.35	1.026	0.83

313.1 K		313.1 K		313.0 K	
0.145	0.11	0.158	0.19	0.153	0.11
0.332	0.25	0.318	0.37	0.301	0.21
0.437	0.35	0.471	0.53	0.459	0.31
0.614	0.47	0.623	0.69	0.613	0.40
0.810	0.60	0.770	0.84	0.895	0.57
1.015	0.73	1.003	1.07	1.037	0.65

Table 3: Dual-Mode Sorption Model parameters for ethane and ethylene In the studied films and respective average absolute deviation in percentage (AAD%)

		T ^a	K _D ^b	C' _H ^c	b ^d	AAD (%)
C ₂ H ₆	Annealed PLA 80:20	283.1	0.29	2.20	0.90	0.9
		293.1	0.26	2.16	0.61	2.0
		303.1	0.25	2.00	0.44	2.8
		313.1	0.24	1.90	0.34	2.0
	Annealed PLA 98:2	283.1	0.36	7.18	0.32	3.9
		293.0	0.24	5.97	0.31	1.2
		303.1	0.19	5.34	0.25	4.0
		313.1	0.12	4.90	0.23	1.4
	Melted PLA 98:2	283.0	0.16	2.78	0.97	1.0
		293.1	0.14	2.45	0.67	0.7
		303.0	0.12	2.28	0.44	0.6
		313.0	0.11	2.19	0.30	1.0
C ₂ H ₄	Annealed PLA 80:20	283.06	0.90	9.00	1.20	4.6
		293.04	0.74	8.01	0.64	3.0
		303.31	0.62	7.60	0.30	6.4
		313.23	0.47	6.49	0.16	3.3
	Annealed PLA 98:2	283.4	0.66	7.30	0.39	1.9
		292.7	0.58	6.20	0.34	3.4
		302.6	0.55	5.20	0.30	2.2
		312.1	0.52	4.30	0.28	1.3
	Melted PLA 98:2	283.0	0.39	7.90	0.29	3.1
		294.3	0.35	7.15	0.25	3.7
		303.2	0.32	5.85	0.24	2.6
		313.1	0.30	5.40	0.23	2.4

^aT/(K); ^bK_D/(cm³(STP) cm⁻³ bar⁻¹); ^cC'_H/(cm³(STP) cm⁻³); ^db/(bar⁻¹)