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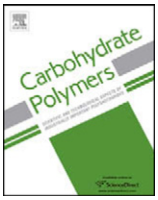

Preparation and evaluation of the barrier properties of cellophane membranes modified with fatty acids

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ABSTRACT

Cellophane (regenerated cellulose) membranes with tailored properties regarding hydrophobic character and barrier effects were prepared by their controlled heterogeneous esterification with two fatty acid derivatives (hexanoyl and dodecanoyl chlorides). The characterization of the modified membranes was performed by FTIR spectroscopy, X-ray diffraction, and thermogravimetry, confirming the success of the heterogeneous modification reaction while keeping cellophane membranes structural properties. Contact angle measurements clearly confirm the enhanced hydrophobic character displayed by the modified cellophane membranes. The evaluation of their barrier properties was carried out by determining the permeability towards water vapor at different relative humidities and the permeability towards nitrogen, oxygen and carbon dioxide, using the time-lag method, in both wet and dry states. A decrease in both the water permeation and the permeability towards these gases in the wet state was observed for the modified membranes. No significant differences in behavior were found between the membranes prepared with hexanoyl and dodecanoyl chloride regarding hydrophobicity but the different lengths of the chain allowed a fine tune of the permeability. The obtained cellophane membranes are a good example of the development of new bio-based materials with improved surface and barrier properties.

1. Introduction

The knowledge of the transport properties of water vapor and gases in polymers is a relevant parameter for packaging applications. These features depend on the free volume and segmental mobility of the polymer chains, which in turn are affected by the extent of crosslinking and crystallinity (George & Thomas, 2001). Hydrophilic polymeric membranes, such as cellophane, normally have very low permeability towards gases in the dry state, since polymer chains mobility is restricted by the extension of the hydrogen bond network between the cellulose chains. However, permeability in these membranes can dramatically change when they are in the swollen state, which promotes the cleavage of hydrogen bonds, causing a massive expansion of the amorphous regions and increasing chain segmental motion (Liu, Chakma, & Feng, 2008; Wu & Yuan, 2002).

Cellophane is a very well known material due to its good mechanical properties and hydrophilicity. It finds applications in two main areas: as semipermeable membranes for haemodialysis and in the packaging industry. Nevertheless, in the last decades, cellophane has lost ground for conventional polymers mainly due to its high production costs and environmental problems raised from the processing route. Additionally, its high hydrophilicity also plays an important role in the breakdown of cellophane use, since most applications require more hydrophobic/water stable polymers. Another important consequence of cellophane high hydrophilicity is the dramatic change in its barrier properties when in contact with atmospheric humidity.

Chemical modification of macromolecular materials is an attractive alternative for tailoring important properties for specific applications. Several strategies for the modification of cellulose substrates (as well as for other polysaccharides), in both homogeneous and heterogeneous conditions, had been suggested, during the last decades, including the reaction with anhydrides, acyl chlorides, isocyanates, oxiranes, among others (Belgacem & Gandini, 2008). For example, the modification with fatty acids has been reported as an interesting and efficient way to prepare new cellulose-based materials, due to the abundance, renewable and

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biodegradable nature of fatty acids (Chauvelon et al., 1999; Kwatra, Caruthers, & Tao, 1992; Satgé et al., 2002; Sealey, Samaranayake, Todd, & Glasser, 1996; Vaca-Garcia & Borredon, 1999). The controlled heterogeneous modification of cellulose in particular is a relatively recent research domain (Jandura, Riedl, & Kokta, 2000; Pasquini, Belgacem, Gandini, & Curvelo, 2006), which is gaining growing attention since the reaction can be restricted to the groups present in the accessible regions of cellulose macromolecules or fibers, as opposed to homogeneous conditions where the supramolecular structure of cellulose is destroyed and the original physical and mechanical properties are lost. Recently, Freire, Silvestre, Neto, Belgacem, and Gandini (2006) proposed a controlled heterogeneous modification of cellulose fibers with fatty acid derivatives, which reduces their hydrophilic character, while maintaining their structural properties. These acylated cellulose fibers were successfully tested as reinforcing elements for composites with low-density polyethylene (LDPE) (Freire et al., 2008).

Following our interest in the development of new materials based on cellulose substrates, in this work the preparation of novel cellophane derivatives using hexanoic and dodecanoic acids in controlled heterogeneous conditions was carried out. This approach is particularly important because the prepared membranes will keep cellophane interesting properties (transparency, dimensional stability, *etc.*), while the high hydrophilic behavior, which limits cellophane applications, will be reduced. The characterization of these membranes and the evaluation of the barrier properties, such as permeability towards water vapor at different relative humidities, and permeability towards nitrogen, oxygen and carbon dioxide in both wet and dry states of the membranes are presented and discussed. The two carboxylic acids were used so that the effect of the chain length in the barrier properties could be accessed. The obtained results provide an interesting example of the preparation of new bio-based materials with improved surface and barrier properties.

2. Experimental

2.1. Materials

Cellophane (regenerated cellulose) membranes were obtained from Sigma–Aldrich (D9402) and vacuum-dried at 40 °C for 48 h before use. Fatty acids (hexanoic 99% and dodecanoic 99%) were purchased from Sigma–Aldrich and high purity thionyl chloride was supplied by Fluka. Hexanoyl chloride and dodecanoyl chloride were prepared from the corresponding commercial acids by the reaction with thionyl chloride following a known procedure (Freire et al., 2006). Toluene was dried over sodium wire. Pyridine was purified and dried by distillation over sodium hydroxide. All other reagents were of analytical grade and used as received.

Carbon dioxide (CO_2), oxygen (O_2) and nitrogen (N_2) with 99.999% were purchased from Air Liquid. Gases were used with no further purification.

2.2. Membranes modification

Cellophane membranes were esterified with hexanoyl and dodecanoyl chlorides using the cellulose/fatty acyl chloride/pyridine system, following an established procedure (Freire et al., 2006). In order to avoid degradation/disintegration of the membranes, the optimum reaction conditions (time and temperature) were previously optimized. These were found to be 30 and 50 min at 80 °C, for cellophane membranes modified with hexanoyl or dodecanoyl chloride, respectively. At the end of reaction, the esterified membranes were washed with acetone, ethanol, water, and again with ethanol and acetone for removing any trace of fatty acyl chloride and other impurities. Finally, esterified cellophane membranes were dried at 60 °C for 24 h.

2.3. Characterization methods

FTIR spectra were recorded with a Brücker IFS 55 FTIR spectrometer equipped with a single horizontal Golden Gate ATR cell, with a resolution of 8 cm^{-1} after 128 scans. Spectra were collected from 4000 to 500 cm^{-1}.

X-ray diffraction (XRD) patterns were measured with a Phillips X'pert MPD diffractometer using Cu Kα radiation. The scattered radiation was detected in the angular range from 5° to 40° (2θ). The crystallinity index (CI) was estimated by the height ratio between the diffraction peaks using the Eq. (1):

$$\mathrm{CI} = \frac{I_{CR} - I_{AM}}{I_{CR}} \times 100 \qquad (1)$$

where I_{CR} is the intensity of diffraction peak for the crystalline phase ($2\theta = 18–22°$ for cellulose type II) and I_{AM} is the intensity of diffraction peak for the amorphous counterpart ($2\theta = 13–15°$ for cellulose type II) (de Menezes, Pasquini, Curvelo, & Gandini, 2009).

A thermogravimetric analyser Shimadzu TGA-50 equipped with a platinum cell was used to study the dynamic thermal degradation. The dynamic tests were run at a constant heating rate of 10 °C min^{-1} from room temperature up to 800 °C, under a nitrogen flow of 0.02 L min^{-1}. The thermal decomposition temperature was taken at the onset of a significant ($\geq$0.5%) weight loss, after moisture loss.

Contact angles (θ) were measured using water, formamide, ethylene glycol and diiodomethane with a "surface energy evaluation system" commercialized by Brno University (Czech Republic). Each θ value is the average of three independent determinations acquired immediately after the drop deposition. These values were used to calculate the polar and dispersive components of the surface energy of the cellophane membranes using the Owens–Wendt's approach (Owens & Wendt, 1969).

2.4. Water vapor permeability (WVP) measurements

The permeability towards water vapor was obtained by using an apparatus described elsewhere (Santos, Seabra, Veleirinho, Delgadillo, & Lopes da Silva, 2006) and a method based on the ASTM E96-95 – standard test methods for water vapor transmission of materials. Different relative humidity (RH) environments were established inside the test chamber using saturated aqueous solutions of different salts: magnesium chloride (32% of RH at 26 °C); magnesium nitrate (45% of RH at 26 °C); sodium chloride (72% of RH at 26 °C); and barium chloride (80% of RH at 26 °C). Membrane samples were conditioned in these environments during 48 h before their weights were recorded. Before testing, the thickness of the membrane samples was measured using a digital micrometer (model MDC-25S, Mitutoya Corp., Tokyo, Japan). Mean thickness was calculated from five measurements taken at different locations in each membrane sample. At least, three samples of each type of membrane were measured.

2.5. Gas permeation measurements

Usually two methods have been used to measure the permeation of pure gases through dense polymer membranes: differential and integral methods (Felder, 1978). All these methods are based on the dynamic response obtained from a sudden change in the membrane boundary conditions (Taveira, Mendes, & Costa, 2003). Despite the advantages and disadvantages of these methods, the most used is undoubtedly the integral method, known as time-lag, which allows the simultaneous determination of permeability

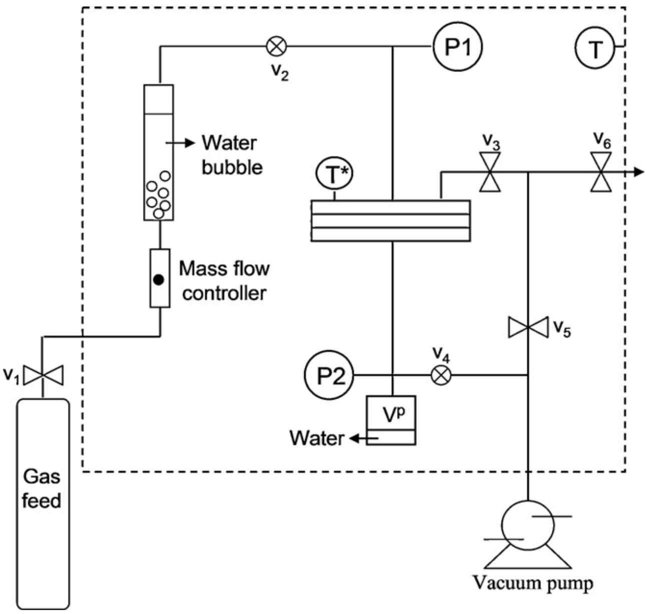

Fig. 1. Diagram of the time-lag apparatus. P represents the pressure sensors, V the manual and electric valves, V^p the permeate tank, T* the temperature controller in the permeation cell and T the thermostatic air bath.

and diffusivity (Hands, 1999). Typically, a time-lag apparatus is composed by two tanks, feed and permeate, connected to the permeation cell. The permeation cell consists of two compartments (feed and permeate chambers) separated by the membrane under study. Initially, both chambers and the permeate tank are evacuated. At a given instant it is made a step pressure perturbation in the feed chamber. As the testing gas permeates the membrane the permeate pressure rises. If the permeate tank volume is known, it is possible to obtain the permeation flowrate from the pressure history, as long as this pressure stills low compared to the feed – approximate constant driving force (Brandão, Madeira, & Mendes, 2007; Taveira et al., 2003).

Two different time-lag apparatuses were used in this work: one for the permeation of gases in the dry state and the other for the wet state measurements. The permeation of gases in the dry state through both unmodified cellophane and acylated cellophane samples was measured in a time-lag apparatus using a permeation cell with a surface area of 13.9 cm^2 connected to permeate tank with a volume of (34.2 ± 0.2) cm^3. The pressure variations in the permeate tank were measured with a high precision absolute pressure sensor (MKS e-Baratron, ref. 628, 133 mbar). It was applied 1 bar feed pressure and the permeate tank was evacuated below 1 mbar. Cellophane membranes used for permeability measurements in dry state were degassed under vacuum during 48 h inside the permeation apparatus.

The experimental set-up used for the wet state time-lag experiments is shown schematically in Fig. 1. This apparatus is very similar to the one used for dry gases with two main differences: (i) a water bubble column was inserted in the line before the permeation cell, in order to saturate the probe gas; (ii) the permeate tank also has water inside (25.0 cm^3) to assure that the membrane is in equilibrium throughout the experiment and thus no partial pressure difference exists between the two sides of the membrane. The permeation cell, with 11.04 cm^2 of effective area, comprises a sintered disk used to support the membrane and a viton O-ring to seal the cell. To control the pressure variations in the permeate tank, with a volume total of (80.7 ± 0.3) cm^3, a precision absolute pressure sensor (Druck, ref. PMP 4010, 350 mbar) was used. The time-lag unit was placed inside a thermostatic cabinet and the experiments were performed at 25.0 °C. The feed pressure was atmospheric and the initial permeate pressure was 31.67 mbar (water vapor pressure at 25 °C).

Assuming ideal gas behavior, the permeate flux (Q) can be obtained (Brandão et al., 2007; Taveira et al., 2003):

$$Q = \frac{n}{At} = \frac{V^p \Delta P}{AtRT} \tag{2}$$

where A is the effective area of dense membrane, ΔP is the variation of downstream pressure, V^p is the permeate volume, t is the time, n is the quantity of mater, R is the gas constant and T is the temperature. The permeability (P) is obtained from:

$$P = \frac{Q}{\Delta p / \ell} \tag{3}$$

where ℓ is the membrane thickness and Δp is the difference in pressure (driving force). The time-lag parameter (θ) relates to the diffusivity coefficient (D) and can be obtained, before the steady-state flux is achieved, from:

$$D = \frac{l^2}{6\theta} \tag{4}$$

For the gas permeation experiments at 100% of RH, the unmodified and modified cellophane membranes were previously equilibrated at the water vapor pressure at 25 °C, inside the permeation apparatus, during 12 h before the beginning of the measurements. This procedure ensured that membranes were in the wet stationary state and in this case the diffusivity coefficients cannot be determined. The thickness of the membranes was measured immediately after testing. Average thickness was calculated from five measurements.

All permeation data were determined for at least three samples in order to confirm the reproducibility of the experimental results.

3. Results and discussion

3.1. Characterization of the modified membranes

In this work cellophane membranes (Cell) were esterified with hexanoyl and dodecanoyl chlorides and the products were named $CellC_6$ and $CellC_{12}$, respectively. The success of the reaction of esterification was clearly confirmed by FTIR analyses (Fig. 2(a)), on the basis of the appearance of a new ester carbonyl band at 1735 cm^{-1} and an increase in the intensity of the C–H band in the range 2860–2900 cm^{-1} arising from the aliphatic acid chain (Bellamy, 1975). Additional proofs of the successful esterification are the decrease in intensity of the broad band at about 3400 cm^{-1} assigned to the cellophane O–H vibrations (Bellamy, 1975; Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998) and the appearance of a band around 700 cm^{-1}, typical of CH_2 vibrations in compounds bearing carbon chains with more than four CH_2 groups.

The unmodified cellophane membranes displayed the typical XRD pattern of cellulose II (Meshitsuka & Isogai, 1995), with the main diffraction signal at around $2\theta = 12.3°$, 20.3° and 21.7°, normally assigned to the diffraction planes $1\,\bar{1}\,0$, $1\,1\,0$ and $2\,0\,0$, respectively (Zhang, Ruan, & Zhou, 2001). All the esterified membranes preserved this XRD pattern (Fig. 2(b)) suggesting that the modification occurred predominantly on the outmost and amorphous regions without affecting the internal structure of the membranes. However, there is a slight increase at 2θ between 15° and 20° for both $CellC_6$ and $CellC_{12}$, which is normally attributed to the less ordered regions of cellulose chains. The calculated values of the crystallinity index are 40, 37, and 36% for Cell, $CellC_6$ and $CellC_{12}$, respectively, showing only a slight decrease of this index after the heterogeneous modification.

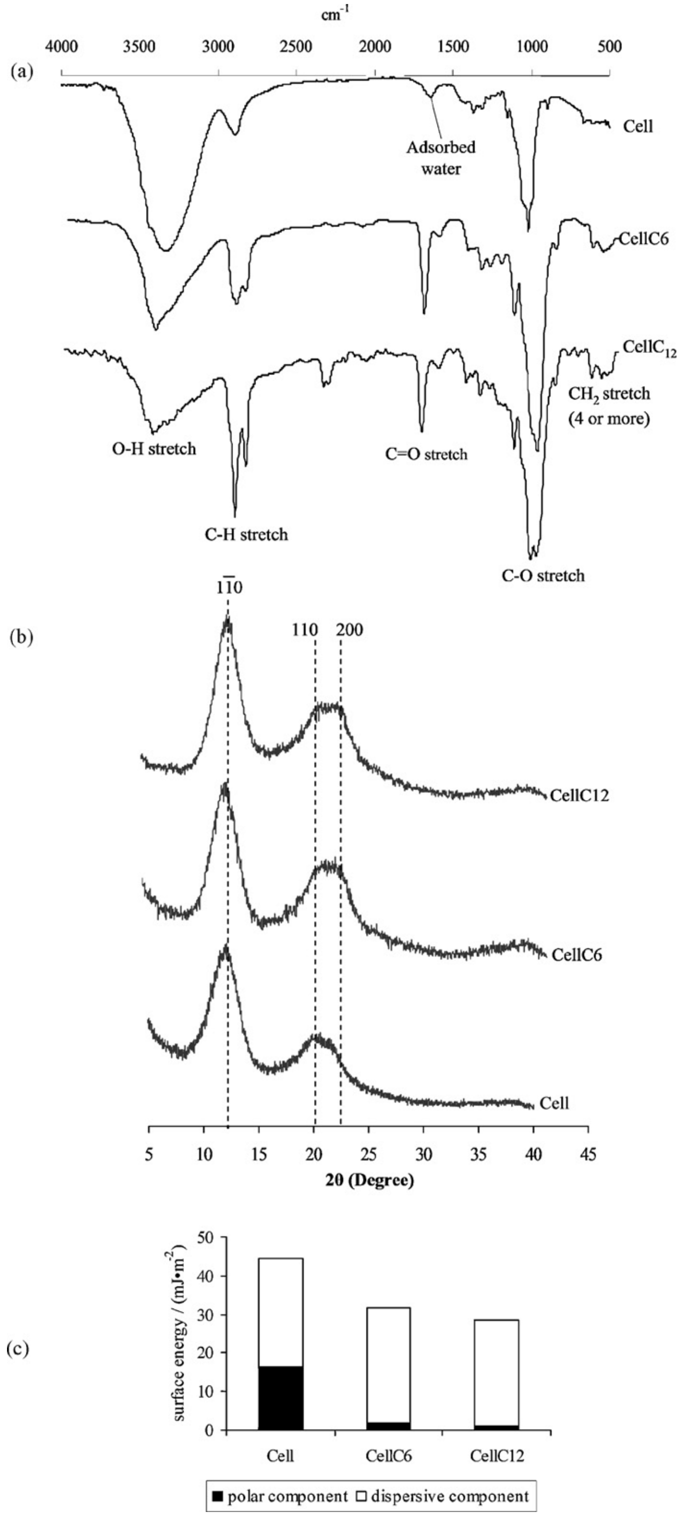

Fig. 2. (a) FTIR-ATR spectra, (b) X-ray diffractograms, and (c) Surface energies of cellophane membranes before (Cell) and after esterification with hexanoyl ($CellC_6$) and dodecanoyl ($CellC_{12}$) chlorides.

Table 1
Thermogravimetric (TGA) features and contact angles (θ,°) for different liquids of cellophane membranes before and after esterification.

Samples	Cell	$CellC_6$	$CellC_{12}$
TGA			
Weight loss at 100 °C (%)	8.94	5.42	3.38
Td_i (°C)	255	190	175
Td_1 (°C)	353 (57)[a]	268 (29)	260 (30)
Td_2 (°C)	–	350 (49)	313 (45)
Contact angles (θ,°)			
Water	54.2 ± 5.8	90.7 ± 0.5	94.0 ± 1.6
Formamide	51.6 ± 0.8	75.5 ± 0.8	77.6 ± 1.0
Ethylene glycol	48.4 ± 0.8	63.7 ± 3.0	76.2 ± 0.5
Diiodomethane	42.9 ± 1.6	50.8 ± 1.6	54.1 ± 0.5

Error analysis was obtained by the standard deviation of three independent determinations after drop deposition.

[a] Number in parentheses refers to the percentage of decomposition attained at Td_1 and Td_2.

The thermal stability of the membranes was assessed by thermogravimetrical analysis. Table 1 gives the relevant thermogravimetric features of cellophane membranes before and after the esterification reactions. The TGA tracing related to unmodified cellophane membranes follows a single weight-loss step starting at 255 °C (Td_i) and with a maximum decomposition at about 353 °C, which is in perfect agreement with data reported in the literature (Kawano & Logarezzi, 1995). The thermograms of esterified membranes showed two main separate degradation steps: the first step (Td_1) is attributed to the degradation of the esterified fraction, while the second step (Td_2) is associated with the unmodified fraction of cellophane (Freire et al., 2006). According to Table 1, the modified cellophane membranes are less stable, since they started to decompose at temperatures substantially lower than unmodified cellophane membranes. This behavior is attributed to the decrease in crystallinity associated with the esterification reaction, as already reported for cellulose fibers by Jandura et al. (2000) and Freire et al. (2006). The TGA results also indicated an increase in membrane hydrophobicity after esterification, as shown by the lower weight loss at 100 °C, assigned to water release, compared to the unmodified cellophane membranes.

The surface energy of solids can be determined from the measurement of the contact angles formed by liquids with different surface energies on their surface (Briggs, Rance, & Briscoe, 1989). Table 1 gives the average contact angle of liquids with different polarities deposited onto the surface of the cellophane membranes. The considerable enhancement in the hydrophobic character of the surface of modified cellophane membranes was clearly demonstrated by the increase in contact angles with polar liquids (water, formamide and ethylene glycol). This behavior had already been reported for cellulose fibers modified with hexanoyl and dodecanoyl chloride (Freire et al., 2006). Total surface energy as well as their polar and dispersive components for unmodified and acylated cellophane samples are displayed in Fig. 2(c). It can be concluded that the decrease in the surface energy of the cellophane membranes after esterification was mostly induced by the drastic reduction in the polar contribution, resulting from the surface functionalization of hydroxyl groups by acyl groups with non-polar aliphatic chains.

3.2. Water vapor permeability

The cellophane water vapor permeability (WVP) before and after esterification with hexanoyl and dodecanoyl chlorides is shown in Fig. 3(a). The obtained results confirm that unmodified cellophane membranes have a hydrophilic nature, as also shown by the contact angles previously presented in this work, and have poor water barrier properties when compared to conventional polymers, such as polyethylene. For example, Morillon, Debeaufort, Capelle, Blond, and Voilley (2000) reported for the same conditions that polyethylene has a permeability towards water vapor one order of magnitude lower than that of cellophane membranes. The cellophane water vapor permeability for different relative humidities obtained in this work is in general one order of magnitude lower than the values reported by other

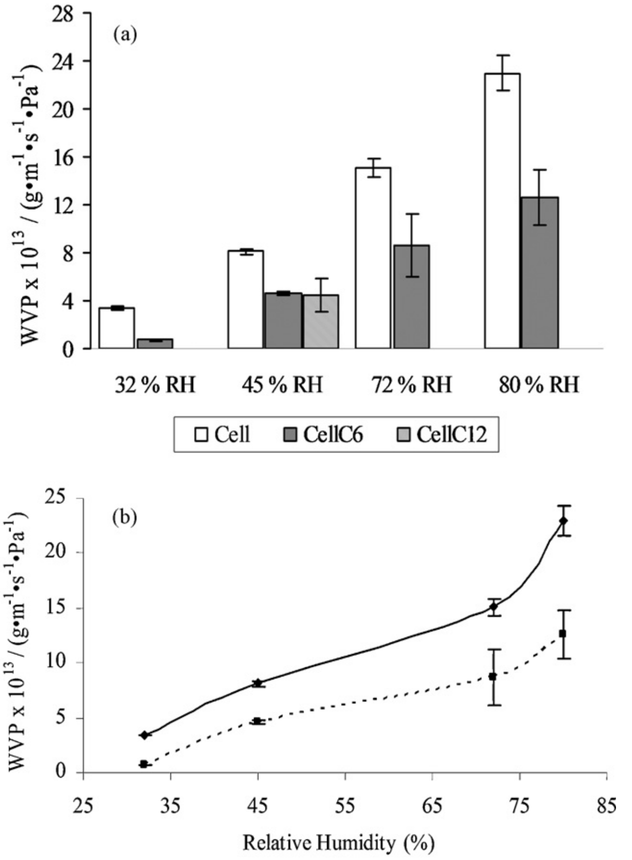

Fig. 3. (a) Cellophane permeability towards water vapor (WVP) before (Cell) and after esterification with hexanoyl ($CellC_6$) and dodecanoyl ($CellC_{12}$) chloride at different relative humidities (RHs). (b) Cellophane permeability behavior towards water vapor (WVP) before (solid line) and after (dashed line) esterification with hexanoyl chloride as a function of the relative humidity. Standard deviations were calculated based on three experimental replicas.

authors for the same material (Debeaufort, Voilley, & Meares, 1994; Martinpolo, Mauguin, & Voilley, 1992; Morillon et al., 2000). This difference can be due to the different methods and the conditions involved in measuring the permeability towards water vapor, as well as to the nature of the cellophane membrane. Indeed, the water vapor transmission rate for cellophane membranes obtained in this work $(8.3 \pm 0.3) \times 10^{-3}\,\mathrm{g\,m^{-2}\,s^{-1}}$ at 26 °C and 72% of RH is similar to the one reported by Debeaufort and Voilley (1994), $(5.0 \pm 2.5) \times 10^{-3}\,\mathrm{g\,m^{-2}\,s^{-1}}$ at 25 °C and 70% of RH.

As expected the esterification of cellophane membranes with hexanoyl chloride causes a significant decrease in the permeability towards water vapor at all the relative humidities. Fig. 3(a) shows that the esterification of cellophane with hexanoyl chloride causes a decrease of approximately 50% in permeability towards water vapor for all relative humidity conditions studied, confirming the increase in hydrophobicity after the modification. This decrease occurs due to the insertion of fatty aliphatic chains on surface of the membrane, causing a decrease in the affinity of cellophane membranes for the water molecules. The permeability towards water vapor of unmodified cellophane and modified with hexanoyl chloride increases with relative humidity, in a nonlinearly manner. Fig. 3(b) shows that the permeability behavior as a function of the relative humidity for pristine and modified with hexanoyl chloride cellophane membranes is roughly the same. This behavior is identical to that shown in the literature for other polysaccharide (starch) (Liu, 2005). The sigmoidal shape of the water sorption isotherms indicates that the water transport through hydrophilic polymers is a complex phenomenon (Morillon et al., 2000), which depends on the amount of water sorbed. It has been proposed (Despond, Espuche, & Domard, 2001) that at low relative humidity (<40%), the water molecules are sorbed in the amorphous phase of the hydrogen bond active sites while for higher relative humidities, especially after 80% of RH, the water molecules are predominantly clustered instead of sorbed on those active sites; this way, the solubility is drastically increased. In the present results (Fig. 3(b)), these two major changes in the permeability towards water vapor can be clearly distinguished. The first one is observed around 45% of RH and the second significant change occurs approximately at 80% of RH. For higher relative humidities, the plasticization effect leads to a dramatic increase in the permeability towards water vapor.

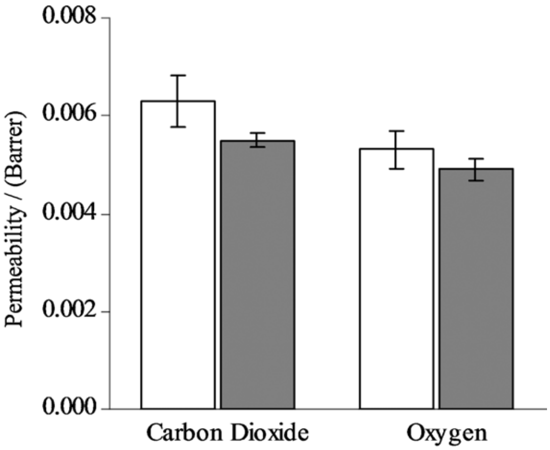

Fig. 4. Permeability towards carbon dioxide and oxygen in dry state cellophane before (Cell) and after esterification with hexanoyl chloride ($CellC_6$), at 25 °C. The error bars, based on the uncertainties in measured variable, were obtained for 95% confidence interval (*t*-distribution) based on three experiments.

The effect of the esterification of cellophane membranes with dodecanoyl chloride in the water permeation was also evaluated at 22 °C and 45% of RH (Fig. 3(a)) and no significant differences were observed in the water permeation between the $CellC_6$ and $CellC_{12}$ membranes. These results are consistent with the small differences in contact angles measurements (Table 1) and in the surface energy (Fig. 2(c)) values observed for these membranes as described above.

3.3. *Gas permeation*

Two probe gases, O_2 and CO_2, were selected for characterizing the dry state cellophane membranes at 25 °C. It was not possible to accurately determine the time-lag due to its very small value and subsequent large experimental errors. For that reason, the diffusion and solubility coefficients are not presented. The permeability coefficients were obtained for steady-state conditions, i.e. when the permeating gas flux is constant with time. The permeability results for dry Cell and $CellC_6$ membranes are shown in Fig. 4. The dry Cell membrane shows a very low absolute permeability to both CO_2 and O_2 compared to other conventional barrier polymers, such as low-density polyethylene (LDPE), polystyrene (PS) and polyvinyl chloride (PVC) (Brandrup, Immergut, & Grulke, 1999), as can be verified in Table 2. However, the results obtained are similar to those reported by other authors for cellophane membranes (Kamide & Iijima, 1994; Kamiya & Takahashi, 1977; Wu & Yuan, 2002) and analogous to those reported for other hydrophilic polymers (Kim, Park, Youm, & Lee, 2004; Liu et al., 2008). These small permeability values are due to the dense structure of these membranes in the dry state since the high level of hydrogen bonds decreases void space (George & Thomas, 2001). As expected, the heterogeneous chemical modification of cellophane membranes with hexanoyl chloride has not affected the permeability to both gases in dry

Table 2
Comparison of the CO_2 and O_2 permeability of dry cellophane membrane and some conventional polymers at 25 °C. Solubility and diffusivity of different gases in water at 25 °C (Lide, 2006–2007).

Polymers	CO_2 permeability (Barrer)	O_2 permeability (Barrer)	
Cell	0.0063	0.0053	This work
LDPE	12.7	2.9	Ref. Brandrup et al. (1999)
PS	10.5	2.7	
PVC	0.2	0.05	

Gases	Solubility ($cm^3_{STP}\ cm^{-3}\ cmHg^{-1}$)	Diffusivity ($cm^2\ s^{-1}$)	Permeability (Barrer)[a]
CO_2	1.01×10^{-2}	1.91×10^{-5}	1923
O_2	3.76×10^{-4}	2.42×10^{-5}	91.0
N_2	1.94×10^{-4}	2.00×10^{-5}	38.7

[a] Permeability of gas in water was estimated from solubility and diffusivity.

membranes, since the modification was limited to the outmost layers of the membranes, without affecting their bulk properties. Liu et al. (2008) showed that the gas permeability through these types of dry membranes is dominated by the diffusion of the gas in the polymer matrix. Consequently, the small changes in the permeability of dry cellophane membranes for both gases should be related to the slight decrease in crystallinity of the $CellC_6$ sample caused by the modification reaction and not directly by surface energy decrease.

As previously mentioned, cellophane is a very good gas barrier under dry conditions, but it loses this property at a high relative humidity. In order to evaluate if the proposed chemical modification with hexanoyl chloride improved the barrier properties of the cellophane membranes to 100% humidified gases, CO_2, O_2 and N_2 were used as probe gases in the permeability experiments at 25 °C. The CO_2 and O_2 permeation rates on the wet Cell membrane are 19.8 and 2.0 Barrer, respectively. These permeation rates are 3300 and 400 times higher than those of dry state membranes. These results show that water plays an important role in the transport process in wet membranes. Fig. 5 also shows the permeability towards the different humidified gases for the modified cellophane membranes. Comparing these results with the parameters listed in Table 2 for the three studied gases (CO_2, O_2 and N_2) in water it can be concluded that the permeation behavior through wet state cellophane membranes follows the same order as the gas permeation in water. As expected, all the cellophane membranes showed a higher permeation rate for CO_2 when compared with O_2 and N_2. This could be explained by the higher solubility of CO_2 in water than the other two gases, due to the strong CO_2–water interactions (Lide, 2006–2007). As shown in Fig. 5, at 25 °C and 100% of RH, the $CellC_6$ and $CellC_{12}$ show a significant decrease of the gas permeability when compared to the Cell membranes: CO_2 (42 and 56%), O_2 (43 and 59%) and N_2 (33 and 57%), respectively. This decrease occurs due to the reduction of surface energy and consequent increase of their hydrophobic character, which led to a lower affinity to water molecules, as well as lower permeability towards gases.

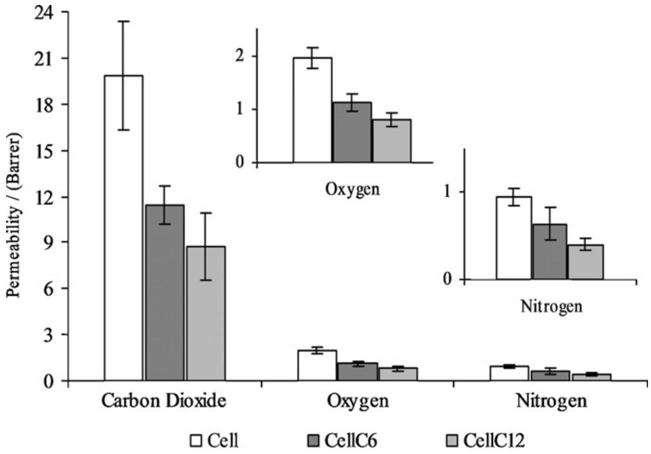

Fig. 5. Permeability towards carbon dioxide, oxygen and nitrogen in wet state cellophane before (Cell) and after esterification with hexanoyl ($CellC_6$) and dodecanoyl ($CellC_{12}$) chloride, at 25 °C and 100% of relative humidity. The error bars, based on the uncertainties in measured variable, were obtained for 95% confidence interval (*t*-distribution) based on three experiments.

4. Conclusions

The heterogeneous modification of cellophane membranes with two acyl chlorides was successfully achieved. As expected, the ensuing modified membranes preserved the bulk structure of the pristine material, while showing quite different surface energy values, resulting in an increased hydrophobic surface character. However, these membranes have lower thermal stability than the starting materials.

Finally, the well-known barrier properties of cellophane membranes to water and gases changed significantly with the proposed surface modification. A decrease in the permeability towards water vapor, for all the tested conditions, and in the permeability towards gases in the wet state was verified for the modified membranes. However, no change was observed for permeability towards gases in the dry conditions, when compared to the pristine material.

The surface modification described in this work provides an interesting example of preparation of new bio-based polymeric material with surface and barrier properties greatly improved.

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