Transport of Water and Gases through EVA/PVC blend films – Permeation and DSC investigations.

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ABSTRACT

The transport of water vapor and gases (oxygen and carbon dioxide) through poly(ethylene-co-vinyl acetate) (EVA) films of different VA content, poly(vinylchloride) (PVC) and EVA/PVC blend films, was analysed from permeation measurements.

A plasticization effect of water on the material was observed for EVA films with more than 19% wt. of VA content and for the EVA/PVC blends, while for gas permeation practically all the experimental curves are characterized by a constant diffusion coefficient, whatever the VA content of the copolymer used. The increase in water absorption with the VA content leads to a steady increase in the water permeability of the EVA copolymers. By mixing the glassy PVC polymer with the EVA copolymer (in a rubbery state) reduced water and gas permeability is observed, resulting mainly from the decrease of the diffusivity due to the low segment mobility of the dense PVC material able to create hydrogen bonds between the hydrogen atoms and the Cl-substituted carbon of PVC with VA carbonyls. Compared to EVA copolymers, the EVA/PVC blends with equivalent VA contents are better in terms of selectivity.

Keywords : EVA copolymers, EVA/PVC blends, water and gases permeation, DSC.

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1-Introduction

Fresh fruit and vegetables, which are living matter, sometimes need to be shipped and stored until their consumption. In order to extend their life time, it is necessary to reduce the rates of biochemical reactions which consume oxygen and produce carbon dioxide, ethylene and water [1]. There is an opposite relationship between the respiratory intensity and the storage time of the fruit and vegetables. Anaerobic fermentation of bio-components under high water and CO_2 contents often leads to bad taste and smell of fruit and vegetables. A better preservation of this type of food can thus be obtained by decreasing the respiratory intensity and the anaerobic fermentation rate *via* control of oxygen, carbon dioxyde and water vapor permeabilities. This can be obtained with packaging materials exhibiting high H_2O/CO_2 and CO_2/O_2 selectivities.

To obtain a more favorable atmosphere for the preservation of some foodstuffs, micro perforation of hydrophobic films like bioriented polypropylene is currently used. The permeability of all gases is enhanced due to the additional convection flow through the created holes. As the bulk flow through holes is much faster than that through the dense polymer, but is non-selective [1], such films are only suitable for certain foodstuffs like cheese, where water vapor and CO_2 buildup must be avoided.

In the present work, we investigate the use of copolymers and blends as selective packaging materials. Changes in copolymer or blend composition make it possible to vary the film permeability and selectivity properties. As ethylene-vinyl acetate (EVA) copolymers with vinyl acetate content varying from 2% to 70%. are commercially available, they are worth being studied as packaging materials.

In previous papers, the transport of water, oxygen and carbon dioxide through ethylene-co-vinyl acetate copolymers films have been studied [2,3]. In this paper, we focused our study on the transport properties for water, and pure carbon dioxide and oxygen through miscible binary blends of EVA with polyvinylchloride. The interest of mixing PVC in EVA copolymers is the possibility to introduce a glassy polymer well-known to be compatible with our EVA series (which are in a rubbery state) and which is a barrier to gas permeation, and so be able to improve gas selectivities by changing permeation properties (permeability, diffusivity and solubility). Usually, glassy polymers are recognised to be more selective than rubbery more permeable polymers.

2-Theoretical Background

The mathematical treatment of diffusion transport is based on the following assumptions [4,5] :

– The polymer film is homogeneous,

– The process is Fickian, i.e. not time-dependent,

– The interfacial sorption (penetrent/polymer) equilibrium is instantaneous and steady,

– The mass transfer occurs in the perpendicular direction to the plane sheet.

Permeation

Concentration and flux profiles, $C(x,t)$ and $J(x,t)$, are described by Fick's laws and the boundary conditions used are :

$$
\begin{aligned}
&for\ \ t = 0,\ \ C(x,0) = 0 \quad \forall x \in]0,L[\\
&at\ x = 0, \quad C(0,t) = C_{eq} \quad \forall t \\
&at\ x = L, \quad C(L,t) = 0 \quad \forall t
\end{aligned}
\qquad (1.)
$$

For water (H_2O) and oxygen (O_2), the measurement principle and procedure were described in previous papers [6,7] . When the upstream face of an initially dry film is suddenly brought into contact with an atmosphere at fixed water or oxygen concentration, while the downstream face is swept with a dry gas at a flow rate (f), a permeation flux J occurs through the film. The initially nil flux increases progressively with time up to a limit J_{st}, which is the typical steady state flux. The variations with time of the reduced water or oxygen flux J/J_{st} are obtained by integration of Fick's laws according to our specific boundary conditions.

For carbon dioxide (CO_2), the measurement of the transport parameters by the time-lag method is based on the variation of the downstream pressure with time. When the upstream face of an initially dry film is suddenly brought into contact with an atmosphere at fixed carbon dioxide pressure, while the downstream face is kept at a low pressure (under vaccum, 10^{-3} mbar), the carbon dioxide permeation through the film leads to a pressure build-up which is monitored.

The permeability coefficient is the product of gas flux and film thickness divided by the pressure difference Δp between the two faces of the film (or activities Δa). From the steady state permeation flux J, it is possible to determine the permeability coefficient P:

$$P = \frac{J_{st}L}{\Delta X} \qquad (2.)$$

where L is the thickness of the polymer film, J_{st} the stationnary flux, $\Delta X = \Delta p$ for CO_2 time-lag permeation tests [8] and $\Delta X = \Delta a$ for H_2O and O_2 permeation tests. In pervaporation, at the upstream interface with pure water, $\Delta a \approx a_h = 1$. In permeation, $a_h = p_h/p_{st}$, where p_h and p_{st} are vapor and saturated vapor pressures, respectively. Usually P is expressed in barrer (cc STP.cm / $cm^2 s^{-1} cmHg$).

On the other hand, for CO_2 time-lag permeation, the stationnary flux J_{st} is obtained from the slope of the steady-state part i.e. when the curve of the amount Q =f(t) is similar to an asymptotic line which corresponds to

$$Q = \frac{DC_{eq}S}{L}(t - t_L) = J_{st}S.(t - t_L) \qquad (3.)$$

where t_L, called time-lag, is the intercept on the time axis of the asymptotic line of the curve Qt=f(t); S the exposed area and D the diffusion coefficient. Thus, for carbon dioxide, the permeability coefficient P can be calculated directly by using eqn. (4) or indirectly knowing that

$$Q = S \int_{t=o}^{t} J(L,t)dt \qquad (4.)$$

One of the main problem in the determination of the values of the different quantities which occur in these equations is linked to the determination of the ad-hoc value (or expression) of the diffusion coefficient D. If we assume that D is constant, its value can be calculated by at least two differents ways:

i) from the time-lag time-lag t_L [9]:

$$D_L = \frac{L^2}{6t_L} \qquad (5.)$$

ii) from the time $t_{0.24}$ corresponding to a value of $J/J_{st} = 0.24$, i.e. at the inflexion point I of the transient permeation curve [7]:

$$D_I = \frac{0.091.L^2}{t_{0.24}} \qquad (6.)$$

The calculated value of D_L usually obtained from the curve Q=f(t) can also be determined on the transient permeation curve at the J point corresponding to a value of $J/J_{st} = 0.6167$, for which $t=t_L$.

If D_L is practically found equal to D_I, the assumption D=constant can be generally accepted. In permeation, the particular case of D constant is characterized by the reduced curve j=f(τ) (j=J/J$_{st}$) and/or q=f(τ) (q =Q/SLC$_{eq}$) with τ=Dt/L^2

$$q = \tau - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{(-n^2\pi^2\tau)} \qquad (7.)$$

$$j = 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{(-n^2\pi^2\tau)} \qquad (8.)$$

This reduced curve j=f(τ) shows an inflexion point I(τ_I=0.091, j$_I$=0.24). At this inflexion point I of the plot of the dimensionless flux J/J$_{st}$ versus the reduced time τ=Dt/L^2, the slope α (=Δj/$\Delta\tau$) depends on the D variation law. The slope α could be used as a significant parameter of the concentration dependence.

If D_L is different from D_I, a model which takes into account a possible variation of D with the concentration C of sorbed molecules must be tested. The interpretation of the experimental curves is then more complex and requires the numerical integration of the experimental data. Assuming that the diffusion coefficient generally increases exponentially with the local permeant concentration in the film during the course of water penetration [10,11] an empirical equation is then used and represents the diffusion plasticization effect of water on the materials [8,9] :

$$D = D_0\, e^{\gamma C} \qquad (9.)$$

where D_0 is the limit diffusion coefficient , γ is the plasticization coefficient and C the local permeant concentration. To determine the two parameters of this diffusion law, we may use a new method which is described in more detail in a separate paper [12]. During the fitting procedure of the experimental transient flux data, the values of D_M (=$D_o e^{\gamma C_{eq}}$), D_o, γ, C_{eq} and $\bar{D}$ are computed. C_{eq} is the penetrant concentration in the polymer at sorption equilibrium and

$\bar{D} = \frac{1}{C_{eq}} \int_0^{C_{eq}} D(c)\,dC$ is an integral mean diffusion coefficient which can be used to characterize the average diffusion coefficient of water in the materials.

Now, on the basis of a mean diffusion coefficient $\overline{D}$, the solubility coefficient S can be deduced from the general relation [13]

$$P = \overline{D} \cdot S \qquad (10.)$$

Finally, the fundamental parameters characterizing membrane separation performance are the permeability coefficient, P, and the ideal selectivity, $\alpha_{A/B}$. Ideal gas selectivity is the ratio of permeability coefficients of two gases [14] :

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A S_A}{D_B S_B} \tag{11.}$$

where P_A is the permeability of the more permeable gas and P_B is the permeability of the less permeable gas in the binary mixture.

3-Experimental

3.1-Preparation of membranes

Poly(ethylene-*co*-vinylacetate) films (EVA) of low vinyl acetate (VA) content (up to 19 wt. %) were kindly provided by 3M Corp (Health Care Specialties, 3M Center St Paul, USA). For the sake of simplicity, the weight per cent of vinylacetate is indicated as a subscript of the copolymer name : EVA_x stands for the copolymer of x wt. % VA content. Poly(ethylene-*co*-vinylacetate) of high vinyl acetate content, which is not available in the form of films, were prepared by casting a solution of the appropriate sample (Baymod type, kindly provided by Bayer Corp. Paris, France) in dichloromethane (10% w/w CH_2Cl_2, at 30°C with agitation until complete dissolution, c.a. 10 hours) on a glass plate. After solvent evaporation (under vacuum at 25°C for 24 hours then 80°C for 8 hours), the film was unstuck from the glass plate by soaking it with pure water.

For the blend of Polyvinylchloride (PVC from Aldrich Chemical Company, Mn=55000) with EVA of different vinyl acetate content, a solution of 20 wt. % of PVC and EVA in tetrahydrofuran was cast into films on a glass plate. Based on literature data showing good result for these blends in terms of miscibility [15,16], the composition used in this work is EVA_x/PVC (A/B % w/w) with A % = -0.4.x + 78 and B=100-A.. After solvent evaporation as described previously, the films were stored in a dessiccator over phosphorus pentoxide until their use.

The films used in the present study have different thichnesses, ranging from ca. 100 to 250 µm. Corrections were applied to the data in order to make the comparison of the film transport properties possible, assuming eqn. (2) valid for these films.

3.2-Methods

3.2.1- Permeation methods

    a) For water and oxygen: gas sweeping technique

    The permeation apparatus consists of a measurement cell, a dry nitrogen supply, a hygrometric unit consisting of two sensors and an <u>oxygen concentration</u> analyzer. The first sensor, a capacitance type hygrometer (gold-plated alumina device, from Shaw Ltd., Bradford, England), was selected because of its fast-response (response time shorter than 3 s), and the second one (chilled mirror hygrometer, General Eastern Instruments, Massachussetts, USA) was used for its high accuracy (±0.07 part per million (volume) of water vapor in a gas). The oxymeter ("Quartz 650L", Cosma, Igny, France) is equipped with an electrochemical gauge which allows the measurement of oxygen concentration from oxygen partial pressures on both sides of a zirconium oxyde partition. This system give the oxygen concentration in ppmV with a response time shorter than 5 s. The precision is ± 1% of the full scale (10 ppm, 100 ppm, 1000 ppm, 1%, 10%, et 100%) and the reliability ± 0,5%.

    The previously dried film was placed in the cell and dry nitrogen was flushed in both compartments for many hours until a dew point lower than -70°C was obtained. Next, a stream of pure oxygen or liquid water was pumped through the upstream compartment, then the oxygen or water concentration in the initially dry sweeping gas was monitored in the downstream compartment.*via* the oxymeter and hygrometers and a data acquisition system.

    The flux J(L,t) at the dry interface is obtained from:

$$J(L,t) = \frac{f}{S} \cdot 10^{-6} \cdot \frac{(x^{out} - x^{in})}{R.T_r} \cdot p_t \qquad (12.)$$

with S the film surface area (30 cm^2), R, the ideal gas constant, and T_r, the temperature (in K) of the experiment. The pressures x^{in} and x^{out} are directly obtained for oxygen or indirectly obtained for water (from T_{dp} dew point temperature) of the sweeping gas. In this latter case, concentration x (ppmV) is calculated from the water vapor pressure p, which is directly related to the sweeping gas dew points T_{dp} at the inlet and the outlet of the cell (x ppmv = 10^6 p/p_t, p_t being the total pressure, usually 1 atm.)[5].

    b) For carbon dioxide (CO$_2$): Time-lag technique

Due to the lack of CO_2 sensor with high enough sensitivity, the time-lag technique was used for CO_2. The measurement principle of carbon dioxide permeation properties of films is based on the variable pressure method. During all experiments the temperature of permeation apparatus is kept at 25°C. Before measurement, the permeation cell (XX45047 Millipore filtration cell adapted for gas permeation) was completely evacuated by applying vacuum (10^{-3} mbar) on both sides of the film for at least one hour. Then, the upstream side was provided with the gas under test at pressure p_1 (in our case p_1 = 4 bar). The increase of pressure p_2 in the calibrated downstream volume was measured using a sensitive pressure gauge (0-10 mbar, Effa AW-10-T4) linked to a data acquisition system.

These permeation experiments were carried out on 2 or 3 samples, and about 4 measurements were made per sample. Therefore, the permeation parameters (P, D_L and S) were obtained with a precision range from 4 to 10%. The upstream pressure applied to the samples allowed measurements in a reasonnable time (a few tens of minutes). These pressure conditions were also chosen in such a way that no irreversible modification of the polymer occurs, for instance by plasticization effect due to CO_2 [17].

In this study, all permeation experiments were carried out at 25°C in a thermoregulated chamber.

3.2.2- DSC experiments

The most common and most accurate way of measuring the melting and glass transitions in polymers is by Differential Scanning Calorimetry (DSC). In this work, calorimetric measurements were carried out with a 2920 modulated DSC (Thermal Analysis instrument) equipped with a low temperature cell (minimal temperature = -60°C). A range of temperatures -50°C < T < 180°C was used. Calibrations for both the temperature and the enthalpy were achieved from measurements of melting temperature and enthalpy of Indium (T_m = 156.6°C and ΔH_m = 28.45 J.g^{-1}). The mass of the samples was about 15 mg, encapsulated in standard DSC aluminium pans. Experiments were performed under a neutral nitrogen atmosphere. Before tg, samples were stored in a vacuum desiccator over P_2O_5 for at least two weeks to avoid moisture sorption effects.

Appearing as a step in the baseline or heat capacity C_p, the T_g can be calculated by either the half height of the C_p step, the onset of the transition obtained by extrapolating the tangent of the inflection point to the initial baseline, the inflection point of the step, or the ½ ΔC_p between the baselines. In our case we will estimate the T_g by the inflection point of the step.

Melting is characterized by the peak temperature and by the melt peak area used to estimate the degree of crystallinity (DoC).

4-RESULTS AND DISCUSSION

Structural properties

DSC experiments were used to characterize the structure of EVA copolymers/blends of different VA content and to correlate results with permeation properties. **Fig. 1** shows the results of DSC measurements on all samples. DSC thermograms allow to <u>determine the glass transition</u> T_g (T_g being defined as the midpoint glass transition temperature) and the endothermic step defined by

$$\Delta C_p = (C_{p,l} - C_{p,g})_{T=Tg} \qquad (13.)$$

where $C_{p,l}$ is the specific thermal heat capacity in the liquid-like state and $C_{p,g}$ is the thermal heat capacity in the glassy state.

The DSC curves of EVA_{70}, PVC and EVA_{70}/PVC are characteristic of wholly amorphous materials. Only an enthalpic step in the DSC curve is detected. The curves relating to EVA19, EVA50, EVA_{19}/PVC and EVA_{50}/PVC exhibit one or two endothermic peaks. When the V.A. content decreases, the area of this endothermic peak increases. This peak corresponds to the melting of a crystalline phase present in the material. Glass transition is also observed for these samples except for the EVA_{19} sample for which the glass transition step is too weak to be detected with good accuracy due to the small change in heat capacity and presence of a crystalline phase. Nevertheless, it is clear that all these observations allow the conclusion that these samples are characterised by important modifications of their crystalline fractions. However, assuming that the melting enthalpy of polyethylene crystal is $\Delta H_{m(theo)} = 293$ J/g, we may estimate the degree of crystallinity phase DoC from $\Delta H_m/\Delta H_{m(theo)}$ where ΔH_m is the measured enthalpy of each EVA copolymer. In agreement with the literature, the degree of crystallinity decreases with the increase of the VA content. Concerning the EVA copolymers-PVC blends, the estimation of DoC is more complicated. In these blends, PVC is a wholly amorphous material. Thus, for each blend, the calculation of the degree of crystallinity is made by taking into account the fraction of EVA copolymer in the blend. These estimated values of DoC for each sample are reported in **Table. 1**. From these results and considering

errors in peak area measurements, it appears clearly that the blend does not affect the degree of crystallinity of the EVA part.

The determination of the glass transition (temperature and heat capacity change) allows indications about the miscibility of blends to be obtained. Immiscible blends will retain the glass transition temperature of the original components, whereas miscible blends will show only one glass transition temperature at a level reflecting the weight fractions of the components. In our case, only one glass transition is observed for each blend (EVA_{19}/PVC, EVA_{50}/PVC and EVA_{70}/PVC). So, in a first approach, it seems that our binary systems are miscible blends. Various equations have been proposed to predict the glass transition temperatures of blends from properties of the pure components [18,19,20]. The most commonly used is the Fox equation [18], which was originally proposed for calculating the T_g's of copolymers but which has also found some applicability in polymer blend studies :

$$\frac{1}{T_g} = \frac{w_{EVA}}{T_{g,EVA}} + \frac{w_{PVC}}{T_{g,PVC}} \tag{14.}$$

where w_{EVA} and w_{PVC} are the respective weight fractions of the pure components, and $T_{g,EVA}$ and $T_{g,PVC}$ are their glass transition temperatures ; T_g is the glass transition temperature of the blend. Estimating glass transition temperature for each pure component, we found that the Fox expression describes quite well our experimental results. However it predicts values which are higher than experimental values (**Table 1**). Although the calculated value does not coincide with the experimental data, one can conclude the the components are miscible. The difference observed may be due to the difficulty of estimating the glass transition temperature from DSC curves.

The Tg values determined from DSC measurements for our EVA copolymers and EVA/PVC blends are given in **Table 1**. Taking into account the weak amplitude of the glass transition, it is interesting to note that for EVA copolymers the glass transition temperature is not drastically modified between 19% w/w and 50 % w/w V.A. content. This has been observed by Thaumaturgo et Monteiro [21]. A slightly higer value of Tg is found for 70% w/w V.A. content. The same behavior is observed with miscible EVA/PVC blends but with higher Tg values. This shift to higher Tg values results from the glassy state of PVC characterized by a high Tg value (83°C).

The increase in the concentration of the acetate groups caused the rearrangement of polymer chains because of the large difference of polarity between polyethylene and poly(vinyl acetate). It was shown that important modifications concerning the crystalline morphology and the degree of crystallinity exist as the content of VA increases in these copolymers. For

content of 70% (w/w) V.A., samples are wholly amorphous while for 19% (w/w) V.A., the crystallinity is close to 20%. The ratio amorphous/crystalline phase increases with the VA content. This increase is not linear and it is found that VA molecules create enough disorder in PE to limit its ability to crystallise [2,3]. Thus, the presence of V.A. groups significantly reduces the crystalline volume fraction in the entire copolymer. Since the concentration in V.A. content become high(> 50% w/w), the crystalline volume fraction vanishes and the hydrogen bond interactions between polar groups are favoured and that can lead to an increase of Tg.

H$_2$O permeability, diffusivity and solubility coefficient

Fig. 3 is a plot of the thickness-corrected fluxes of water permeating through the polymer films when water activity step (from zero to one) is applied on the film's upstream face at time zero of the transient regime as a function of the thickness-corrected time t/L^2. It is known that in the reduced time scale τ, the diffusion coefficient D is free from the geometry of the film, $\tau/D=t/L^2$. This plot takes into account the effect of the film's thickness on the water diffusion and the permeation flux, so that the differences in the permeation patterns represent the intrinsic behavior of the materials. The correction is based on the assumption that the materials are homogeneous, i.e. uniform in properties; this assumption is acceptable insofar as the films were made of dense polymers and were not restricted to any specific orientation. **Fig. 3** shows that the steady-state water permeation flux and, hence, the permeability (as the applied driving force is the same in all experiments), increases according to the order:

For EVA copolymers EVA$_{19}$ < EVA$_{50}$ < EVA$_{70}$, this order being not respected in blends EVA$_{19}$/PVC (13 % w/w V.A.) < EVA$_{70}$/PVC (35 % w/w V.A.) < EVA$_{50}$/PVC (29 % w/w V.A.).

The water permeability increases steadily with the VA content as one would expect from the increase in the average number of polar groups (carboxyl) in the statistical copolymer. In the case of EVA/PVC blends, this number is not the predominant factor in the water permeability coefficient (**Figs. 3, 4a**). The unexpected decrease of the permeability coefficient for the EVA$_{70}$/PVC blend is rather linked to the increase of the amount of PVC which is a glassy polymer (at room temperature) able to interact with acetate groups of EVA and characterized by a low water permeability coefficient (see **Table 2**). However, to have a better approach to the water permeability for our materials it is necessary to examine the diffusivity data.

Dependence of water diffusion coefficient on local water content in polymer films

The lack of suitable methods for the determination of the diffusion laws when the diffusion coefficient is concentration dependent generally limits the analysis of the transient permeation regime to the case of constant diffusion coefficient [22]. However, it is easy to show the dependance of the diffusion coefficient with the penetrant concentration in the polymer when transient permeation data are available: on the basis of a Fickian process assuming D constant (see eqn.8), the values of the diffusion coefficient calculated at different points of the transient permeation flux are no longer the same [23,24]. The values of D_I and D_L corresponding to the transient permeation extents of $J/Jst=0.24$ and $J/Jst=0.62$, respectively (see eqns. 5-6), are different for all polymers, except for the EVA of 19wt. % VA. **Table 2** shows that the D_L value is larger than the D_I value for the EVA series and EVA/PVC blends. As the former value corresponds to an earlier period of the transient regime compared with the latter one, the smaller D_I means that the water diffusivity increases as the permeation proceeds from the starting point, where the film is dry. Such an increase in the diffusivity is generally attributed to plasticization of the materials by the permeant (water), though the origin of the increase in diffusivity with the permeation extent cannot be determined by the transient permeation experiments.

Another way to show the change in the diffusion with the permeation extent is to compare the experimental transient permeation curve with the one calculated with the flux obtained in the case of constant diffusivity: the experimental water transient fluxes through the polar polymers are lower than the calculated flux in the early part of the permeation, at times smaller than t_I , when the polar films are mostly dry. As the permeation proceeds further, more water molecules penetrate into the polar films, plasticize them, leading to larger experimental fluxes compared with the calculated ones (**Fig. 5**). When the transient fluxes are computed according to the procedure described in a previous paper [10], an excellent agreement between the calculated (see eqn. 9) and the experimental fluxes is obtained with a positive plasticization factor [24].

The value of the integral mean diffusion coefficient $\overline{D}$ represents the overall diffusivity of water in the considered polymer; it takes into account the plasticization effect, i.e., the enhancement of water mobility in the polymer due to the presence of sorbed water under

given experimental conditions. This means that the increase in the free volume, thus the increase in the diffusivity, due to the added free volume of water, is proportional to VA content in EVA films.

Compared to the EVA series, the EVA/PVC blends show smaller water diffusion coefficients (**Table 2**). The smallest diffusion coefficient in the dry polymer blend (D_0) can be explained either by it having the largest density of the materials, or the smallest chain segment mobility due to the high PVC density and Tg compared with those of the EVA components, althought these blends are in the rubbery state (Tg values of the EVA/PVC blends being higher than EVA ones). The low segment mobility in these miscible blends can also be caused by the interactions between the two polymer components. Such interactions should be hydrogen bonds between the hydrogen atoms and the Cl-substituted carbon of PVC with VA carbonyls. Similar H bonds were already shown for PVC-poly(caprolactones)[25]. However, the fact that the plasticization coefficient is larger for the blend with PVC suggests that the chain segment mobility is greatly enhanced by the presence of water molecules.

In comparison with EVA series, the lower overall water diffusivity in the miscible EVA/PVC blends can be explained by the very low intrinsic free volume of the PVC material. This can be seen in the low values of D_0, i.e. the water diffusion coefficient in the dry polymers.

The plasticization factor (γC) increases with the VA content in the same way as the permeability (**Table 2**). However, a detailed analysis of the transient fluxes through the EVA films of different VA contents reveals some interesting features. The 19 wt. % VA sample does not experience any plasticization effect on the water diffusion from water molecules. This apparent absence of plasticization can be the result of antagonistic effects: judicious cancellation of a negative (due to water clustering) and a positive (due to a free volume increase) plasticization effects. The copolymer samples containing 50 and 70 wt. % VA , exhibit increasing plasticization factor with the VA content. The increase in the plasticization factor is mainly due to the increase in the water concentration at the polymer face in contact with liquid water (i. e. the water concentration in the materials in equilibrium with liquid water C_{eq}). On the other hand, water seems not to have a very strong plasticization effect on the water diffusivity through EVA copolymers and EVA/PVC blends too, even at high VA contents (see γ values in **Table 2**). This behavior can be explained by the relatively high free volume existing in the copolymers (relatively high D_0 values, **Table 2**).

If we admit that the negative plasticization effect is due to aggregation of the water molecules in the hydrophobic environment of the polymer matrix, the fact that this effect vanishes [2], then is reversed when the content ofn polar VA groups increases, suggests that the behavior of water in the copolymer is governed more by an average interaction field rather than by site interactions. This behavior is consistent with the random nature of the monomer unit distribution in EVA copolymers.

To discuss the role played by the nature and the structure of EVA copolymers and their mixture with PVC on the water diffusivity, and taking into account the dependance of D with C, we have plotted the mean diffusion coefficient $\overline{D}$ versus V.A. content. As shown in **Fig. 4b**, for the EVAx series and EVAx/PVC blends, the same behavior is observed when the content of polar group increases. This variation can be explained by the fact that for high V.A. content, the amount of amorphous phase and the associated amount of polar groups are large enough to govern the diffusion process. The presence of V.A. units reduces the crystallinity of the polymer material and thus enhances the diffusivity by decreasing the tortuosity of the diffusion path. On the other hand, polar and bulky acetyl groups also reduce the chain segment mobility. This reduced mobility is enhanced with the addition of PVC which interacts with V.A. groups in the blends and whose Tg and density are higher (see diffusion coefficients in **Table 2**).

In terms of water solubility, keeping in mind the concentration dependent diffusion coefficient, it is more judicious to compare the calculated water concentrations C_{eq} than solubility coefficients S deduced from eqn. (10).

The amount of water sorbed by the blend of EVA with PVC is very low in spite of the polar character of PVC, it is twice as small as that of the pure EVAx film of equivalent overall VA content (see **Table 2**). Again, this behavior can be explained by the interactions between the two polymers. The interactions between the two polymers reduces the number of polar groups available for interactions with water in the materials.

O$_2$, CO$_2$ permeability, diffusivity and solubility coefficient

As for water permeation with the EVA/PVC blends, the permeability coefficient for O$_2$ and CO$_2$, does not depend on the increase in the average number of polar groups. For both gases with the EVA series and EVA/PVC blends, the increase of P follows the order: EVA$_{70}$/blend < EVA$_{19}$/blend < EVA$_{50}$/blend.

The VA content is not the predominant factor in the gas permeability coefficient (**Fig. 4a**).

It is clear that the origin of this variation of the permeability coefficient is in the variation of the diffusion coefficient (**Tables 3,4**). It seems that no correlation exists between the time-lag diffusivity, D_L, and the chemical composition of the materials. In fact, the diffusivity of a gas molecule, for which the sorption coefficient varies moderately with chemical composition, depends on both the segment mobility in the amorphous phase and the crystallinity of the polymer materials. On the one hand, polar and bulky acetyl groups reduce the chain segment mobility, but on the other hand, the presence of VA units also reduces the crystallinity of the polymer materials, thus enhancing the diffusivity by decreasing the tortuosity of the diffusion path. As shown in **Fig. 2**, for EVA copolymers and EVA/PVC blends, the glass transition temperature increases and then decreases when the VA content increases. Assuming that gases, small permeants, have practically no affinity with polymeric materials, the diffusivity is mainly governed by the structure of the material. In this case, the variation of the gas diffusivity is in good concordance with the variation of Tg, i.e. the gas diffusion coefficient varies in reverse to the glass transition temperature.

The normalized experimental flux curves obtained with pure oxygen are presented in **Fig. 6**. It is found for the EVA series and EVA/PVC blends that D_I and D_L values are practically identical (**Table 3**). Moreover the comparison between experimental curves and the calculated curve with D constant allows us to consider that oxygen transport through EVA copolymers and blends can be described with a model assuming a constant diffusion coefficient. The same behavior has been observed with carbon dioxide. It is well-known that with polymeric materials the diffusion process of gases is usually characterized by a Fickian diffusion assuming D constant. However, slight deviations of experimental flux curves with the Fickian curve (D constant) show opposite behaviors between EVA series and EVA/PVC blends (**Fig. 6**). In particular, with the EVA_{70}/PVC blend a significant decrease of D can be observed. This surprising result could be explained, in part, by a time-dependent diffusion coefficient, this linked to a relaxation phenomenon. We must keep in mind that among our systems, the EVA_{70}/PVC blend is characterized by the highest Tg value close to the ambient temperature.

In terms of solubility, on the basis of a constant diffusion coefficient D, the solubility coefficient S is calculated from eqn. (10). These solubility values, estimated for the EVA series and EVA/PVC blends, are reported in **Tables 3, 4**. Since gas molecules are small permeants having low affinities for polymers, the transport mechanism can be described according to the Henry's Law, keeping in mind that these penetrants are characterized by low solubility coefficients. Indeed, as there are no polar interactions between oxygen molecules

and polymer groups, the sorption coefficient for O_2 is much lower than that for CO_2, and varies randomly with the VA content. For CO_2, the sorption coefficient S increases with VA content in the copolymer (**Fig. 4c**, **Table 4**). This result is in agreement with the data reported by Bondar et al 'for poly(ether-block-amide) copolymers' [26]. The blending of the EVA copolymer with the glassy PVC leads to a decrease in the sorption coefficient.

Ideal selectivities

Keeping in mind that ideal selectivity coefficients correspond to the permeability ratio and so are the product of contributions from both diffusivity and solubility, **Table 5** gathers the values of the calculated ideal selectivity for different permeant pairs. The selectivity to water ($\alpha_{H2O/O2}$ and $\alpha_{H2O/CO2}$) increases with the VA content in the EVA copolymers and in the EVA/PVC blends, and is highest for the copolymer EVA_{70}. By mixing PVC with the EVA copolymer, a decrease of the water selectivity (except for EVA_{19}/PVC) and the gas selectivity ($\alpha_{CO2/O2}$) can be observed. The CO_2/O_2 selectivity is the lowest for the blend of EVA_{70} with PVC. Nevertheless, it is interesting to note that for water selectivity, with equivalent V.A. content, the EVA/PVC blends are better than EVA copolymers while for gas the selectivity is practically unchanged (EVA_{70}/PVC with 35% VA content and EVA_{33} with 33% VA). These results can be explained, in part, by the intrinsic properties of PVC which offers high water selectivity and low gas selectivity.

From the application viewpoint, PVC/EVA blend is a good candidate for the packaging of bio-products which are sensitive to water vapor build-up due to biological activities: it limits the respiratory activity *via* its low permeability, and removes efficiently the generated water vapor. With regard to both CO_2 and water selectivity over oxygen, the copolymer film with 70% VA content offers the best performance.

Figure Captions

Figure 1 : DSC thermograms of EVA copolymers/blends of different VA contents.

Figure 2 : Variations of the Tg values with the V.A. content in the EVA_x and EVA_x/PVC blends.

Figure 3 : Thickness-corrected fluxes of water permeating through the EVA_x and and the EVA_x/PVC blend films.

Figure 4 : Transport parameters for water, oxygen and carbon dioxide with EVA series and EVA/PVC blends a) permeability coefficients, b) diffusivity coefficients, c) solubility coefficients.

Figure 5 : Normalized water transient fluxes through EVA_x copolymers and EVA_x/PVC blends.

Figure 6 : Normalized oxygen transient fluxes through EVA_x copolymers and EVA_x/PVC blends.

Tables

Table 1 : Values of T_g, ΔC_p, T_m, ΔH_m and DoC.

Samples	% VA	T_g (°C)	$T_{g\ Fox}$ (°C)	$\Delta C_{p,exp}$ (J/g.K)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	DoC (%)
EVA$_{19}$	19	-25	-	0.14	48	83	86	29
EVA$_{50}$	50	-31	-	0.40	-	-	18	6
EVA$_{70}$	70	-18	-	0.47	-	-	0	0
EVA$_{19}$/PVC	13	-18	*0*	0.24	46	84	64	22/32*
EVA$_{50}$/PVC	29	-20	*6*	0.37	30	-	6	2/3.5*
EVA$_{70}$/PVC	35	16	*24*	0.42	-	-	0	0
PVC	0	83	-	0.38	-	-	0	0

(*) Degree of crystallinity calculated taking into account the fraction of EVA copolymer in the blend.

Table 2 : Values of the different water diffusion-law parameters obtained for the EVA and EVA/PVC blends : diffusion coefficient in the dry polymer D_0, integral mean diffusion coefficient $\overline{D}$, plasticization factor γC_{eq}, plasticization coefficient γ, and the water concentration in the polymer in equilibrium with liquid water C_{eq}. Concentration-dependent diffusion law used was : $D = D_0 [\exp(\gamma C)]$.

	EVA % V.A.	P Barrer *	D_0 x10^8 cm^{2}s^{-1}	D_I x10^8 cm^{2}s^{-1}	D_L x10^8 cm^{2}s^{-1}	$\overline{D}$ x10^8 cm^{2}s^{-1}	γC_{eq}	γ cm^3/mmol	C_{eq} mmol/.cm^3
EVA$_x$	**19** (EVA$_{19}$)	1134	4.5	4.5	4.7	4.5	0	0	0.26
	50 (EVA$_{50}$)	9357	13.3	20.5	25.4	39.8	1.88	7.4	0.25
	70 (EVA$_{70}$)	12287	5.1	8.1	10.0	15.7	1.95	2.3	0.83
EVA$_x$/PVC	**13** (EVA$_{19}$/PVC)	678	0.6	2.2	3.3	6.2	3.56	29.7	0.12
	29 (EVA$_{50}$/PVC)	1995	7.3	8.8	9.9	12.6	0.99	6.2	0.16
	35 (EVA$_{70}$/PVC)	1141	1.7	2.3	2.7	3.8	1.44	4.5	0.32
	PVC	239	0.4	0.7	0.9	1.4	2.26	13.3	0.17

*1 barrer = 10^{-10} cm^3(STP).cm/cm^2.s.cmHg

Table 3 : Values of the permeability, diffusivity and solubility coefficients from the transient permeation data obtained with pure O_2 at 25°C through EVA copolymers/blends of different V.A. contents

	EVA % V.A.	PVC wt. %	P Barrer	D_I $10^8.cm^2s^{-1}$	D_L $10^8.cm^2s^{-1}$	S $cm^3STP/cm^3.cmHg$
EVA_x	**19** (EVA$_{19}$)	0	5.3	35.1	38.5	0.0014
	50 (EVA$_{50}$)	0	8.1	58.0	62.8	0.0013
	70 (EVA$_{70}$)	0	3.6	24.5	24.7	0.0015
EVA_x/PVC	**13** (EVA$_{19}$/PVC)	30	1.6	15.0	14.9	0.0011
	29 (EVA$_{50}$/PVC)	42	2.4	26.3	25.2	0.0010
	35 (EVA$_{70}$/PVC)	50	0.8	4.3	3.2	0.0026
PVC	**0**	100	0.08	-	0.84	0.0009

Table 4 : Values of CO_2 permeability, diffusivity and solubility coefficients in EVA copolymers/blends of different VA contents obtained at 25°C with the time-lag technique.

	EVA % V.A.	PVC wt. %	P Barrer	D_L $10^8.cm^2s^{-1}$	S $cm^3STP/cm^3.cmHg$
EVA_x	**19** (EVA$_{19}$)	0	57	45.9	0.012
	50 (EVA$_{50}$)	0	70	22.5	0.031
	70 (EVA$_{70}$)	0	30	7.8	0.038
EVA_x/PVC	**13** (EVA$_{19}$/PVC)	30	11.7	10.8	0.011
	29 (EVA$_{50}$/PVC)	42	13.4	7.4	0.018
	35 (EVA$_{70}$/PVC)	50	2.3	1.11	0.021
PVC	**0**	100	0.28	0.16	0.018

Table 5 : Values of the ideal selectivity coefficients from the transient permeation data obtained at 25°C through EVA copolymers/blends of different V.A. contents

	% V.A.	$\alpha_{H2O/O2}$	$\alpha_{H2O/CO2}$	$\alpha_{CO2/O2}$
EVA$_x$	**19** (EVA$_{19}$)	214	20	10.8
	33 (EVA$_{33}$)	351	134	2.8
	50 (EVA$_{50}$)	1155	134	8.6
	70 (EVA$_{70}$)	3413	410	8.3
EVA$_x$/PVC	**13** (EVA$_{19}$/PVC)	424	58	7.3
	29 (EVA$_{50}$/PVC)	716	128	5.6
	35 (EVA$_{70}$/PVC)	1375	496	2.8
PVC	**0**	3034	856	3.5

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