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Sorption, Diffusion and Permeation Properties of Oxygen and Water in Copolymer of Ethylene and Polar Monomers

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Summary: Asymmetric membranes, based on Poly[ethylene-*co*-(vinyl acetate)] (EVA) containing 70 wt.% of vinyl acetate, were prepared by a treatment of unilateral hydrolysis using solutions of sodium hydroxide dissolved in a mixture of water and methanol. The depth of hydrolyzed layers and the concentration of hydroxyl groups in the membranes were controlled by the reaction time. The oxygen permeability, P_{O2}, of these membranes decrease with the reaction time while the water permeability, P_{H2O}, reaches maximum at 30 min. The ideal separation factors of P_{H2O} to P_{O2} of the EVA membranes treated for 1h to 4h are in the range of 3840 to 13500, and are greater than that of the EVA membranes. The plasticization effect of the membrane depends on the depth and concentration of hydroxyl groups and the concentration gradient of water in the membranes.

Introduction

Barrier properties for packaging materials have been improved. The films protecting foods from the oxidation and the moisture have sufficient performances, which are poly(ethylene terephtalate), polyethylene, polypropyrene, and poly(vinylidene chloride), etc. As well, poly[ethylene-*co*-(vinyl acetate)] (EVA) completely hydrolyzed, leading to poly[ethylene-*co*-(vinyl alcohol)], is one of the most impermeable polymers at the dry state. Their perfect gas barrier properties for water and oxygen, however, are not suitable for fresh fruits and vegetables. These foods, which are perishable, need to be stored until their consumptions. They are the sources of biochemical reactions for the period of preservation, which consume oxygen and produce carbon dioxide and water. The reactions are quantified by the respiratory intensity. There is a trade-off between the respiratory intensity and the period of their conservation. It is necessary to reduce the respiratory intensity for the longer life-time, that can be achieved by the reduction of partial pressure of oxygen in the packaging

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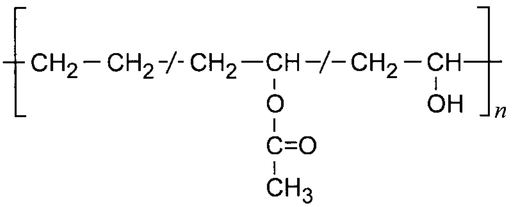
materials. Moreover, the condensation of water, generated by the biochemical reactions induces moulds, and also an anaeorobic fermentation of bio-components under high water and CO_2 contents often lead to a bad taste and smell. For a better preservation of fresh fruits and vegetables, increasing in the water permeability and keeping the low permeability for oxygen are required to reduce the respiratory intensity and the anaerobic fermentation rate.

From these considerations, the aim of this study was to prepare membranes exhibiting high H_2O/O_2 permselectivities. We have reported that the H_2O/O_2 permselectivities of membranes of copolymers of ethylene with vinylacetate increased with the vinyl acetate contents (from 2 to 70 wt.%)[1]. In order to improve their permselectivities, asymmetric membranes, based on EVA containing 70 wt.% of vinyl acetate groups, were prepared by a treatment of unilateral hydrolysis using solutions of sodium hydroxide dissolved in a mixture of water and methanol. The chemical structure of the treated layer contained poly[ethylene-*co*-(vinyl acetate)-*co*-(vinyl alcohol)].



$$\left[-\mathrm{CH_2}-\mathrm{CH_2}-/-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH}}-/-\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{CH}}-\right]_n$$

Poly(ethylene-co-vinyl acetate-co-vinyl alcohol)

The depth of the hydrolyzed layers and the concentration of hydroxyl groups in the EVA membranes were controlled by the treatment time in the solutions and were characterized by means of IR spectroscopy and fluorescent microscopy. The transport properties of water and oxygen through the asymmetric membranes were studied by permeation and sorption measurements.

Experimental Part

Polymer film preparation

Poly[ethylene-*co*-(vinyl acetate)] (EVA) containing 70 wt.% of vinyl acetate was Baymod type, kindly provided by Bayer Corp. Dense films of EVA were prepared by casting from dichloromethane (10 wt.%) solutions onto a glass plate. The obtained film is dried for 12h at atmospheric pressure at room temperature and then dried in an oven for 7h at 80°C. After cooling it at room temperature, the margin of the films was crimped like a boat as a part of film measuring 130 by 150 mm was left onto the glass plate. A 120 ml solution of a 0.8 molar NaOH and containing 75 vol.% of methanol and 25 vol.% of water was spread in the boat. Different reaction times of hydrolysis were used from 30 minutes to 16 hours. The reaction was terminated by adding 150 ml of a 3.0 M HCl solution. After 15 minutes, the films were soaked in water to remove HCl. Finally, they were unstuck from the glass plate and then transferred on polyethylene sheets in non-treated side, and then were exposed in the air for 24h and were dried with P_2O_5 in a desiccator at room temperature under vacuum for 24h. Their thickness was approximately 150μm. In order to estimate the depth of hydrolyzed layer of the membranes, the cross-section view of the membranes dyed by Rhodamine 6G (Aldrich) was observed by microscope using fluorescent light. Prior to the observation, the membranes were treated as follows; Rhodamine 6G was dissolved into the methanol solution containing 25 vol.% of water. The membranes were stored in the solution for 24h and then were rinced until the water was uncolored. After drying, the membranes were used.

IR spectroscopy

The IR spectra were obtained by using ATR method (Attenuated total reflection), and by collecting and averaging 32 scans, at a resolution of 4 cm^{-1}.

Permeation measurement

Gas sweeping technique for water and oxygen (differential permeation)

The water, oxygen permeabilities of through the membranes were measured using two hygrometric sensors and an oxymeter analyzer according to the experimental method developped by Marais et al.[2]. The new exposed area of the cell was reduced, A(=0.00049 m^2), this in order to avoid the convection flow inside the cell than the initially developed cell (A=0.0030 m^2). The previously dried film was placed in the cell putting its treated surface at the feed side and dry nitrogen was flushed in both compartments 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 pure sweeping nitrogen 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:

$$J(L,t) = \frac{f}{A} \cdot 10^{-6} \cdot \frac{x^{out} - x^{in}}{RT} \cdot p_t \tag{1}$$

with R, the gas constant and T, the temperature (in K) of the experiment. The fractions x^{in} and x^{out} are directly obtained for oxygen or indirectly obtained for water (from dew point temperature T_{dp}) of the sweeping gas whose flow-rate, f, is 9.3×10^{-6} m^3s^{-1} (optimal flow necessary for using a mirror hygrometer). In this latter case, the value of x in ppm 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 ppm = $10^6\,p/p_t$, p_t being the total pressure, usually 1.013×10^5 Pa)[3]. The permeability coefficient is the product of the steady gas flux and film thickness divided by the difference of gas or vapor pressures Δp between the two faces of the film:

$$P = \frac{J_{st} L}{\Delta p} \tag{2}$$

where L is the thickness of the polymer film and J_{st} the stationary flux.

Time-lag technique for oxygen

Since the oxygen permeation properties of the samples indicate high barrier properties, the vacuum-pressure method was used. The permeation measurements were carried out for pure O_2 at 25°C in a thermoregulated chamber. The gases were supplied by Airliquid and used without further purification. The feed side pressure was 4×10^5 Pa. The pressure on the permeate side never exceeded 1000 Pa during the permeation measurement. The oxygen permeability coefficient was determined from a steady-state slope of the time dependent pressure curve using following equation[4]:

$$P = (dp/dt) \cdot \{273V/760(273+T)\} \cdot (l/Ap_t) \tag{3}$$

where P is the permeability coefficient; l is the membrane thickness; dp/dt is the increase of pressure per unit time on the permeate side; V is the volume of the permeate side (9.813×10^{-5} m^3); T is the absolute temperature of experiment; and A is the effective area of the membrane (1.134×10^{-3} m^2).

Sorption measurement

An IGA microbalance (Intelligent Gravimetric Analyser, from Hiden Analytical Ltd., Warrington, UK) was used for an accurate measurement of sorption rate of water vapor in the films. The microbalance and the operation procedure were described in a previous paper[1]. The sorption chamber was maintained at 25°C. The percentage mass gain Δm of the film at time t, was defined on the basis of the dry mass of film M_o. The EVA membrane and two hydrolyzed films, which were treated for 30 min and 2h, were studied in O_2 and water vapor sorption experiments.

Results and Discussion

Preparation of asymmetric membranes

The attenuated total reflection (ATR) spectrum reflects the average surface structure of the materials in limited depth (1 to 4μm). The ATR method does not give information about the total amount of functional groups in the samples. However, this method permits the comparison between the treated and the untreated surface structures of the membranes. Figure 1 shows the hydrolysis degree of the hydrolyzed and untreated surface layers of the membranes. In the EVA membrane, the 1730 cm^{-1} band was attributed to the carbonyl group due to the vinyl acetate structure. The relative intensities of carbonyl group normalized with the peak area of the carbonyl group of EVA membrane, $A_{1730}/A_{1730(EVA)}$ are plotted. It can be observed that for the treated surfaces of the membranes, the relative intensity decreases as the reaction time increases while, for the untreated surfaces, the relative intensity is not changed up to 3h of the reaction time, after which, it decreases. This observation indicates that the EVA layer exists at the untreated side of the membranes for which the reaction time is less than 3h, and the membranes treated for more than 4h have a gradient of hydrolysis in all the thickness.

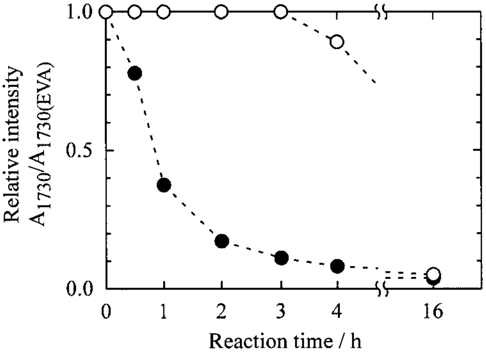


Figure 1. Hydrolysis degree of the surface vs. reaction time from ATR-mode FTIR spectra; ● hydrolyzed and ○ non-treated surfaces.

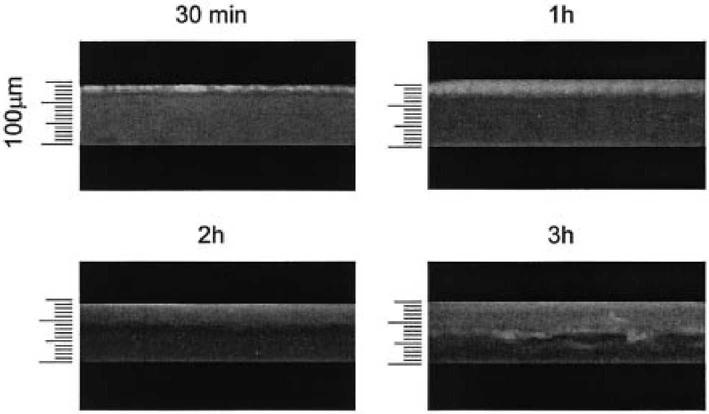


Figure 2. Cross-section views of the EVA membrane before and after hydrolysis.

The cross-sectional views of the EVA membranes treated from 30 min to 3h obtained by fluorescent microscopic are shown in Figure 2. The Rhodamine 6G solution was uptaken in the membranes, and then was desorbed only in the hydrolyzed layer by washing in water. The upper sides of the membranes, which are light color, are the hydrolyzed layers and their down sides, which are dark color, are the EVA layers. The hydrolyzed layers expand from 27μm to 80μm with the reaction time.

Examination of the specimen surface by the ATR spectra and the fluorescent microscopic reveals that the membranes after unilateral hydrolysis are asymmetric and are characterized by different depth of hydrolyzed layers and different concentration of hydroxyl groups.

Dependencies of oxygen transport properties on the reaction time

The relationship between the reaction time and the permeability coefficient for O_2 in the EVA and asymmetric membranes treated (for less than 4h) is shown in Figure 3. The permeability coefficients in the asymmetric membranes decrease with reaction time. The diffusion and solubility coefficients for O_2 in the EVA membranes before and after unilateral hydrolysis (1h and 2h) are shown in Table 1. The diffusion coefficients were calculated using the time lag t_L. This t_L value is the time at which the value of the normalized flux $(J/J_{st}) = 0.62$ is reached[2]. Dividing P by D gives S. These parameters for the two asymmetric membranes of the different reaction time (1h and 2h) are apparent values because these membranes are asymmetric in the direction of permeation as mentioned previously.

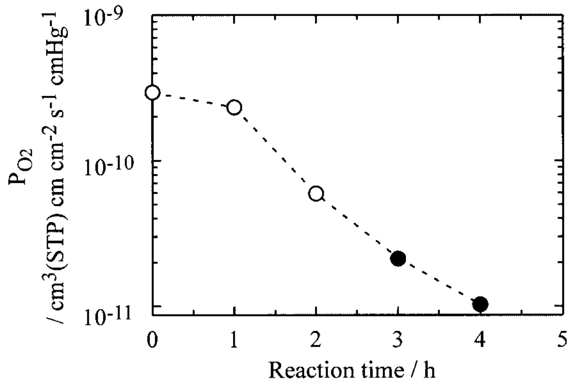


Figure 3. Plots of permeability coefficient for O_2 vs. reaction time of the hydrolysis for EVA membranes.

Table 1. Diffusion and solubility coefficients of oxygen for the EVA membranes before and after hydrolysis (1h and 2h)

Sample	$D_{time-lag} = \frac{L^2}{6t_L}$	$S = \frac{P}{D}$
	cm^2/s	$cm^3(STP)/\ cm^3\ cmHg$
EVA	2.0×10^{-7}	0.00149
EVA-1h	1.6×10^{-7}	0.00145
EVA-2h	1.3×10^{-7}	0.00046

The diffusivity and solubility coefficients of oxygen in the asymmetric membranes decrease. The hydrolyzed layers in the asymmetric membranes contain the hydroxyl group of vinyl alcohol. Each hydroxyl group is bound by inter- and intra-hydrogen bonds. It is well-known that poly(vinyl alcohol) has a crystalline region formed by hydrogen bond[5]. The oxygen molecules are not able to diffuse and soluble in the crystalline regions in polymers, which means the regions act as impermeable barriers analogous to filler particles[6]. We considered that the hydrolyzed layers in the asymmetric membranes become more impermeable for oxygen by the hydrogen bond between the hydroxyl groups more than the unaffected layers.

Dependencies of water transport properties on the reaction time

Figure 4 shows the relationship between the reaction time and the permeability coefficient for water in the EVA and asymmetric membranes. In the case of water permeation and compared to O_2 permeation, a different tendency is observed. The permeability coefficients for O_2 through the hydrolyzed membranes for 30 min and 1h are slightly greater than that of the EVA membrane. After 2h of treatment, the oxygen permeability significantly decreases as a function of the reaction time.

It has been previously reported that, in poly(ethylene-*co*-vinyl acetate) containing the different amount of vinyl acetate, the water permeability increases steadily with the increasing vinyl acetate content mainly due to the increasing water sorption and plasticization effect in the membranes[1]. In this study, the water permeability decreases in spite of the increasing vinyl alcohol content and depth of the hydrolyzed layers. It is thought that the hydroxyl group is more hydrophilic and more strongly interacts with water than the vinyl acetate while the interaction of each hydroxyl group is very strong due to the hydrogen bond. The behavior of water permeation in hydrophilic materials is more complex than oxygen permeation one. The different effect between the water diffusivity and solubility on the hydrolyzed layers is suggested.

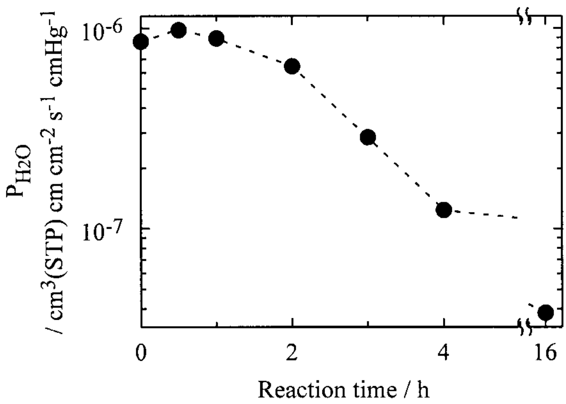


Figure 4. Plots of permeability coefficient of H_2O vs. reaction time of hydrolysis of the EVA membranes.

Figure 5 shows the relationship between diffusion coefficient D_l of water and the reaction time. D_l is calculated from the time $t_{0.24}$ corresponding to a value of J/J_{st} = 0.24 ($D_l=0.091L^2/t_{0.24}$)[2].

As the diffusion coefficient of gases through homogeneous materials is constant, D_l is equal to another diffusion coefficient calculated from the time-lag method. The value of D_l in the asymmetric membranes decreases with the reaction time.

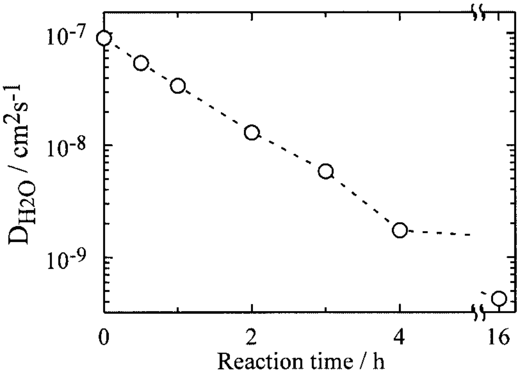


Figure 5. Plots of diffusion coefficients (D_l) of H_2O vs. reaction time of hydrolysis of the EVA membranes.

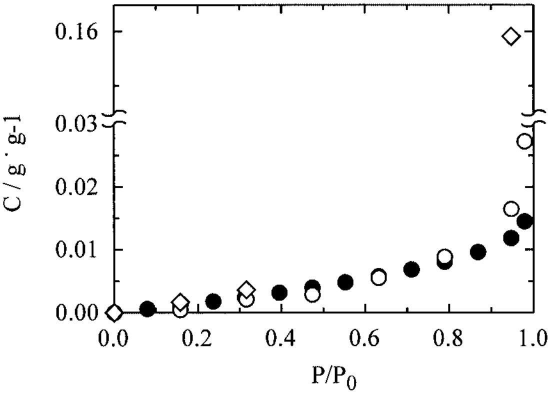


Figure 6. Sorption isotherm for water at 25°C in the EVA membrane before and after hydrolysis; ● EVA, ○ EVA-30min, ◇ EVA-2h.

Figure 6 shows the sorption isotherm for water at 25°C in the EVA membrane before and after hydrolysis (30 min and 2h). At low activities of the water vapor, the difference of water sorption in the membranes is small but the uptake of water molecules in the EVA-2h membrane is much greater than that of water molecules in the EVA and EVA-30min membranes at the high activity in contrast with the behavior of their oxygen solubilities. We can consider that the maximum of water permeability of the EVA membrane treated for 30 min is due to the relative increase of its water solubility exceeding the decrease of its water diffusivity compared with the EVA membrane. In spite of the significantly high sorption of water of the EVA membrane treated for 2h at the high activity, its water permeability was lower than that of the EVA membrane. These phenomena might be explained by the plasticization behavior of the hydrolyzed layers by water.

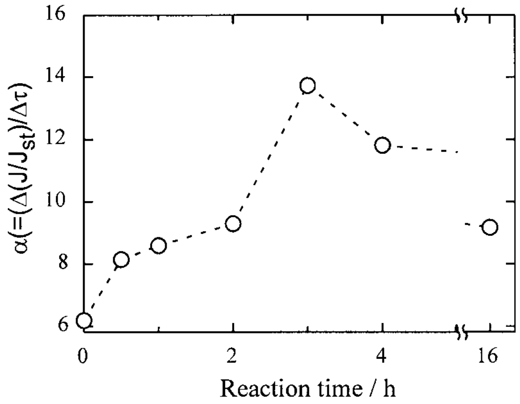


Figure 7. Influence of the reaction time upon the slope α at an inflexion point on the normalized experimental curves of the EVA membrane before and after hydrolysis.

Figure 7 shows the influence of the reaction time upon the slope α at the inflection point on the normalized experimental curves of the EVA membrane before and after hydrolysis. The transient permeation curves normalized by dimensionless time τ ($=D_Jt/L^2$) have an inflexion point at (τ, J/J_{st}) = (0.091, 0.24). As the slope α at the inflexion point is equal to 5.82, a diffusion coefficient is constant[2]. In the case of homogeneous materials, the slope $\alpha > 5.82$ means the materials are plasticized by the sorbed water in the materials[2]. Even though the EVA membrane is homogeneous, the water diffusivity of the EVA membrane exhibits a concentration dependence. In all the membranes used in this study, the value of α of the asymmetric membranes exhibits greater values than that for constant D. It is suggested that, in all the asymmetric membranes, the chain mobility in the hydrolyzed layer is enhanced by penetrating water molecules from the beginning of the permeation to the steady state of the permeation because the hydrogen bond of hydroxyl groups in the hydrolyzed layers is cut by the sorbed water. However, the behavior of the plasticization of the hydrolyzed layers might be different among the asymmetric membranes because the value of α has a maximum at 3h.

Hodge et al[5,7] have been reported that, in the case of poly(vinyl alcohol), the sorbed water in hydroxyl groups promotes chain mobility and disrupts hydrogen bond. Water molecules diffuse initially through the amorphous region of the polymer and attach themselves to hydroxyl side groups, disrupting inter and intra hydrogen bond and swelling the polymer. In the latter stages of water absorption, the action of water molecules attaching to the hydroxyl groups on the polymers destroys crystalline. After the vast majority of crystalline has been destroyed, the water molecules in the polymers form small aggregations with the increasing water content.

In the case of the permeation experiment, the concentration of water at the permeation side keep zero and the activity of water is 1 at the feed side, which means a steady state in non-equilibrium. In contrast, the sorption of water is measured in equilibrium. In the permeation experiment, gradients of water concentration exist in membranes.

In our case, the significant increase of the water sorption at the high water activity can be due to such an aggregation of water molecules. If all the hydrogen bonds between hydroxyl groups in the hydrolyzed layers were destroyed by the absorption of water, the water diffusivity in the layers would enhance with the increasing reaction time because of the plasticization effect. In fact, the water diffusivity decreased with the reaction time.

The gradient of water concentration in membranes decrease toward the permeation side. It seems reasonable to suppose that the surface of the membrane at the feed side is completely plasticized contacting liquid water, while a part of the hydrolyzed layers inside the membrane are not sufficiently plasticized by the decreasing water concentration in the layers. In the same way as for the oxygen diffusivity through the asymmetric membranes, the insufficiently plasticized layers act as an obstacle to the diffusion of water molecules by the hydrogen bond between hydroxyl groups.

From our experimental results of IR spectra, the asymmetric membranes treated for less than 3h have the untreated layers that consist of EVA. In the boundary phase between the hydrolyzed layer and the untreated layer in the asymmetric membranes, the concentration of water would not be zero by its concentration gradient in the membrane. Since the permeation side of the membrane keep the dry state during the permeation experiment, in the case of the asymmetric membranes treated for more than 4h, the water molecules cannot destroy most of the hydrogen bonds of hydroxyl groups exposed at the permeation side. Therefore, the plasticization effect of the membranes treated for more than 4h decreases.

Ideal selectivities

The ideal separation factors $\alpha_{H_2O/O_2}(= P_{H_2O} / P_{O_2})$ were evaluated from the values of the experimental permeability coefficients. These value of the EVA membranes treated for 1h to 4h were in the range of 3840 to 13500, and were greater than that of the EVA membrane (α_{H_2O/O_2}=2900). There is a trade-off between the water permeability and the ideal separation factor.

Conclusion

The unilateral hydrolysis of the EVA membrane improves the ideal selectivity of water to oxygen. The hydrolyzed layers of the asymmetric membranes act as an obstacle of the diffusion and solution of oxygen molecules by the presence of hydrogen bonds between hydroxyl groups. In the case of the EVA membranes treated for 30 min and 1h, which relatively has the thinner hydrolyzed layers, the water permeability is improved by the interaction between water molecules and hydroxyl groups. The water permeabilities of the other asymmetric membranes were lower than that of the EVA membrane. The plasticization effect of the membrane depends on the depth and concentration of hydroxyl groups and the concentration gradient of water in the membranes.

[1] S. Marais, Y. Hirata, D. Langevin, C. Chappey, Q.T. Nguyen, M. Métayer, *Material Research Inovvation*, accepted.

[2] S. Marais, M. Métayer, M. Labbé, *J.App.Polym.Sci.* **1999**, *74*, 3380.

[3] M. Métayer, M. Labbé, S. Marais, D. Langevin, M. Brainville, C. Chappey, F. Dreux, P. Belliard, *Polym. Testing* **1999**, *18*, 533.

[4] C. Rogers, J.A. Meyer, V. Stannet, M. Szwarc, *Tappi* **1956**, *39*, 737.

[5] R.M. Hodge, G.H. Edward, G.P. Simon, *Polymer* **1996**, *37*, 1371.

[6] D.R. Paul, *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 294.

[7] R.M. Hodge, T.J. Bastow, G.H. Edward, G.P. Simon, A.J. Hill, *Macromolecules* **1996**, *29*, 8137.