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Dense hydrophilic composite membranes for ultrafiltration

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Abstract

Dense hydrophilic composite membranes for ultrafiltration were prepared from an asymmetric porous PVDF support coated with a thin (< 1 μm) layer of polyether-*block*-polyamide copolymer. Membranes with a molecular weight cut-off between 800 and 4500 g/mol and water permeability between 2.3 and 9.4 l h^{-1} m^{-2} bar^{-1} were obtained. The dry membrane surface was characterized as a dense non-porous layer when observed by scanning electron microscopy. When compared to other commercial membranes and to the non-coated porous PVDF support in the ultrafiltration of oil–water waste, the performance of the composite membranes was comparable to the Amicon YM30 cellulose membrane with lower susceptibility to fouling.

Keywords: Fouling; Polyether-*block*-polyamide copolymer; Ultrafiltration

1. Introduction

Ultrafiltration has been well established as an alternative to other separation processes and in many cases it is an unique separation solution. It has been widely used in waste water treatment and in the food industry [1,2]. Since new environmental regulations are being settled, ultrafiltration has become even more attractive for applications such as oil–water separation. In this field, two main users should profit from new developments in the membrane science: (i) In the metal industry, oil–water emulsions are frequently used and have to be treated before being discharged; (ii) In offshore oil production and further onshore operations, a considerable amount of waste is generated from the injection of water for oil recovery. European regulations today require an oil content lower than 40 mg/l in the wastewater. Much lower values are being considered for the near future or are already used in other countries specially for structures near the shore or for wastes discharged in rivers.

An undesirable phenomenon, flux decline during the ultrafiltration process has been, however, frequently observed, limiting the efficiency of the method [3]. Fouling is still a serious problem caused by solute adsorption on the membrane surface and pore blocking. The phenomenon is mainly irreversible and much work has been done to control it. Solute adsorption involves hydrophobic interactions and hydrophobic membranes have therefore a higher susceptibility to fouling. However many hydrophobic membranes are still the most useful ones for ultrafiltration due to their superior characteristics of chemical and thermal stability. Surface modification [4–9] and blending [10,11] with more hydrophilic polymers have been described as an attempt to successfully combine hydrophilicity, chemical stability and good permselective characteristics.

The aim of this work was to investigate the performance of dense hydrophilic composite membranes in

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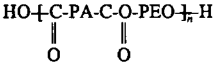
ultrafiltration. An asymmetric porous structure of a poly(vinylidene fluoride) support should be responsible for the required mechanical stability. A very thin and dense hydrophilic layer should minimize fouling, inhibiting the solute adsorption on the surface and the solute access to the porous structure below it. The high hydrophilicity should also allow a high water flow through the membrane.

2. Material

Polyether-*block*-polyamide copolymers



$HO\left[\underset{\underset{O}{\|}}{C}-PA-\underset{\underset{O}{\|}}{C}-O-PEO\right]_n H$

PEBAX® 4011 and 1074 were kindly supplied by Elf Aquitaine, France. The polyether segment is poly(ethylene oxide) and the polyamide is polyamide 6 (PEBAX® 4011) or 12 (PEBAX® 1074). The polyether content in each case was confirmed by elemental analysis as 59 and 55 wt%, giving a high hydrophilicity to the polymer. After 24 h immersion in water, PEBAX® 4011 absorves 119% and PEBAX® 1074, 48% its weight. Due to the polyamide block, the copolymers are insoluble in most of the solvents. Poly(vinylidene fluoride) (PVDF) Foraflon F6000/6000 HD was also purchased from Elf Aquitaine/Atochem and the polyester non-woven Viledon FO 2403 was produced by Carl Freudenberg, Germany.

3. Experimental

3.1. Membrane preparation

Porous asymmetric PVDF membranes were obtained by phase inversion from a *N,N*-dimethyl acetamide solution, cast on a polyester non-woven and coagulated in water in a continuous machine. The porous membranes were carefully washed with water and dried. Except when mentioned in the text, membranes were obtained by coating the porous PVDF membrane with a 0.75% PEBAX® solution in 1-butanol. The solution was obtained after at least 30 h reflux in butanol. The membranes were dried during 2 h at room temperature and further 2 h at 70°C to eliminate the solvent. Membranes were also obtained with mixtures of different PEBAX® grades.

3.2. Permeability and cut-off evaluation

The membrane permeability to water was measured in ultrafiltration cells with pressures between 5 and 10 bar. The membrane selectivity was evaluated by measuring the solute retention in stirred dead-end ultrafiltration cells with 400 ml maximum feed volume. A 0.5 wt% poly(ethylene glycol) (PEG) aqueous solution was used as feed, containing equal amounts of PEG with the following molecular weights: 1500, 3000, 6000, 10 000 and 40 000 g/mol. Membranes with higher retention for low molecular weight solutes were also tested with raffinose (molecular weight 595 g/mol). Permeate and retentate samples were analyzed using a high performance liquid chromatograph with a Ultrahydrogel T00861 column and differencial refractometer. Retention of a 0.2 wt% aqueous solution of rutine sulfate sodium salt (molecular weight ca. 800 g/mol) was analyzed by visible absorption spectroscopy (422 nm). Cut-off was considered the minimum molecular weight of solutes with 90% retention.

Also the membrane selectivity to organic solvents was evaluated using aqueous solutions saturated with toluene, xylene and phenol. The organic concentration was measured by UV-spectroscopy and gas chromatography.

3.3. Membrane morphology

The membrane surfaces were covered with chromium by sputtering and observed in a Jeol field emission scanning electron microscope. Micrographs of the membrane cross section were obtained in a similar way, after fracture in liquid nitrogen. The dry membranes were observed with higher magnification on an atomic force microscope (AFM) without any previous treatment.

4. Results and discussion

The composite membranes obtained here are asymmetric, with a quite dense hydrophilic layer coating a porous PVDF support. Fig. 1 shows the retention

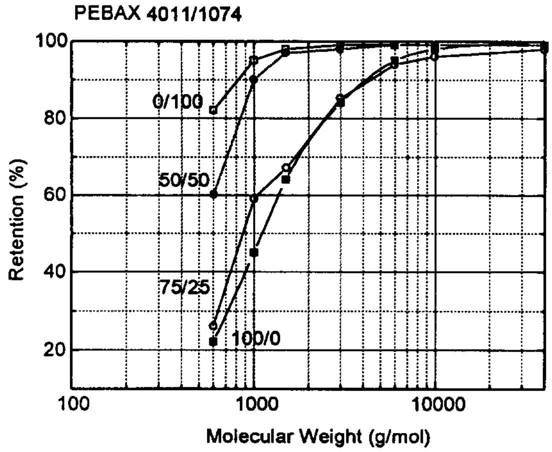


Fig. 1. Retention curves of composite membranes obtained from mixtures of PEBAX 4011 and 1074 with the following composition: (□) 0/100, (●)50/50, (○) 75/25, (■)100/0.

Table 1
Cut-off and water permeability of PEBAX membranes

PEBAX 4011/1074 composition	Solution concentration (%)	Cut-off (g/mol)	Water permeability ($l\,h^{-1}\,m^{-2}\,bar^{-1}$)
0/100	0.20	900	6.4
0/100	0.75	800	2.3
50/50	0.75	1000	4.5
75/25	0.75	4500	8.4
100/0	0.75	4500	9.4

Table 2
Retention of PEBAX membranes to organic solvents

Membrane	Retention	
	Toluene	Xylene
PEBAX 4011	49–77	>81
PEBAX 1074	>92	80

curves for membranes obtained with PEBAX® 4011, 1074 and mixtures of both grades.

The membranes were prepared with 0.75% copolymer solutions. Table 1 shows the cut-off for each kind of membrane and the water permeability. Cut-off values of four different membranes showed variations up to 16%. The permeability varied up to 6%.

The PVDF membranes without the PEBAX® layer had a permeability of 70 $l\,h^{-1}\,m^{-2}\,bar^{-1}$ with a cut-off higher than 100 000 g/mol. Among the hydrophilic composite membranes, those prepared with PEBAX® 4011 were the most permeable. Using PEBAX® 1074, a lower water permeability was obtained, but the molecular weight cut-off was considerably improved, already in the range of nanofiltration. Intermediary values were obtained with the mixtures.

An improvement of the characteristics of PEBAX® 1074 membranes was obtained by decreasing the concentration of the casting solution. Membranes obtained from a 0.2% copolymer solution had a small increase of the cut-off value (from 800 to 900 g/mol) but a water permeability almost three times higher (6.4 $l\,h^{-1}\,m^{-2}\,bar^{-1}$). The use of even lower polymer concentrations led to a jump of the cut-off value out of the range of interest.

The selectivity of the membranes to organic solvents were then evaluated and the results are shown in Table 2. Experiments were performed using saturated aqueous solutions as feed. Salt (NaCl) retention is lower than 5%. High organic solvent rejection and lower salt retention are desirable requirements for many membrane applications such as oil–water separation in wastes from oil recovering off-shore plants.

4.1. Membrane morphology

The morphology of the composite membrane was investigated by scanning electron and atomic force microscopy. Fig. 2 shows the membrane cross-section observed by scanning electron microscopy. A dense PEBAX® layer, thinner than 1 μm, can be seen on the surface of the asymmetric porous PVDF structure, when 0.75% PEBAX® 4011 cast solutions are used. A much thinner layer is obtained with a 0.2% PEBAX® 1074 solution.

In Fig. 3a, the porous structure of the PVDF support can be clearly seen, as observed also by field emission scanning electron microscopy. No pores were observed when the same PVDF membrane was coated with the blockcopolymer layer (Fig. 3b).

The atomic force microscope allows a higher magnification. Both composite membrane and PVDF support surfaces are shown in Fig. 4. A much smoother surface is observed in case of the composite membrane but a few cavities could indicate the presence of pores.

In order to further check the presence of pores, the gas selectivity of the dry membranes were measured

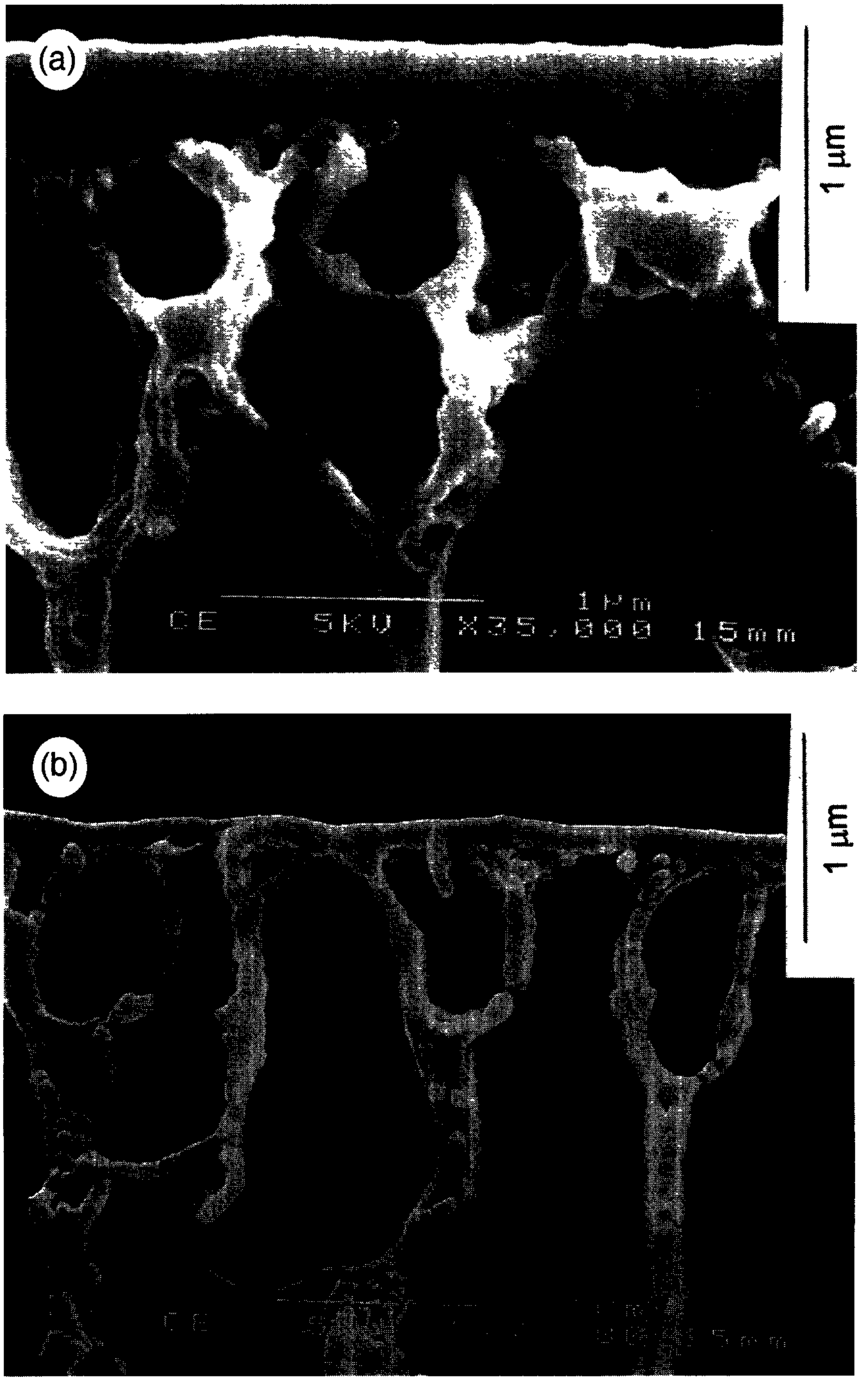


Fig. 2. Cross section observed by scanning electron microscopy of (a) a PEBAX 4011/ PVDF composite membrane obtained from a 0.75% casting solution and (b) a PEBAX 1074/PVDF composite membrane obtained from a 0.2% casting solution.

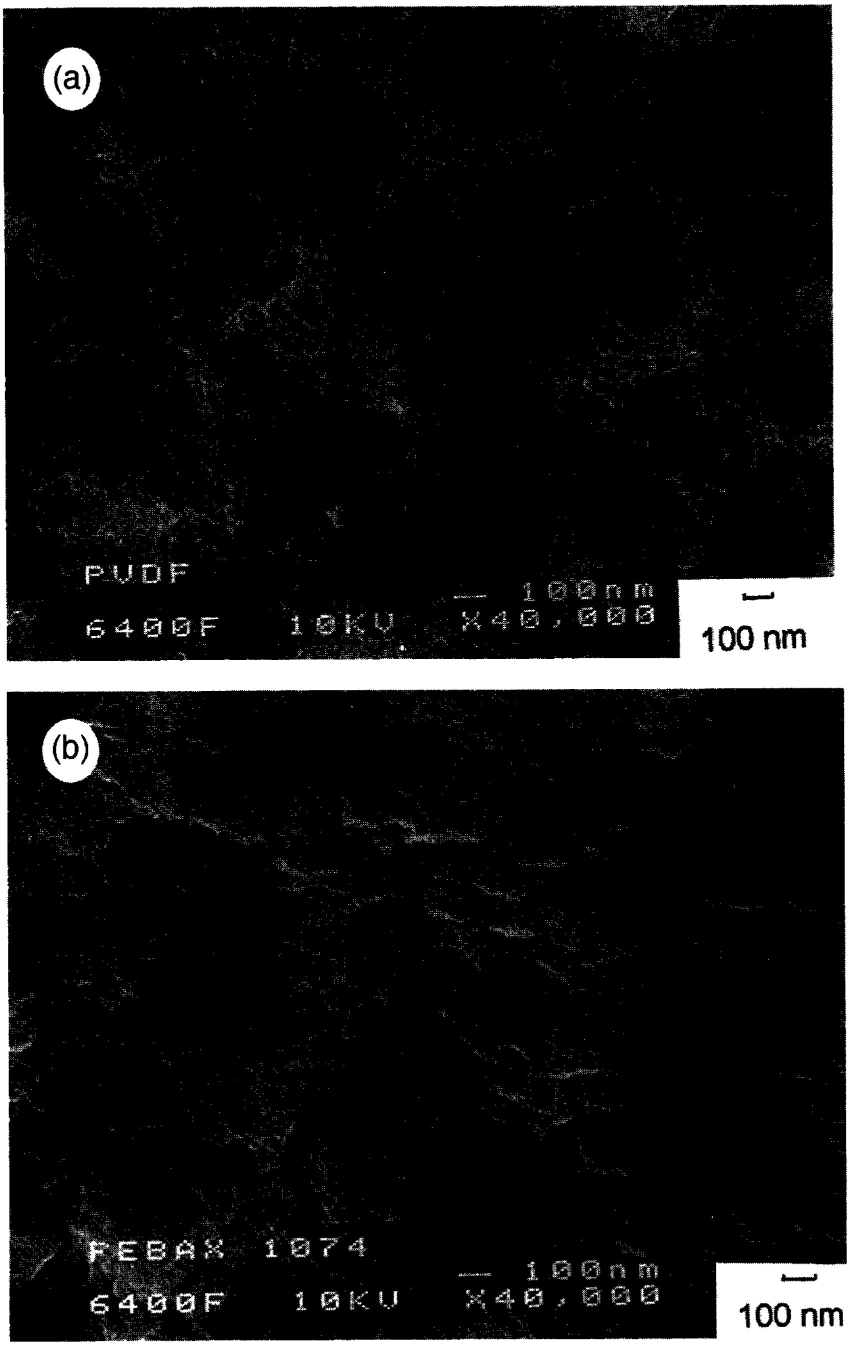


Fig. 3. (a) Porous PVDF and (b) PEBAX/PVDF composite membrane surface, observed by field emission scanning electron microscopy.

and compared to that of porous UF-membranes Desalination E100 and Film Tec FT30. N_2 and CO_2 flows through a 36 cm^2 membrane area were evaluated. The porous membranes show only the Knudsen-selectivity, which is about 0.8 for CO_2/N_2 or no gas selectivity at all. On the other hand, the PEBAX® 4011 membrane may have a selectivity factor of ca. 40, and the 1074 a selectivity factor of ca. 20, as an evidence for the

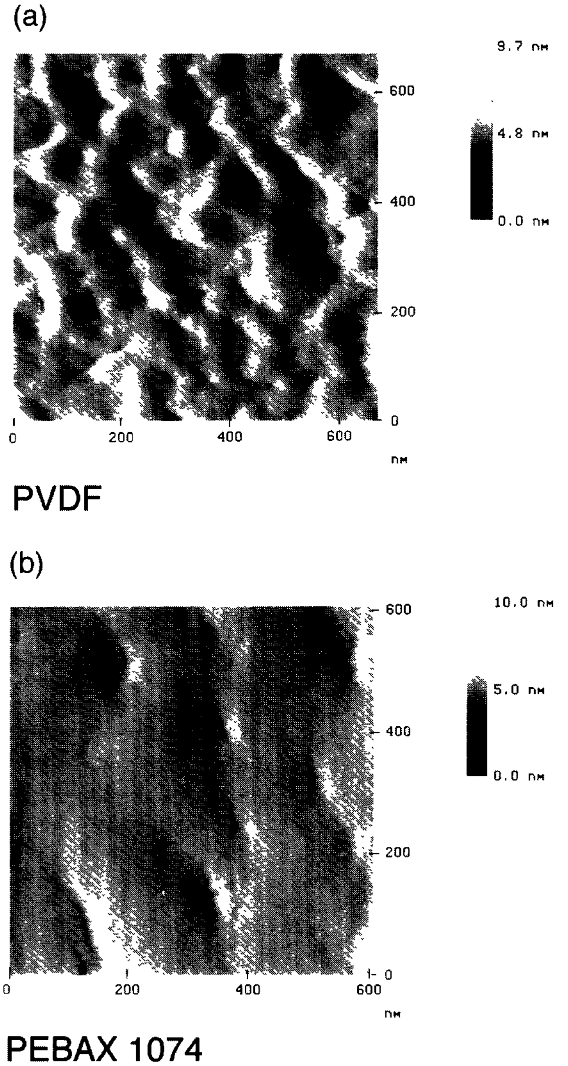


Fig. 4. (a) Porous PVDF and (b) PEBAX/PVDF composite membrane surface, observed by atomic force microscopy.

absence of pores, at least when the membranes are dry. During the ultrafiltration, the hydrophilic copolymer layer considerably swells and the membrane may rather behaviour as an open gel. Even the transport of quite large solutes, which in some cases have a molecular weight up to 4500 g/mol, is allowed through the copolymer "gel". If the selective layer is crosslinked, swelling in water is minimized, the gel structure is not so expanded anymore and a considerable change in the membrane cut-off may be observed. That was the case when the membrane was exposed to high energy electrons. Some PEBAX® 4011 membranes irradiated with 100 kGy doses had a permeability decrease from 9 to 5 l h^{-1} m^{-2} bar^{-1} and the retention of 1500 g/mol solutes increased from 65 to 93%.

4.2. Fouling behaviour

One of the main purposes of this work was to minimize the membrane susceptibility to fouling. In this sense, the performance of the PEBAX® 4011 membranes were compared to that of commercial ones in conditions much nearer the real application. During ca. 8 h, ultrafiltration experiments on the dead-end stirring cell were performed, using as feed an oil–water emulsion from the metal working industry. 400 ml of the waste water was concentrated at 8 bar. The flux decline was measured during the UF-experiment. The oil-in-water emulsions contained 6 wt% oil. They are normally used for reducing friction, cooling tools and rust protection. After use, they become dark and turbid, being a complex mixture of emulsifiers, bactericides, dirt, debris, etc., beside oil and water with several components contributing to fouling. The oily emulsion have

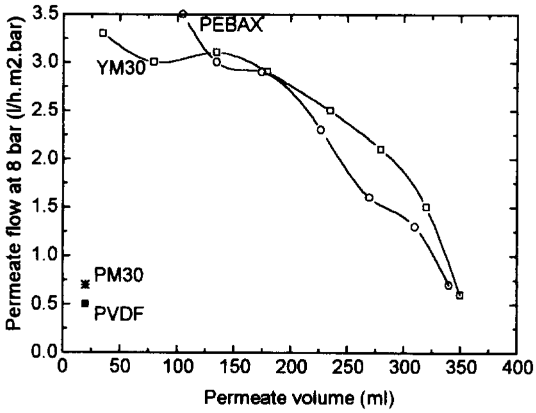


Fig. 5. Ultrafiltration of a oil–water emulsion containing 6% oil with different membranes: (○) PEBAX 4011, (■) PVDF support, (★) PM30 and (□) YM30.

Table 3
Water permeability of different membranes used in the UF-experiment of Fig. 5

Membrane	Water permeability (l h^{-1} m^{-2} bar^{-1})
PEBAX 4011	8
YM30	290
PM30	1130
PVDF	70

to be discharged and ultrafiltration may be a convenient method to purify the water before that. For comparison, the commercial membranes, YM30 cellulose and PM30 polysulfone from Amicon and the PVDF porous membrane used as support for the composite PEBAX® membrane were chosen. YM30 and PM30 are recognized in the literature [12] as suitable membranes for oil–water separation. The flow decline during the experiment is shown in Fig. 5.

The initial feed volume was always 400 ml and the pressure was 8 bar. A dead end UF-cell was used and retentate was concentrated during the experiment. Part of the decrease of the permeate flow was due to a concentration increase in the retentate, but the main reason for flow decrease was fouling. The behavior of the different membranes could be compared at the same situation. The permeate composition was not analyzed, since the feed was a quite complex mixture, but in all cases a clear transparent solution was obtained in contrast to the dark and opaque feed. The flow decline, as an evidence of fouling, was the more important aspect. Table 3 shows the membrane permeability to pure water.

Membranes such as PM30 or even the PVDF support are very permeable to pure water. However, when used for filtration of the oil–water emulsion, they showed to be very susceptible to fouling, with a flow decrease down to less than 0.7 l h^{-1} m^{-2} bar^{-1} after the first minutes of filtration. The two membranes were rather hydrophobic. On the other hand PEBAX® membranes have a rather low permeability to pure water, when compared to the initial values of other membranes. But when used for filtration of the oil–water emulsion, the permeate flow was considerably higher than that of the PM30 and PVDF membranes. They were comparable to the best tested commercial membrane, YM30, with a low flow decrease. Results confirm that the hydrophilic copolymer membrane is affected by fouling in a much less extent than the investigated hydrophobic membranes.

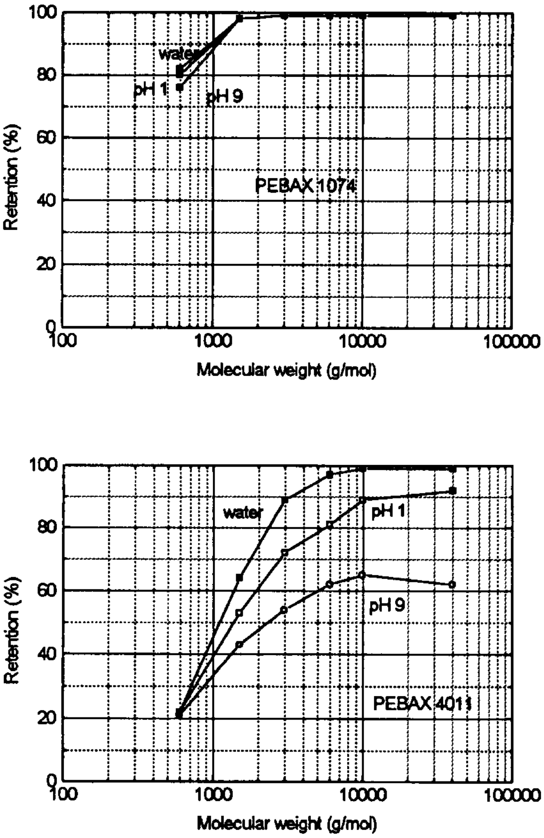


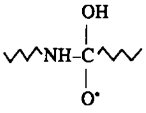
Fig. 6. Retention curves for (a) PEBAX 4011 and (b) PEBAX 1074 membranes after one week in different pH buffers.

A PEBAX® 4011 membrane with initial 6.4 l h^{-1} m^{-2} bar^{-1} water permeability, obtained from a 1% blockcopolymer solution, was also compared to the commercial E100 Desalination polysulfone membrane (initial water permeability of 20 l h^{-1} m^{-2} bar^{-1}) inthe ultrafiltration of 3.5% fat milk. The E100 membrane, normally used for these purpose had a permeability of 0.8 l h^{-1} m^{-2} bar^{-1}, after 6 h of ultrafiltration. The blockcopolymer membrane had a permeability of 1.1 l h^{-1} m^{-2} bar^{-1}. If the initial water flow is taken in account and compared to the final permeate flow through the membrane, the performance of the composite membrane was again superior. As already mentioned, hydrophilic membranes are less affected by solute adsorption on their surface. Furthermore, the PEBAX® membrane here is quite dense and pore blocking due to fouling can be neglected, since the membrane in water can be better seen as an expanded gel without macroscopic pores, in opposite to conventional UF-membranes.

4.3. *pH stability*

The stability of the membranes was evaluated in different pH buffers, since for some applications membranes may be used or cleaned in more aggressive conditions. Both PEBAX® 4011 and 1074 membranes were stored during a week in pH 1, 7 and 9 buffers and retention curves were then obtained, as already described. The results are shown in Fig. 6. While the PEBAX® 4011 membrane is not stable specially in alkaline conditions, almost no difference could be detected in the retention curves of PEBAX® 1074 membranes. The polyamide 6 block (PEBAX® 4011) is clearly more affected by extreme pH conditions than the polyamide 12 block (PEBAX® 1074).

In acid solutions, the amide groups hydrolyze forming amine and carboxylic acid. In alkaline solutions,



$$\sim\sim NH-\overset{OH}{\underset{O^{\bullet}}{C}}\sim\sim$$

intermediaries lead to decomposition.

5. Conclusions

Dense hydrophilic composite membranes were obtained from polyether-*block*-polyamide copolymers (PEBAX®) and were succesfully evaluated in ultrafiltration experiments. The membrane cut-off could be varied from 4500 to 800 g/mol, by changing the polyamide block. Water permeability values of ca. 6 l/h m^2 bar could be obtained for the more selective membranes with a dense layer ca. 0.15 μm thick.

Concerning their resistance to fouling, in the ultrafiltration of oil–water emulsions, the performance of the PEBAX® membrane was considerably better than that of the PVDF microporous support without the copolymer layer or commercial polysulfone membranes. The results were comparable to the YM30 cellulose membrane.

Acknowledgements

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