ASYMMETRIC MEMBRANES FROM POLYSTIRENE/POLYOLEFIN BLENDS

M. E. Chiriac, V. Chiriac, C. Vasile[a], M. Pascu[b*]

SC INCERPLAST SA 23 Ziduri Mosi Bucharest, Romania
[a]"P. Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487, Iasi, Romania
[b]"Gr. T. Popa" Medicine and Pharmacy University, 16 University Str., Iasi, Romania

By controlled extraction, asymmetric membranes from PS/PO blends have been prepared. The suitable selection of the membrane, according to their porosity and pores dimensions, allows for utilization in various fields such as: gases separation, concentration of germ solution, proteins and polymeric latex filtration.

1. Introduction

Polyolefins are known for their application in membranes production [1,2]. In our previous papers [3,4] we have obtained blends of compatibilized polystyrene (PS) with either high density polyethylene (PE) or polypropylene (PP) by adding compatibilizing agents, such as SEBS (styrene-ethylene-bytylene-styrene) and, respectively, SEP (styrene-ethylene-propylene) copolymers and by γ-irradiation. By a detailed characterization of the blends, including extraction behaviour, it has been established that porous films can be obtained, having various pores sizes depending on the blend composition, type of used solvent for extraction and extraction time.

The aim of this paper is to test the porous films obtained by extraction of polystyrene from polyolefin matrices, in various fields, indicating the most suitable one for each application.

2. Experimental

2.1. Membrane Preparation

The preparation of the polystyrene (PS)/ polyolefins (PO) membranes consists in three steps: (1) pre-membrane obtaining; (2) treatment of pre-membrane; (3) extraction of the soluble phase to obtain a porous structure.

(1) The PS/high density polyethylene (PE) and PS/polypropylene (PP) blends have been obtained by intensive compounding (mixing-extrusion-granulation) in a HENCKEL mixer provided with a counter-rotating twin screw extruder KO-BUSS MDK type [3,4]. They have been granulated and turned into thin films. The PS/PO blends, as films of 0.05 and 0.1-0.2 mm thickness, have been obtained by the extrusion/injection procedure and by reactive extrusion, respectively on a TRUSSIOMA installation. The extruder, with continuously decreasing volume zones, is provided with a screw having the following characteristics: screw diameter 32 mm; L/D = 20; compression ratio 1/3. The selected processing parameters were: temperatures of extruder zones between 150 and 190 °C and 160-210 °C for PS/PE and PS/PP blends respectively, screw speed 40-60 rpm. A flat die (L=300 mm, h= 0.2 – 0.5 mm) with controlled opening (height) was used. The films were prevailed by a system of pressing cylinders cooled with in air flow on both sides of the film.

---

* Corresponding author: mp@umfiasi.ro

(2) In order to increase the mechanical resistance of the membrane and to stabilize the phase distribution obtained during mixing and processing operations, the γ-irradiation of the pre-membrane films has been performed. An ILU irradiation source with intensity of 8 A which produces a dose of 50 Gy/10 minutes was used. The irradiation time was 10 minutes.

(3) Extraction. The pre-membrane films were cut at 500x300 mm dimensions, folded and laterally sealed, so that the solvent is in contact only with a side of the film. The films have been extracted in a Soxhlet apparatus in chloroform (C) and toluene (T) which dissolve only polystyrene from the blends without interacting with the PO matrix. The extraction time was 1, 8 and 16 hours. The residual solvent was removed by drying in vacuum at 40°C. As it was expected, the membrane thickness is significantly reduced after extraction. The membrane codes include ratio of the components, time of extraction and type of solvent used such as 5PS/5PE 1T or 5 PS/5PE 16C. The composition of the pre-membranes, solvent and extraction time are given in Table 1.

Table 1. Membranes codes and extraction conditions.

Pre-membrane code	Solvent	Extraction time (h)	Membrane code
5PS/5PE	Toluene	1	5PS/5PE 1T
5PS/5PE	Toluene	8	5PS/5PE 8T
5PS/5PE	Toluene	16	5PS/5PE 16T
5PS/5PE	Chloroform	8	5PS/5PE 8C
5PS/5PE	Chloroform	16	5PS/5PE 16C
6PS/4PE	Toluene	1	6PS/4PE 1T
6PS/4PE	Toluene	8	6PS/4PE 8T
6PS/4PE	Chloroform	8	6PS/4PE 8C
7PS/3PE	Toluene	1	7PS/3PE 1T
7PS/3PE	Toluene	8	7PS/3PE 8T
7PS/3PE	Chloroform	8	7PS/3PE 8C
5PS/5PP	Toluene	1	5PS/5PP 1T
6PS/4PP	Toluene	1	6PS/4PP 1T
7PS/3PP	Toluene	8	7PS/3PP 8T
7PS/3PP	Toluene	16	7PS/3PP 16T
7PS/3PP	Chloroform	8	7PS/3PP 8C
7PS/3PP	Chloroform	16	7PS/3PP 16C

3. Results and discussion

3.1 Characterization of the membranes

Pre-membranes and membranes characterization by FT-IR, DSC, TEM, TG/DTG methods have been presented in our previous papers [3,4]. The morphology of the 5PS/5PE and 5PS/5PP pre-membranes is of particles distribution in a continuous matrix. The increase of the amorphous polymer (PS) in the blends composition reduces the spherulites dimensions leading to a stratification of the fibrils along the polystyrene rings. The effect is evidenced by good mechanical performance (high tensile and impact strength of the 7PS/3PO blends) and thermal stability. The shape and size of the pores resulted from the same blend (for example 5PS/5PE, 6PS/4PE 8T and 6PS/4PE 8C) extracted with chloroform and toluene are different. The pores obtained after 16 h extraction in toluene are clear and uniformly distributed, while those obtained after the same duration of time with chloroform are interconnected, big and diffuse ones. To obtain a high porosity, the extraction time should be at least 8h (e.g. 7PS/3PE 8T membrane). The high porosity results in the case of the membrane based on PP. The PS was totally removed after 8 h from 5PS/5PE blend, while from the other blends it is only partially extracted even after 16 h either using toluene or chloroform. The extraction efficiency was higher with chloroform than with toluene.

3.2. Membrane porosity

The membrane porosity was determined using a MILESTONE 2000 porometer PO 4000 type with Hg at a pressure of 2000 bars under an angle of 141° (Table 2).

At short extraction time, micropores and porosity with high values are obtained, while longer extraction time leads to macropores (tens of microns). On the basis of these characteristics, the membranes have been selected and tested for different applications.

Table 2. Average pore radius and porosity and the total volume of the pores of PS/PO membranes toluene extracted.

Membrane code	Average Pores radius (Å)	Average Total volume of pores (mm^3/g)	Average Porosity (%)
5PS/5PE 1T	133	277.6	35.6
5PS/5PE 16T	5692	706.7	61
6PS/4PE 1T	200	61.6	16.1
6PS/4PE 8T	600	661.7	58
7PS/3PE 1T	245	61.4	13
7PS/3PE 8T	846	730.1	63
5PS/5PP 1T	266	217.7	41
6PS/4PP 1T	372	101.2	30
7PS/3PP 16T	2154	754.6	73.2

3.3. Membrane testing

3.3.1. Permeability to gases

There were selected the membranes having small pores dimensions: 6PS/4PE 1T, 6PS/4PE 1C, 7PS/3PE 1T and 7PS/3PE 1C. Permeability to gases was performed using a manometric method; the permeation cell and the working conditions were according to standard method ASTM D1434. Permeation rate and separation factor have been determined: The obtained results are given in table 3 and Fig. 1.

Table 3. Permeation rate (Q in cm^3/m^2, 24h 1atm at 20 ^oC) of the PS/PO membranes.

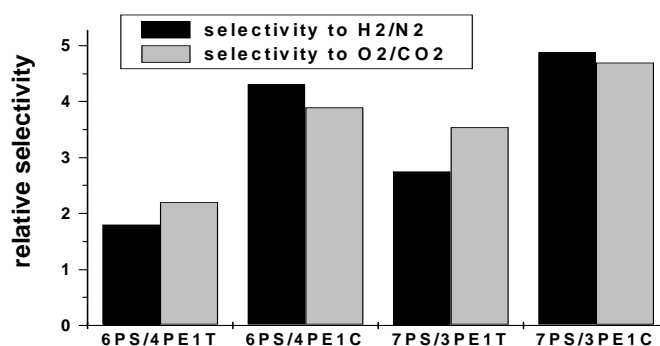| Conditions	6PS/4PE 1T	6PS/4PE 1C	7PS/3PE 1T	7PS/3PE 1C
Air, p_1=1 atm, p_2=2 atm	$1.2 \cdot 10^{10}$	$3.75 \cdot 10^8$	$3.4 \cdot 10^7$	$0.8 \cdot 10^4$
Argon, p_1=0 atm, p_2=1.5 atm	$1.3 \cdot 10^{10}$	$2.2 \cdot 10^8$	$3.1 \cdot 10^7$	$0.8 \cdot 10^4$
Oxygen p_1=10^{-4} torr, p_2= 700 torr	$1.5 \cdot 10^{10}$	$4.8 \cdot 10^8$	$2.1 \cdot 10^7$	$1.0 \cdot 10^4$
Nitrogen p_1=1 atm, p_2=2 atm	$1.8 \cdot 10^{10}$	$2.5 \cdot 10^8$	$5.3 \cdot 10^7$	$0.3 \cdot 10^4$
Carbon dioxide p_1=1 atm, p_2=2 atm	$0.6 \cdot 10^{10}$	$0.5 \cdot 10^8$	$0.5 \cdot 10^7$	$0.5 \cdot 10^4$
Hydrogen p_1=1 atm, p_2=16 atm	$3.8 \cdot 10^{10}$	$7.6 \cdot 10^8$	$8.7 \cdot 10^7$	$1.9 \cdot 10^4$

Fig. 1. Membranes selectivity to gases separation

For the same pressure gradient of the same gas, the membrane 6PS/4PE 1T and 6PS/4PE 1C exhibit permeation rates which differ by two orders of magnitude, while in the case of the 7PS/3PE 1T and 7PS/3PE 1C membrane, the difference is of three orders of magnitude, the faster being the permeation through membranes obtained by extraction in toluene. The explanation of this behaviour is that the pores created by toluene extraction are smooth and discret, while those obtained by extraction with chloroform are interconnected. The membranes 6PS/4PE 1T and 6PS/4PE 1C are of 10^3 or 10^4 times more permeable than 7PS/3PE 1T and 7PS/3PE 1TC membrane, respectively. For both types of membranes obtained by extraction either in toluene or chloroform, the most advanced permeability is for hydrogen and the lowest is for carbon dioxide.

In what is concerning the selectivity of membranes (Fig. 1), it can be remarked that the membranes obtained by extraction with chloroform are superior to those obtained by extraction with toluene. The best results have been obtained with membranes 7PS/3PE 1C and 6PS/4PE 1C. Because of their good selectivity, they are recommended for gases separation.

3.3.2. Permeability to water

All tested membranes are hydrophobic and they do not swell in aqueous medium. There have been determined the permeation flow through the following membranes: 5PS/5PE 8T, 5PS/5PE 16C, 5PS/5PE 16T 6PS/4PE 8T, 6PS/4PE 8C, 7PS/3PP 16T and 7PS/3PP 16C using a microfiltration cell with an area of 5 cm^2 (Figs. 2 a-c).
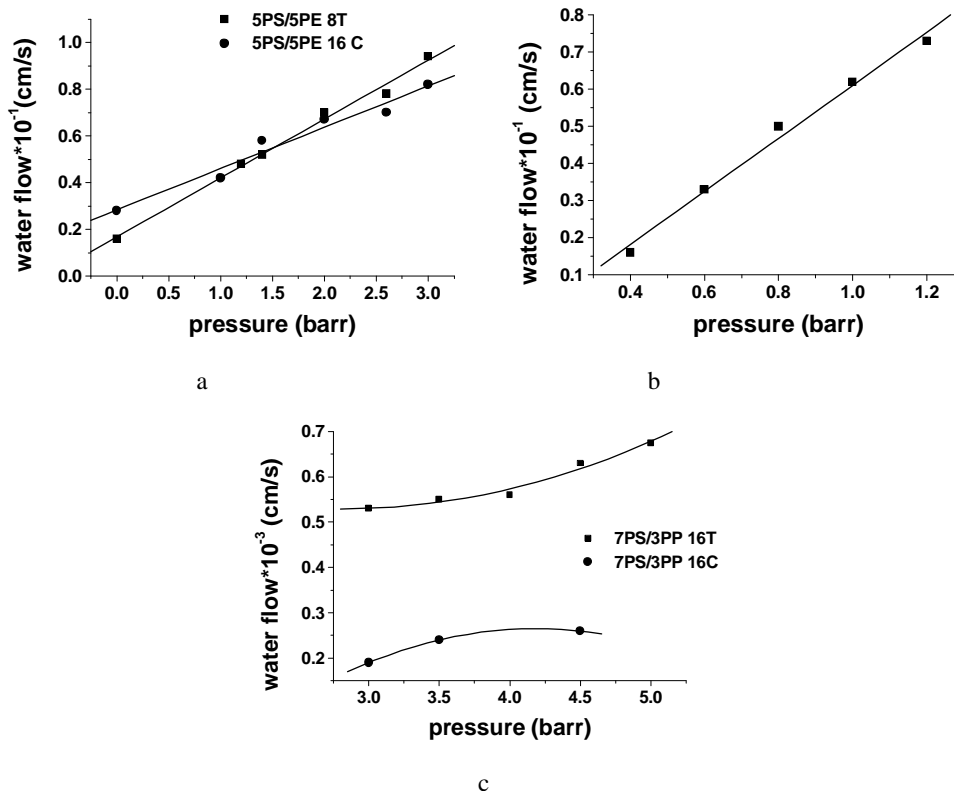

a　　　　　　　　　　　　　　　　　b

c

Fig. 2. Twice distilled water flow (p= 0–4 bars) through PS/PO membranes (a) 5PS/5PE;
(b) 5PS/5PE 16T; (c) 7PS/3PP.

It can be observed that the permeation flow through the 5PS/5PE 8T membrane is comparable with that passing through 5PS/5PE 16C membrane (Fig. 2a), while the permeation flow through the 5PS/5PE 16T membrane is with 40% higher than that passing the 5PS/5PE 8T membrane. The permeation flow through 6PS/4PE 8T and 7PS/3PE 16T membrane is 3 times higher at a p=1 bar and of 10 times higher at p=3 bar, comparatively with the membrane with the same

composition but obtained by extraction for 8h in chloroform. The highest values of the permeation flow, even at low pressure (0.8–1 bars), are obtained with 5PS/5PE 16T membrane.

3.3.3. Concentration of germ suspension

A Candida C38 germs cellular culture has been concentrated on the following membranes: 5PS/5PE 1T, 6PS/4PE 1T and 7PS/3PE 1T, which retain germs on their surfaces using a permeation cell with a surface of 10 cm^2 and a pressure of 0.3 atm. The results are given in Table 4.

Table 4. Results obtained for the concentration of a Candida C38 germs suspension on PS/PE membranes.

Membrane code	Initial concentration (germs/mm^3)	Concentration of suspension retained (germs/mm^3)
5PS/5PE 1T	$7 \cdot 10^7$	$1.2 \cdot 10^5$
6PS/4PE 1T	$7 \cdot 10^7$	$5.9 \cdot 10^6$
7PS/3PE 1T	$7 \cdot 10^7$	$2.01 \cdot 10^7$

Because of the small total volume of the pores (of only 61 mm^3/g) and an average radius of 245 Å, the membrane 7PS/3PE 1T behaves as an ultrafiltration membrane permitting only to water to pass through it and so concentrating the germs culture on its surface. A similar behaviour has the 6PS/4PE 1T membrane with a porosity of 16.1 % and an average pores radius of 200 Å, which at its turn retains a significant amount from initial germs culture.

3.3.4. Protein filtration

Two dilute colloidal solutions to be filtrated were: 1 wt% BSA (Bovine Serum Albumin, ~60 000 a.u.) and 1 wt% BD (Blue Dextran, ~2 000 000 a.u.) dilute solutions in monosodium phosphate buffer solution of pH=6.5 have been filtrated through 5PS/5PE 8T and 5PS/5PP 8T membranes. The colloidal proteinaceous solutions should not reach electrostatic equilibrium at the isoelectric point when coagulate. After passing through the membrane, the solution was diluted 24 times and its UV absorption spectrum was recorded. The absorption band of the aromatic amino acids from solutions is recorded at λ=280 nm. Percentage of permeate flow of proteinaceous solutions through PS/PO membranes varied between 74 and 98 %

Due to the difference between the average radius of pores, the 5PS/5PE 8T membrane filtrates both colloidal proteinaceous solutions, while 5PS/5PP 8T only BSA solution.

3.3.5. Permeation of the surfactant solution

Usually, the real dispersion systems from polymerization installation, contains tensioactive substances which diminish the surface tension of the particle surface. In the processes of polymeric latexes recovery, there are used N-dodecylpiridine, hexadodecylpiridine chloride etc. In this test, a permeation cell with 7 cm^2 surface has been used to study the permeation of the N-dodecylpiridine solution of different concentrations namely 1.2; 1.6; 2.4 and 3 g/dL by the following membranes: 6PS/4PE 8T; 7PS/3PE 8T and 7PS/3PP 8T (figure 3). The decreasing flow through membranes with increasing concentration of surfactant was observed by a bimodal variation, the pores distribution being similar it having an important role. The 6PS/4PE 8T membrane has the highest flow at low surfactant concentration (1.2 g/dL) but this one decreases rapidly at a concentration of 3.0 g/dL. The permeate flow through 7PS/3PE 8T membrane remains at high values of 0.75 g/dL even at the biggest concentration. The 7PS/3PP 8T membrane is the most permeable for all the studied concentrations, due to a wide pore distribution. This test is useful for the next step of membranes application in microfiltration of a polystyrene latex.

3.3.6. Permeation of a disperse system containing polymeric particles

In this case it has been determined the normalized flow of an aqueous solution of polystyrene latex having standardized particles of 0.1 μm, in presence of the dodecylsodium sulfate of a concentration of $8 \cdot 10^{-2}$ mol/L. The used pressure was 1 bar. The following membranes have been tested: 5PS/5PE 16T; 6PS/4PE 8T; 7PS/3PE 8T and 7PS/3PP 16T. The diagrams of the permeating flow are presented in Fig. 4.
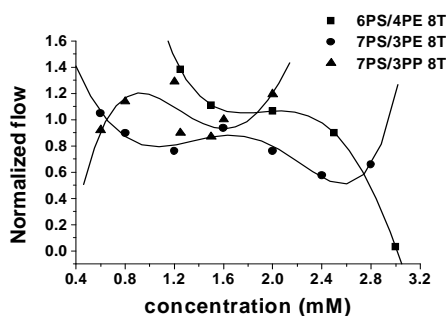
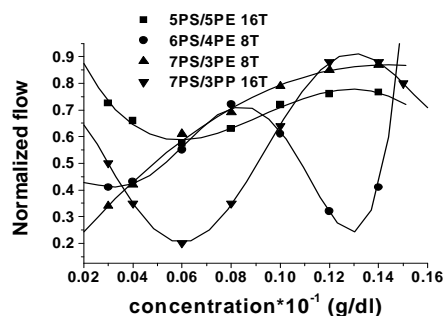Fig. 3. Surfactant flow through PS/PO membranes.   Fig. 4. PS latex flow through PS/PO membranes.

For all the studied membranes, the normalized flow increases with increasing the solution concentration showing also maxima at high concentration values of 0.12–0.15 g/dL, this being a consequence of the wide pores size distribution in the membranes. Three from the four membranes have a good permeation (filtration) to the polystyrene latex namely 5PS/5PE 16T; 7PS/3PE 8T and 7PS/3PP 16T. From these three membranes the most efficient is 7PS/3PP 16T with average pores size of 2154 Å, which behaves as a "perfect sieve" for water particles retaining polystyrene particles on its surface at all studied concentrations and mainly those from 0.09 to 0.15 g/dL.

After each experiment the membranes were washed with water and reused in five consecutive experiments. They preserve their mechanical resistance, filtration quality and pores system. Studying the filtrate, one can observed the total separation of the polystyrene particles at all concentrations, when using 7PS/3PE 8T and 6 PS/4PE 8T membranes. The separation was total at a c<0.1 g/dL. It was not observed any interaction between PS dispersed in solution and PS from the membranes.

4. Conclusions

Porous films of polystyrene/polyolefin have been prepared. The membranes based on such films show excellent filtration properties, which make these membranes good candidates for gas separation, germ, protein and latex filtration.

References

[1] N. S. Vijayalakshmi, R. A. N. Murthy, J. Appl. Polym. Sci. **44**, 1377 (1992).
[2] J. Pionteck, P. Poetchke, U. Schultze, N. Proske, A. Kaya, H. Zhao, H. Malz, Macromolecular Simposia **214**, 279 (2004).
[3] M. Chiriac, G. G. Bumbu, V. Chiriac, C. Vasile, M. Burlacel, B. S. Munteanu, Intern. J. Polym. Mater. **49**, 419 (2001).
[4] M. Chiriac, B. S. Munteanu, G. G.Bumbu, M. Burlacel, A. Ioanid, C. Vasile, Macromol. Mater. Eng. **283**, 26 (2000).