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Hyperfiltration Membranes Prepared by Radiochemical Grafting of Styrene Onto Poly(tetrafluoroethylene). Influence of the Size and Shape of Emulsion Particles Used to Obtain the PTFE Film

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Synopsis

The hyperfiltration performances of membranes obtained from PTFE films sintered with different granulometric distribution emulsions were studied. It has been possible to show that: (1) large spherical particles lead to high flux, poor rejection membranes, and vice versa for small spherical particles; (2) the particle shape affects the membrane properties. "Stick" shaped particles lead to better rejection properties than the spherical and "fibrillar" ones. An attempt was also made to utilize a PTFE/PMMA porous support to make asymmetric membranes.

INTRODUCTION

In preceding studies we have ascertained the promising hyperfiltration properties of membranes obtained from poly(tetrafluoroethylene) (PTFE) films[1-3]; and in this paper we try to point out the contribution to the membrane performance of the base-film structure, with particular reference to the size distribution and shape of the emulsion particles used to cast the PTFE film.

As is well known that among the several methods of making thin PTFE films,[4,5] the best way to get homogeneous films consists[6] of casting the emulsion on a steel sheet, then heating at about 400°C, and repeating the whole operation several times in order to reach the desired film thickness. The films obtained in such a way are called "polydisperse types," and we always used this technique to prepare the membranes studied in this paper.

The emulsion particle sizes were, in our case, restricted within a few tenths of a micron, and by varying their shape and size, the film characteristics should vary, too.

Thus, using different PTFE emulsions, one should get a wide range of different films, and we have therefore tried to show this to be the case.

EXPERIMENTAL PROCEDURES AND GENERALIZED RESULTS

Influence of Particle Size

Radiochemical Grafting Process

The emulsion used to prepare the films had particles of different shape, namely, (1) "balls," (2) "sticks," (3) "fibers." In case (1) four types of emulsions having particles whose dimensions were 0.1, 0.14, 0.22, and 0.3 μ, respectively (conventionally numbered 147, 85, 86, 87 by the Producer, U. Kuhlmann, were used.

In the case of "sticks," the particle dimensions of the four emulsions used were 0.1 × 0.18, 0.14 × 0.26, 0.2 × 0.35, 0.3 × 0.05 μ, bearing the numbers 88, 89, 90, 136. In the case of the small fibers, the dimensions were 0.03 × 0.8 μ and were numbered 138.

The PTFE films obtained from the above-mentioned emulsions were submitted to radiochemical grafting of styrene.[2] The grafting yield was followed as a function of the cross section of the emulsion particles in order to show any eventual influence due to a different monomer penetration into the PTFE matrix.

The experimental results show (Fig. 1) a fairly good constancy of the grafting yield for different shapes and sizes of the emulsion particles, provided that all PTFE films had the same thickness (12 microns).

This fact is, by the way, further evidence that the grafting process takes place inside the PTFE particles and thus involves much smaller structures than particle aggregates.

Hyperfiltration Performances

The grafted films were then sulfonated and hydrolyzed to obtain mem-

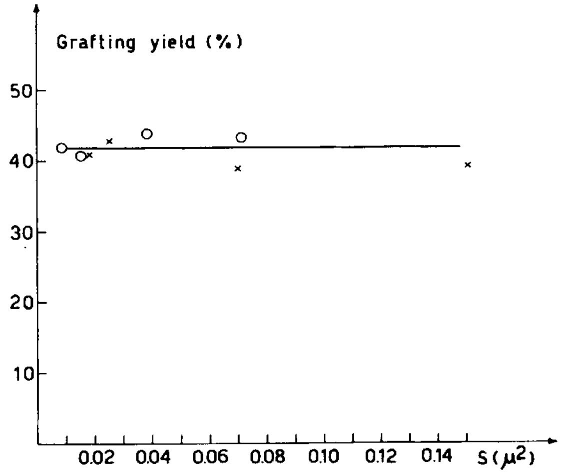

Fig. 1. Grafting yield vs. PTFE particle mean cross section (μ^2): (O) "spherical" particles; (X) "stick" particles.

brane films having an SO_3H group content of 20% w/w. The membranes were then submitted to hyperfiltration tests in a reverse osmosis plant working at 70 atm and with 1% NaCl feed.

In the case of films made from spheroidal particles the experimental results showed an increase of water permeability with the cross section of the particles. The rejection power, usually defined as

$$R\% = \frac{\text{feed concentration} - \text{product concentration}}{\text{feed concentration}} \times 100$$

decreased from 84% to 77% (Figs. 2 and 3).

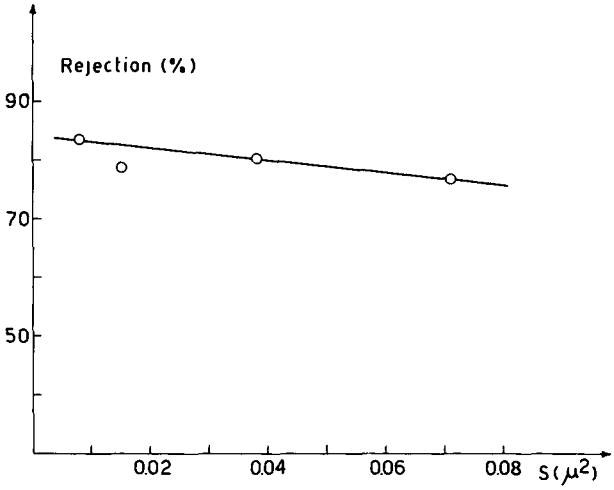

Fig. 2. Salt rejection (%) vs. particle mean cross section (μ^2): "spherical" particles; feed, 10,000 ppm NaCl; pressure, 70 atm.

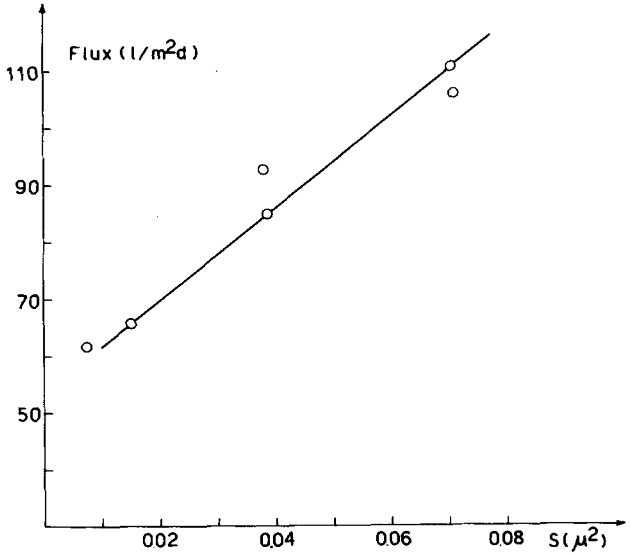

Fig. 3. Water flux (l./m^2d) vs. particles mean cross section (μ^2): "spherical" particles; feed, 10,000 ppm NaCl; pressure, 70 atm.

In the case of films made from oblong particles (sticks), the results (Figs. 4 and 5) showed a similar behavior of the hyperfiltration performances, though the water permeability increase was less marked.

Practically speaking, the change in water flux was 100% in the case of spherical particles, while with oblong particles, it was only 45% (in the same range of particle sections).

In order to check the aggregation degree influence on the membrane performance, some hyperfiltration tests were run on membranes obtained from particle aggregates, having a markedly fiber-like structure (film no. 138).

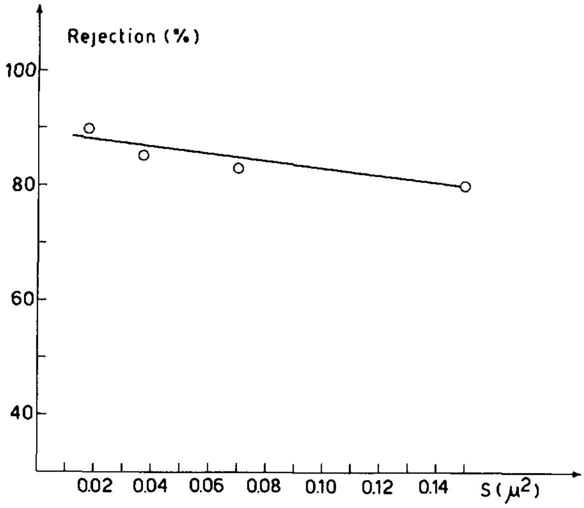

Fig. 4. Salt rejection (%) vs. particle mean cross section (μ^2): "stick" particles; feed, 10,000 ppm NaCl; pressure, 70 atm.

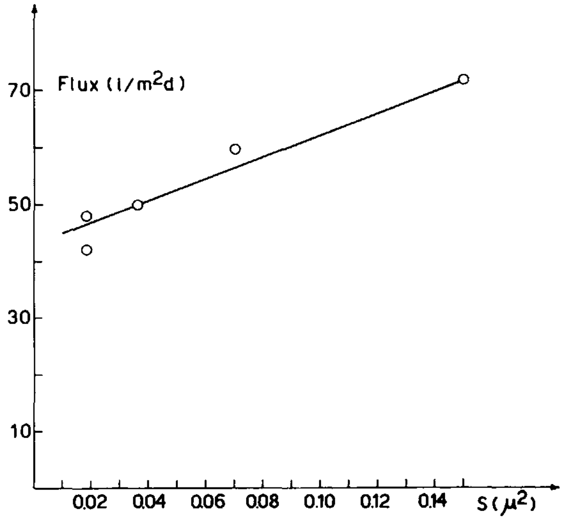

Fig. 5. Water flux (l./m^{2}d) vs. particle mean cross section (μ^2): "stick" particles; feed, 10,000 ppm NaCl; pressure, 70 atm.

These membranes look similar to those obtained with other particles, but the mechanical strength shows the preferential tearing direction is perpendicular to the orientation that the fiber has achieved during the film preparation.

The hyperfiltration tests showed that this kind of PTFE film leads to highly permeable membranes and poor rejection; that is, 30% with a 600 l./m^{2}d water flux and 20% of grafting (other conditions being constant). Moreover, this kind of membrane shows a marked flux reduction due to compaction. This phenomenon has been encountered with other kinds of films, and we shall refer to this later.

Taking into account the different characteristics acquired by PTFE films due to the shape of the particles used, an attempt was made to prepare a membrane starting from a film composite consisting of a double layer of "balls" (0.3 microns diameter) and "sticks" particles (0.6 × 0.4 microns), which is the Ugine Kuhlmann no. 145 film). The results (rejection 86% and flux 80 l./m^{2}d) did not show any noticeable deviation from the mean values for homogeneous membranes.

Crosslinking

Crosslinking was obtained as previously described[1] by adding a crosslinking agent to the grafting monomer.[7] In this case, a mixture of styrene–3% divinylbenzene (DVB) was used.

While the rejection improvement due to crosslinking was about 20% for the membranes previously prepared,[2] in this case the improvement was not so high (see Figs. 6, 7, 8, and 9).

The experimental results nevertheless allow us to say that the crosslinking effect increases with decreasing particle diameter; since the PTFE films used for the above-mentioned membranes[1] came from Dielectrix Co. and were

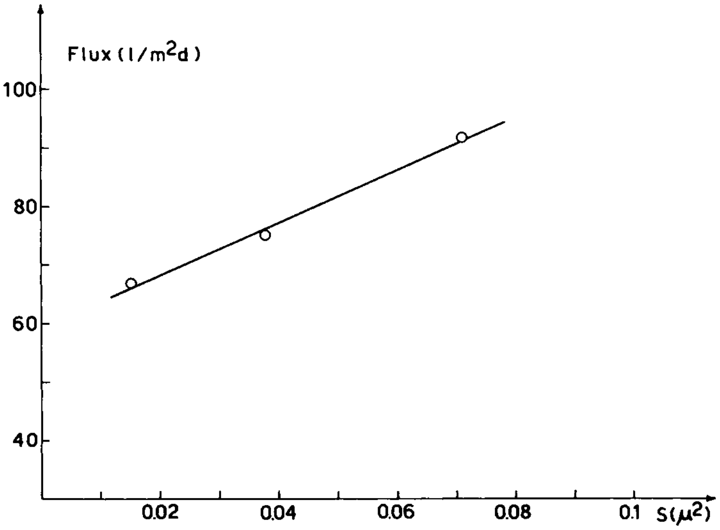

Fig. 6. Water flux (l./m^{2}d) vs. particle mean cross section (μ^2): "spherical" particles; grafting yield, 40% with 3% DVB; feed, NaCl 10,000 ppm; pressure, 70 atm.

manufactured with very small particles, there is no discrepancy with our early data.

It was pointed out that films made from fiber-like particles were more sensitive to the crosslinking action, which caused a 50% rejection increase but halved water flux.

The no. 145 film (having particles of various shapes) did not show any peculiar characteristic in comparison with those having homogeneous particles.

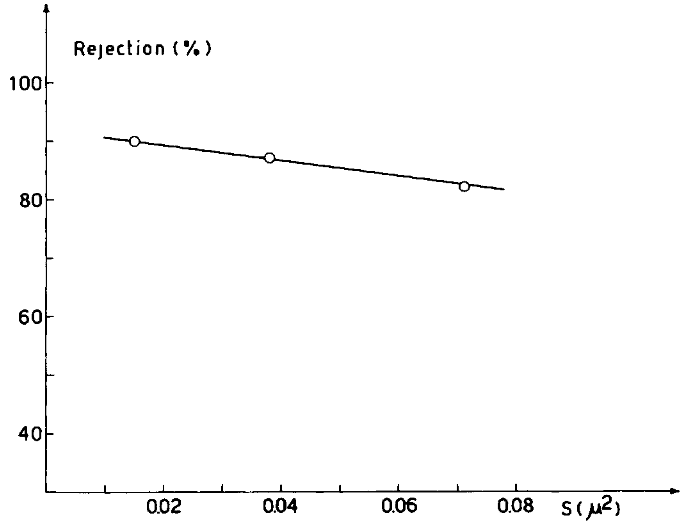

Fig. 7. Salt rejection (%) vs. particle mean cross section (μ^2): "spherical" particles; grafting yield, 40% with 3% DVB; feed, NaCl 10,000 ppm; pressure, 70 atm.

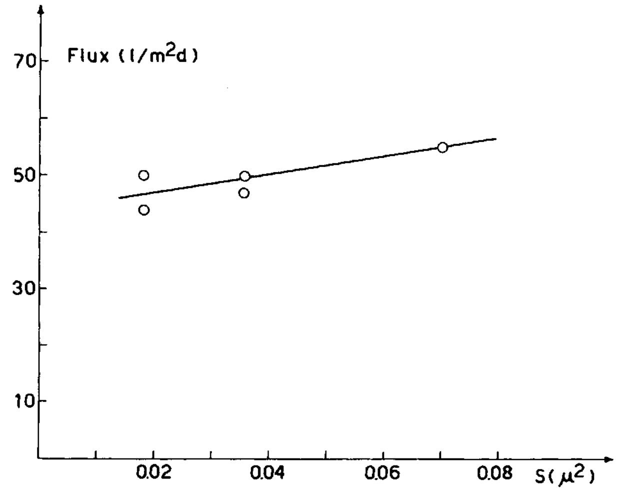

Fig. 8. Water flux F (l./m^{2}d) vs. particle mean cross section (μ^2): "stick" particles; grafting yield 40% with 3% DVB; feed, NaCl 10,000 ppm; pressure: 70 atm.

TABLE I
Characteristics of PMMA/PTFE Films

Film no.	% PMMA	Thickness, μ
143	30	10
163	37.5	15
150	45	12
149	60	12

Films Obtained from PTFE/PMMA Mixtures

In the attempt to obtain highly permeable membranes, Ugine Kuhlmann has produced some experimental films starting from a mixed emulsion of PTFE and poly(methyl methacrylate) (PMMA) particles.

By heating the film at 400°C, the PMMA should decompose, producing large pores in the PTFE matrix (electron microscope investigation seems to confirm this). Thus, varying the PTFE/PMMA ratio, it should be possible to get films at different degrees of porosity. The films used had a thickness ranging between 10 and 15 microns and are listed in Table I.

Some experimental runs showed that the same unsulfonated film exhibits a certain permeability to water but, as expected, no rejection. These films were, as usual, converted in cation exchanging membranes by radiochemical grafting. Very little influence of porosity on the grafting yield was noted.

The results of the hyperfiltration tests showed an initially very high water permeability and poor rejection. As time passed, due to pressure compaction, the rejection increased and flux decreased. The typical behavior of such membranes is reported in Figure 10. The phenomenon seems to be reversible.

After 24 hours of testing, the water flux and rejection became constant. In the plot of Figure 11, the limiting values of flux and rejection are reported as

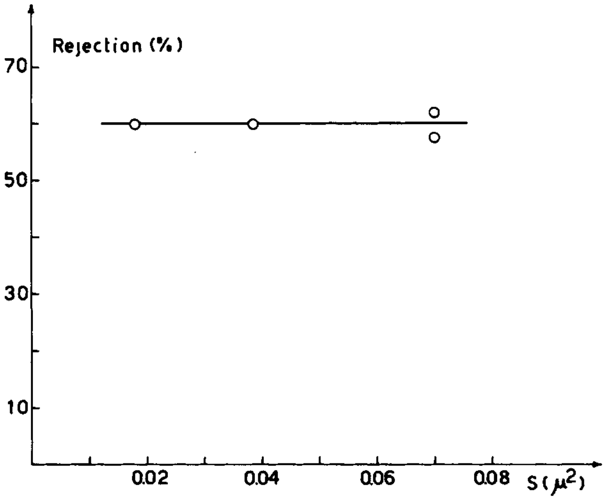

Fig. 9. Salt rejection R (%) vs. particle mean cross section S (μ^2): "stick" particles; grafting yield, 40% with 3% DVB; feed, NaCl 10,000 ppm; pressure, 70 atm.

a function of PMMA percentage in the emulsion and at a constant value of grafting (40%). From this plot, it can be derived that up to 40% of PMMA the film properties remain constant, while above this value, the hyperfiltration performances change dramatically, owing to the largely porous structure of the film.

Asymmetric Membranes

We have shown by the above-mentioned tests that (1) salt rejection increases with decreasing emulsion particle diameter; (2) water permeability in-

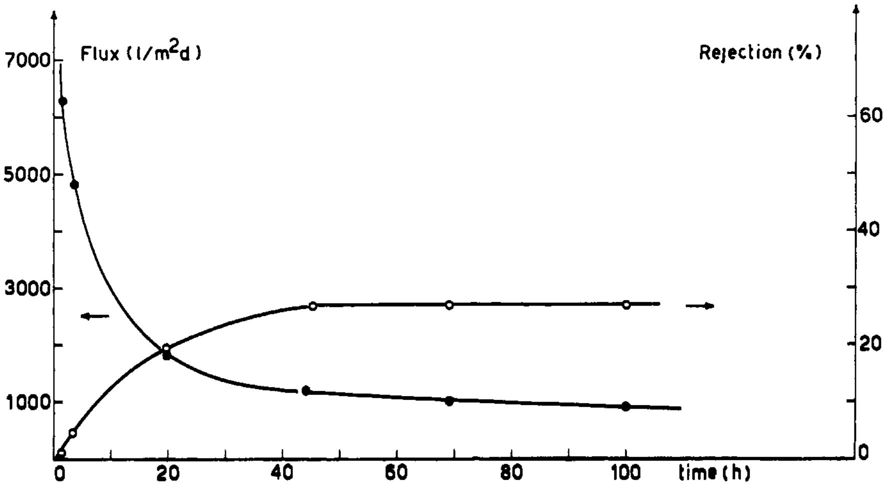

Fig. 10. Salt rejection R% (right) and water flux (left) vs. test time.

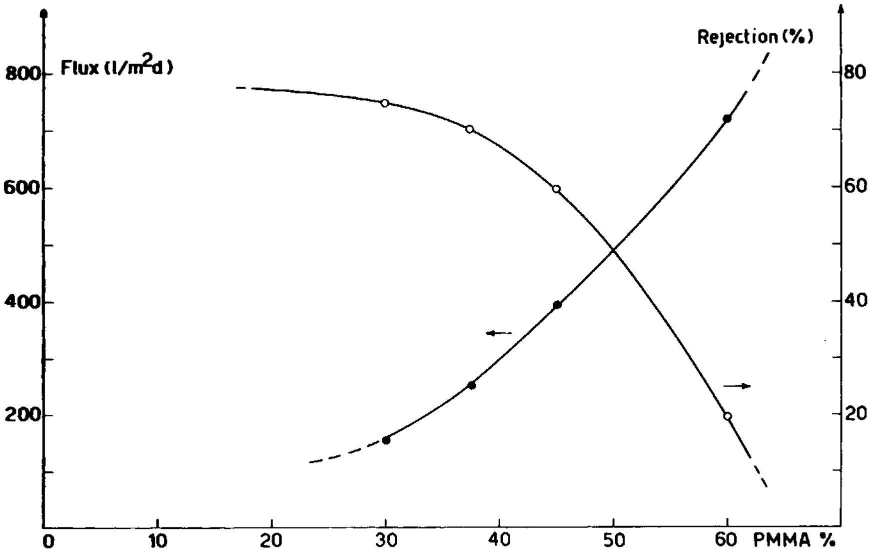

Fig. 11. Water flux F and salt rejection vs. PMMA percentage in the PTFE emulsion.

TABLE II
Rejection and Flux of Asymmetric Membranes

Film no.	*R*	*F*
157	85	84
158	90	98

creases for porous films. The porosity is obtained either by increasing the particle diameter or by using the PMMA technique. We have consequently taken into account the possibility of using these two ways for making an asymmetric membrane, consisting of a very thin layer cast onto a porous support.

With this aim, Ugine Kuhlman has prepared two kinds of asymmetric films, one obtained with a dense layer on a PTFE film sintered from large particles (homogeneous type), and the other by casting the thin layer onto PTFE/PMMA porous films ("heterogeneous" type).

"Homogeneous" Membranes

In order to obtain this type of membrane, the PTFE film was made by casting a thin layer of 0.1-μ-diameter particles onto a support of 0.4-μ-diameter particles. The particles had in all cases a spherical shape. In one case (film no. 157), the thickness of the dense layer was 0.5 μ and that of the porous layer, 14 μ; and in the second case (film no. 158), the thicknesses were 1 μ and 11 μ, respectively.

These films were transformed into membranes by the usual technique and were tested for hyperfiltration under standard conditions (70 atm and 10,000 ppm NaCl). The "dense" layer was always in contact with the feed solution. The results are reported in Table II and show no remarkable change in the mean "symmetric" membrane performances.

The only comment is that in the case of film no. 158, rejection and water permeability are typical of a membrane having as its thickness the sum of the thicknesses of the two layers, whereas in the case of film no. 157, the rejection is slightly smaller, probably due to defects in thin layer.

"Heterogeneous" Membranes

This kind of film was obtained by casting a layer of "stick" particles (0.3 × 0.2 μ size) having a thickness ranging between 0.2 and 2.1 μ onto a porous PTFE/PMMA support.

Unfortunately, the membranes, probably due to defects in the dense layer, possessed the support characteristics.

DISCUSSION AND CONCLUSIONS

On the basis of the experimental results, we are able to answer the question of whether or not the emulsion particle size distribution affects the characteristics of PTFE films obtained by the baking technique and thus the performances of the hyperfiltration membranes derived from them.

To get such results, grafting and sulfonation conditions were maintained rigorously constant and equal to those used for obtaining the previous membranes.[2] In this manner, we think we have ascertained that small particle size leads to high salt rejection–low water permeability membranes and vice versa for large particles. It is difficult to state the true reasons of such behavior, but it can be intuitively related to the voids between the film-forming particles.

The shape of particles itself influences the membrane performances, and this is probably related to the capacity of the particles to arrange themselves in an ordered and compact structure.

Actually, observing the different shapes of the particles examined, one can note that the "sticks" can be arranged in a more ordered manner, similarly to bricks. On the other hand, the tendency of forming ordered fibers has been also encountered in the dry PTFE powder, usually as a result of electrical and mechanical causes.

From the particle size distribution, it is thus possible to predict membrane properties and build up the desired hyperfiltration performances. This can be reasonably applied to electrodialysis properties and others, though it was not investigated in the present paper.

It is, for instance, possible to predict that a membrane having about 3 μ overall thickness, made with stick particles of 0.01 μ^2 cross section having 30% of grafted styrene and 3% of DVB, should represent the best rejection–flux compromise.

We were not successful in transferring the properties of the stick particle film to a film obtained from spherical particles by the simple technique of making the film from mixtures of the two emulsions. This is explained considering that the random mixture of different-shape particles leads to a more disordered structure.

The behavior of membranes obtained both from fiber-like particles (film no. 138) and from PTFE/PMMA mixtures is peculiar and shows high water permeability but poor rejection; furthermore, they exhibit a dramatic compaction under pressure, resulting in flux reduction. The results show that under pressure the membrane undergoes an elastic deformation, and this happens especially at high PMMA contents.

The crosslinking does not affect in any substantial manner the properties of the membranes having spherical and stick particles; on the contrary, it is highly effective in the case of film no. 138 made from fiber-like particles.

It is reasonable to relate this fact to the shape of the "fibers" which, being grafted without DVB, are allowed to maintain a certain independence, similar to the ungrafted film; the DVB addition produces something like polymeric "bridges" between them, which hinder any displacement and keep them close together. This can be supported also by the time–compaction curve, which shows a more "rigid" behavior.

Quite unexpected is the failure of the asymmetric membrane utilizing the PTFE/PMMA support. This fact can nevertheless be explained in terms of (a) mechanical deformation under pressure of the thin layer, due to the rather large pores of the underlying support, with following bursting; (b) destruction or damaging of the thin layer during the baking of the film, due to

PMMA decomposition; (c) defective casting of the thin layer, which, it must be remembered, was made with 0.3 × 0.2 μ particles.

In conclusion, a way to get high rejection and water permeability seems to be to make asymmetric films with the same particle shape, cast with (a) a dense layer of thickness between 0.5 and 1 μ, and (b) a porous support made of PTFE particles of about 1 μ. This does not exclude the use of a heterogeneous support, when some modifications are needed.

We consider very useful for a better understanding an investigation in the following directions: (a) electron microscope study of the membranes, in order to verify their structure and structure changes after grafting and sulfonation; (b) porosity measurement by means of free-water diffusion or by any other technique. We are working on this and hope to be able to report soon on our results.

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