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Scanning Electron Microscopic Study of Microporous Silicone Rubber Membranes for Possible Use in Oxygenators

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ABSTRACT

Microporous membranes were fabricated with Silastic-445 (from Dow Corning of Canada Limited) by using Luperco CST (L-CST) as catalyst and a perchlorate micropore producing additive (MPPA). Gas permeability, percent elongation, and tensile strength data show that membranes prepared with MPPA have high gas transmission rates, high percent elongation, and sufficient mechanical resistance. Scanning electron microscopic analyses reveal that the microporous silicone membranes prepared with a medium concentration of MPPA yield uniform pore distribution, the maximum pore size being $<4\ \mu m$.

INTRODUCTION

Studies [1-35] related to short- and long-term extracorporeal circulation of blood for temporary support of patients suffering from respiratory diseases have revealed that many of the problems encountered in the present-day heart-lung machines can be overcome with the use of membrane oxygenators as these avoid the complications

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of a blood-gas interface thereby reducing the occurrence of fat emboli, microembolic insults, damage to blood proteins [4] and lipoproteins [18].

Clowes [1] was the first to employ an artificial membrane lung as a clinical cardio-pulmonary by-pass. Since then, a number of long-term extracorporeal perfusions in man have been reported, the longest lasting two weeks [19]. In spite of these positive results, the application of membrane lungs is limited due, primarily, to certain shortcomings in the man-made membranes available.

In order to discover the ideal material for the fabrication of membranes, many polymeric substances, viz., polyethylene [3], Teflon [2, 7, 8, 12, 22], other fluoropolymers [25, 28, 33, 34], silicone rubber [10, 14, 16, 20, 29], and even synthetic paper impregnated with silicone [17], have been studied; however, until now, no biocompatible polymeric membrane has been found which can mimic the function of the alveolar membrane within the human lung.

The ideal artificial membrane must be thin, mechanically strong, free from pinholes, nonreactive towards blood, have a high dielectric constant and high gas permeability. Of all the polymeric membranes tested, those fabricated from silicone rubber meet some of the required criteria. It has a considerably higher permeability value for oxygen than most of the permeable nonsilicone plastics. Furthermore, it permits selective transfer of carbon dioxide and allows the diffusion of up to six to eight times (in a gas to gas exchanger) more carbon dioxide than oxygen. Besides having these properties, silicone rubber is also relatively inert. Nevertheless, its treatment with thromboresistant materials [11, 13, 21, 23-27] has been advocated in order to make the exchange membranes better adaptable for use in the human body, i. e., the development of nonthrombogenic blood-compatible membranes which minimize possible damage to proteins and minimize also deposits on the membrane surfaces of cellular materials present in blood.

The principal drawback with thin silicone rubber membranes which have high gas transmission rates is the lack of mechanical strength to withstand high pressure differences. Thick silicone membranes which possess the desired strength do not, however, have the required gas transmission rates. The problem of low mechanical resistance in thin silicone membranes may be corrected by the use of a support material [28, 32, 34], but this introduces other problems, such as pinholes.

There is yet another way of obtaining high gas transmission rates in membranes which have sufficient mechanical strength, obtained through additional thickness; this involves the fabrication of microporous membranes. Such membranes will require less surface for a given gas exchange and consequently a smaller "priming volume". During the last five years, two oxygenators have been built specifically to adapt to microporous membranes [30, 31]; however, the materials used to fabricate the microporous membranes have been restricted so far to polypropylene-supported polymers [33, 34] and Teflon [8, 22] because of the biocompatibility problems.

Keeping these latest developments in mind, it was thought of prime interest to fabricate microporous silicone rubber membranes and to determine their gas transmission rates, mechanical strength, and biocompatibility. Results of a part of this work form the subject of the present communication and are outlined in the following paragraphs.

EXPERIMENTAL

Materials

Polyphenyldimethylsiloxane containing 18.5% silica (Dow-Corning's Silastic 445), polyvinyldimethylsiloxane containing 22% silica (D-C's Silastic 436) and polyvinyldimethylsiloxane containing 15% silica (D-C's Silastic 740) were generously provided by Dow Corning of Canada Limited.

Membrane Preparation

Preparation

Several grams of each Silastic were cut into small pieces and left to soak overnight in a good solvent. The resulting gel was homogenized with a mechanical stirrer, and the volume of the resulting solution was adjusted by evaporation prior to adding two other solvents which brought the Silastic concentration to its critical value and rendered the solution more apt to dissolving larger amounts of MPPA [35]. Luperco CST (L-CST), a specially formulated catalyst containing 2,4-dichlorobenzoyl peroxide, was then added to the solution with vigorous stirring. In order to obtain microporous membranes, various quantities of MPPA were dissolved in a solvent and finally blended into the solution. The resulting solution was clarified by centrifugation.

Casting of the cleared Silastic solutions was done in polytetrafluoroethylene-coated aluminum pans where the thickness of the membranes could be controlled at will. Following the casting process, the solvents were removed by evaporation and the remaining silastic membranes were vulcanized during several minutes. After this, the micropore producing additive was removed from the membranes by leaching for about 1 hr, after which they were air-dried and made ready for characterization.

Characterization of the Membranes

All of the membranes discussed in this study were subjected to the following sequence of tests.

Pinhole Testing. Each membrane was fixed between two horizontal plates, the top plate of which had a 5 cm hole covered with a fine stainless steel screen over which water was poured to a depth of 5 mm to cover the membrane completely. Air under pressure was introduced through the bottom plate under the membrane. When there were pinholes in a membrane, air jets were seen to flow through the screen at fixed locations. If pinholes were detected, no further testing was carried out. The membrane was simply discarded.

Gas Permeability Values. Gas permeability values of the membranes were determined with a volumetric cell according to ASTM method D1434-66 [6] involving Eq. (1):

$$V = P_r \Delta pst/d \tag{1}$$

where V is the volume of gas (ml) flowing through the membrane in time t (sec); P_r is the gas permeability of the membrane expressed in (ml-cm)/(sec-cm^2-cm Hg); Δp is the pressure differential across the membrane in (cm Hg); s is the surface (cm^2) exposed to gas transfer; and d is the thickness of the membrane as measured (in cm) with sliding calipers (Chesterman model 369) equipped with a Mitutoyo dial indicator having a precision of ± 0.00025 cm.

Mechanical Properties. Percent elongation defined as 100 $\Delta L/L$, L being the initial length and ΔL the increase in length at the point of rupture, and tensile strength of the membranes expressed in kPa were measured with an Instron universal testing instrument (model 1130), at a drawing rate of 2 cm/min.

Pore Size and Distribution. A scanning electron microscope, the Cambridge Model S-150 instrument, was used to study the distribution of pore sizes in the fabricated membranes.

RESULTS AND DISCUSSION

In Table 1 are summarized data showing the influence of temperature and time of vulcanization on the gas permeability, the percent elongation, and the tensile strength of nonmicroporous membranes fabricated with D-C Silastic-445 with the use of 4% L-CST. On increasing the temperature of vulcanization from 388 to 458°K while maintaining the same time of vulcanization, the gas permeability values for CO_2 as well as O_2 decreased, as did the percent elongation and the tensile strength of all of the membranes studied. With a fixed temperature, varying the time of vulcanization sixfold resulted in a decrease in the percent elongation of the membranes and in their

TABLE 1. Influence of Temperature and Time of Vulcanization on the Permeability, Percent Elongation and Mechanical Properties of Nonmicroporous Membranes[a]

	Vulcanization conditions		Gas permeability (barrer)[b]		Mechanical properties	
[Silastic]$_0$ concn	Temperature (°K)	Time (min)	CO_2	O_2	Elongation at break (%)	Tensile strength (kPa)
Low	388	30	3945	800	540	3240
Low	418	30	3890	745	430	2180
Low	458	30	3820	640	395	2325
Low	418	10	4025	760	500	3650
Low	418	60	3985	770	385	2030
Medium	418	30	3740	600	540	4270

[a] Membranes fabricated with Silastic-445 using 4% of L-CST but no other additives.
[b] 1 barrer = 1×10^{-10} ml cm/sec cm^2 cm Hg.

TABLE 2. Influence of Catalyst Concentration on the Properties of Nonmicroporous Membranes

			Mechanical properties	
Silastic type	Luperco CST (wt %)	CO_2 permeability (barrer)	Elongation at break (%)	Tensile strength (kPa)
445	2	3930	745	3290
445	4	4080	490	2845
445	7	3875	380	2690
445	12	3985	230	2180
445	20	4190	230	1990
740	4	5170	320	1320
436	7	4720	360	2290

tensile strength; however, their capacity to permeate CO_2 and O_2 did not change. With fixed temperature and time of vulcanization conditions, increasing the weight proportion of Silastic by 25% increased the percent elongation and tensile strength of the membranes but decreased their CO_2 and O_2 permeabilities.

In Table 2 are presented results showing the influence of catalyst concentration on the properties of nonmicroporous silicone membranes. In the case of membranes cast from Silastic-445 solutions, increasing the L-CST from 2 to 20% by weight resulted in a decrease of the percent elongation and tensile strength of the membranes; their permeability to CO_2, however, changed little. On replacing Silastic-445 (18.5% silica) by Silastic-436 (22% silica) or Silastic-740 (15% silica) as the basic material, the permeability of the membranes to CO_2 increased slightly, though their percent elongation and tensile strength decreased slightly. Because of the above results, Silastic-445 was retained as the more appropriate material for further tests. Furthermore, despite the fact that membranes fabricated with only 2% L-CST showed better characteristics, values of 4 and 7% L-CST were retained for subsequent studies, as it was shown that membranes prepared with only 2% of L-CST had low burst strength [29].

In Table 3 are presented some of the properties of microporous membranes fabricated in the present study. The results are compared with data obtained with other types of nonmicroporous membranes. Furthermore, Table 3 also contains data on the surface characterization of the membranes in terms of pore sizes and distributions as obtained from scanning electron microscope photographs shown in Figs. 1-10.

TABLE 3. Properties of Membranes Fabricated under Different Reaction Conditions

Membrane material	Particular fabrication conditions	Membrane thickness (μm)	Gas transmission rate (GTR × 10^{-3})^a		Mechanical properties		Surface characteristics
			of CO_2	of O_2	Elongation at break (%)	Tensile strength (kPa)	
Polydimethylsiloxane [33]	Dow Corning Silastic (reinforced)	190	1110	-	-	-	Nonmicroporous
Poly(carbonate-dimethylsiloxane) [33, 34]	MEM-213 General Electric	50	1275	210	450	18000	Continuous nonmicroporous
Polyalkylsulfone [33]	Propylene supported	25	6625	1585	-	-	Continuous film on porous material
Silastic-445	No additives	100	2680	490	490	2845	Continuous nonmicroporous (Fig. 1)
Silastic-445	Low MPPA Concn	125	2625	645	530	2845	Microporous (Figs. 2, 3, 4) 35% pores 1.0 μm 65% pores 2.5 ± 0.2 μm Uniform distribution
Silastic-445	Medium MPPA Concn	100	44,300	34,100	380	2550	Microporous 65% pores 0.7 ± 0.1 μm 35% pores 3.0 ± 0.5 μm (Fig. 5, Fig. 6, Fig. 7) Uniform distribution

(continued)

TABLE 3 (continued)

Membrane material	Particular fabrication conditions	Membrane thickness (μm)	Gas transmission rate (GTR $\times 10^{-3}$)[a]		Mechanical properties		Surface characteristics
			of CO_2	of O_2	Elongation at break (%)	Tensile strength (kPa)	
Silastic-445	High MPAA concn	75	61,500	55,500	375	2060	Nonuniform distribution of pores of irregular size Maximum pore size > 7 μm (Figs. 8, 9, 10)
Silastic-445	Very high MPAA concn	90	68,400	56,900	360	2060	Irregular pore-size Nonuniform distribution

[a] GTR = 1 cm^3/24 hr-m^2-atm.

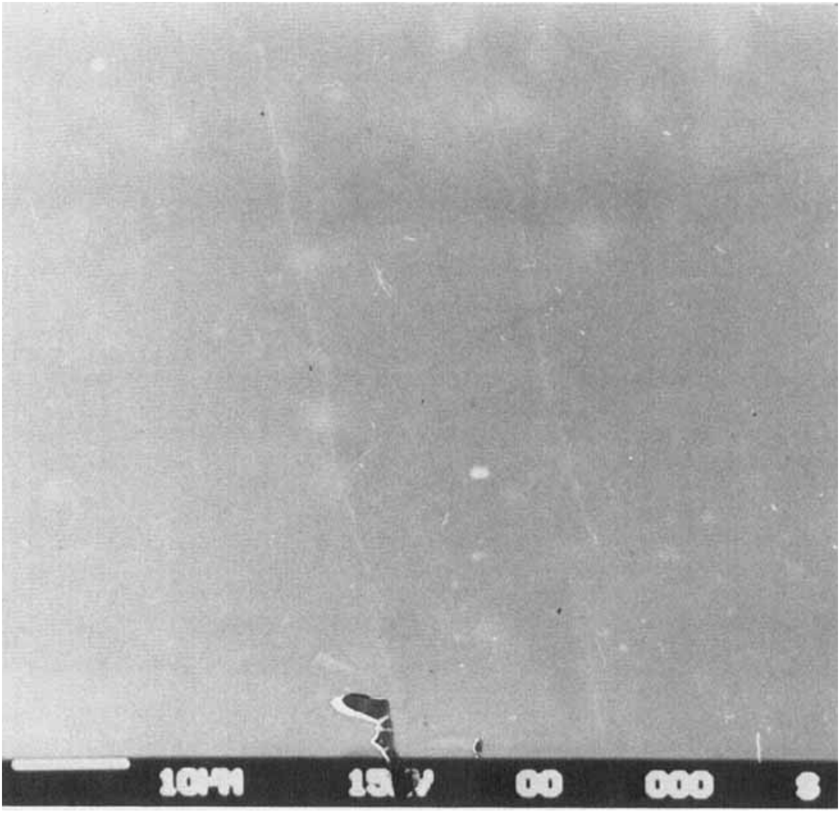

FIG. 1. Scanning electron microscope photograph of a nonmicroporous membrane cast from Silastic-445. Magnifying factor: 2000.

An analysis of the gas transmission rate data given in Table 3 shows that Silastic-445 based microporous membranes fabricated with the addition of medium and high concentrations of MPPA allow 20 to 100 times as much CO_2 and O_2 to pass as do most nonmicroporous membranes fabricated from polyalkylsulfones or the thin poly-(carbonate-dimethylsiloxane) membranes. Moreover, the gas transmission rates of these relatively thick and sturdy Silastic-based microporous membranes are superior by far (10 times or more) to those of the ultra-thin membranes. The gas transmission rate of Silastic-based membranes increases with increasing concentration of MPPA. At high concentrations of this additive, the CO_2 gas transmission rate reaches a maximum value of 6.84×10^7 GTR (see Table 3).

The scanning electron microscope analysis of L-CST-catalyzed membranes prepared with (Figs. 2-10) and without (Fig. 1) the MPPA

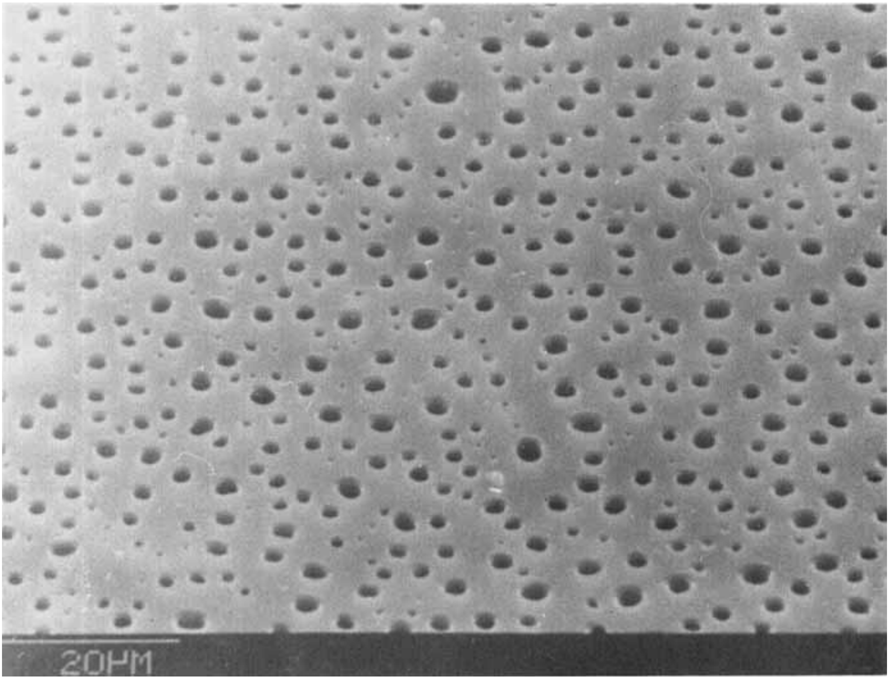

FIG. 2. Scanning electron microscope photograph of the front side of a microporous membrane cast from Silastic-445 at a low concentration of MPPA. Magnifying factor: 1000.

showed that in the latter case the membranes are nonmicroporous, while in the former they are fully microporous.

Microporous membranes prepared with a low concentration of MPPA had uniform pore distributions (Figs. 2-4) with a density of about 4×10^6 pores/cm^2. Furthermore, 35% of the pores had diameters of about 1 μm and 65% about 2.5 ± 0.2 μm. Despite the high pore density observed, the low gas transmission rates (see Table 3) of these membranes indicate that some if not many of the pores do not pass from one side of the membrane to the other. Microporous membranes prepared with a medium concentration of MPPA (Figs. 5-7) showed uniform pore-size distributions, 65% had diameters of 0.7 ± 0.1 μm and 35%, 3.0 ± 0.5 μm (Fig. 6). The pore density of these membranes was calculated at 4.8×10^6 pores/cm^2 including pores of all sizes. If one considers only those pores having a diameter of 3.0 ± 0.5 μm, i. e., those which contribute most towards gas flow, a pore density of 1.7×10^6 pores/cm^2 is obtained (Fig. 5). It would appear that as one increases the concentration of MPPA

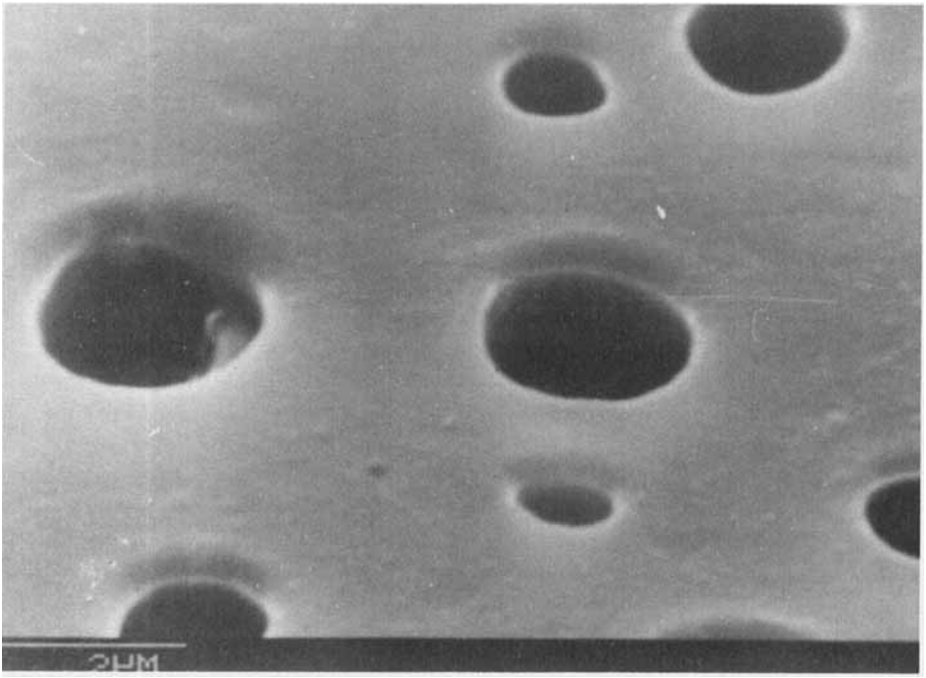

FIG. 3. Scanning electron microscope photograph of the front side of a microporous membrane cast from Silastic-445 at a low concentration of MPPA. Magnifying factor: 10,000.

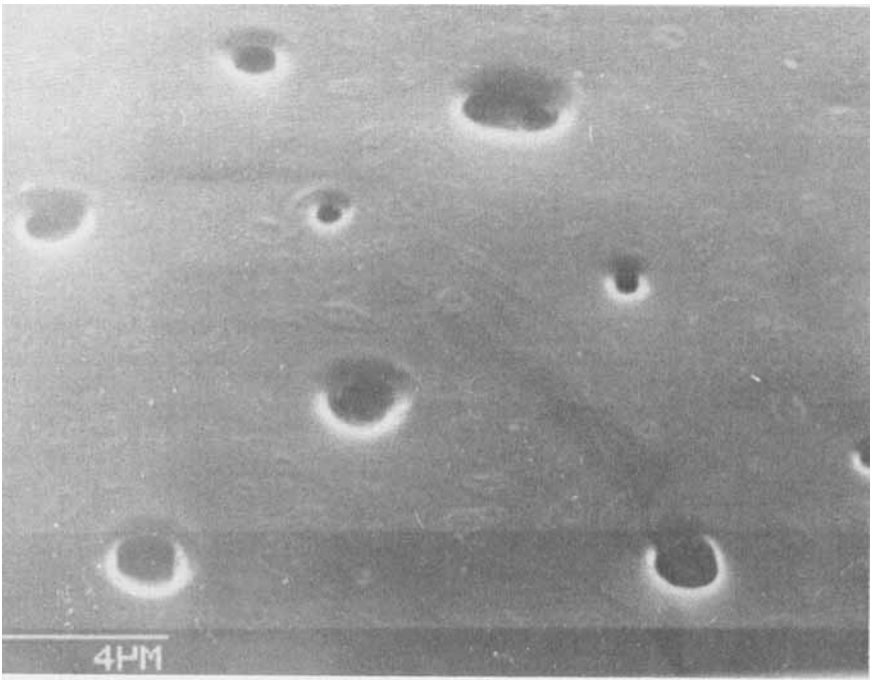

FIG. 4. Scanning electron microscope photograph of the rear side of a microporous membrane cast from Silastic-445 at a low concentration of MPPA. Magnifying factor: 5,000.

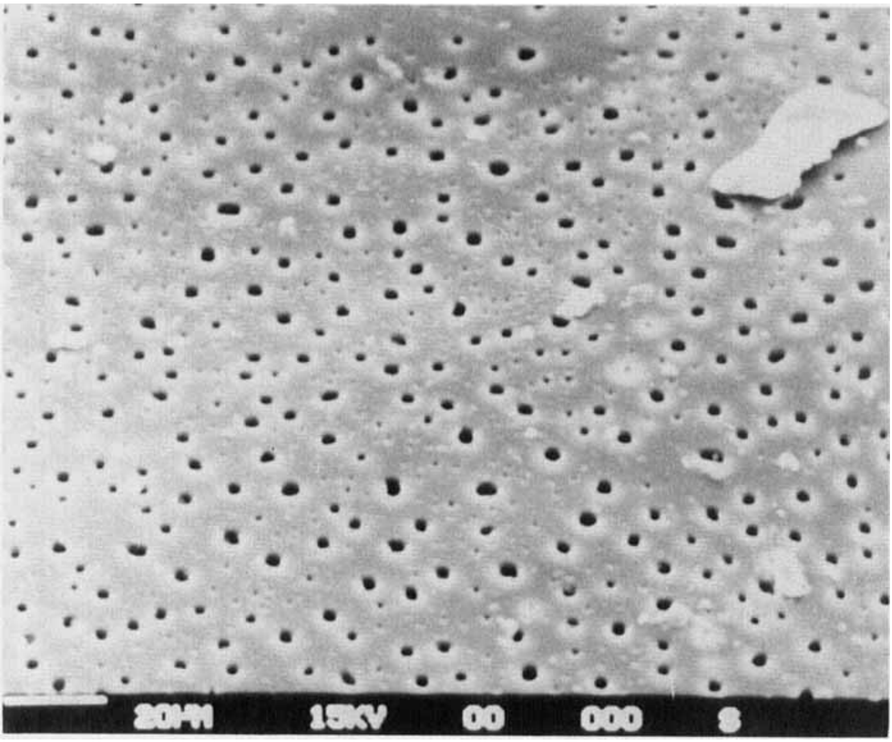

FIG. 5. Scanning electron microscope photograph of the front side of a microporous membrane cast from Silastic-445 at a medium concentration of MPPA. Magnifying factor: 1000.

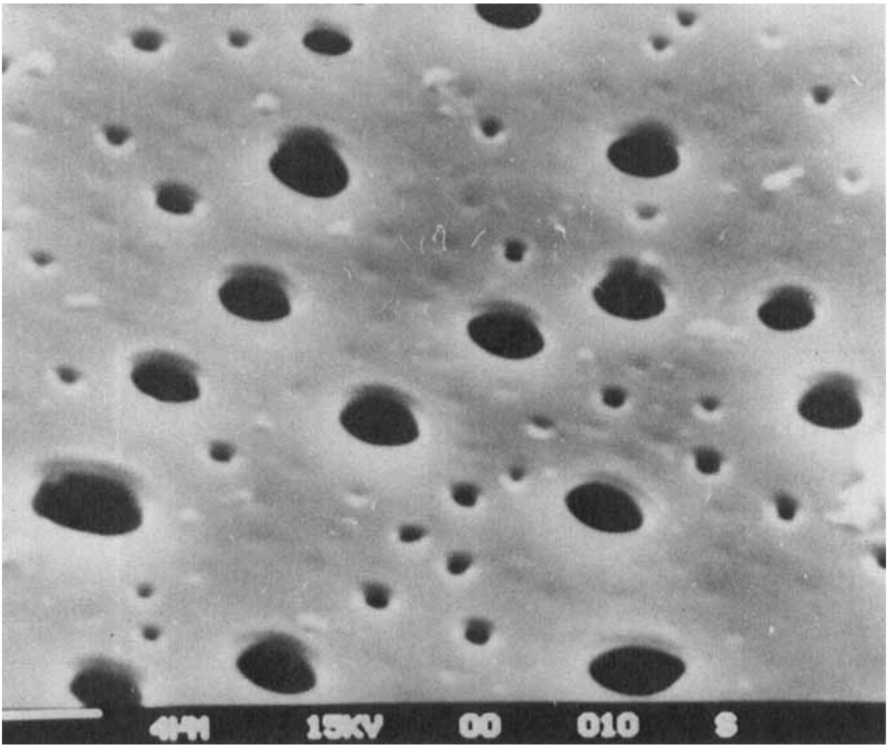

FIG. 6. Scanning electron microscope photograph of the front side of a microporous membrane cast from Silastic-445 at a medium concentration of MPPA. Magnifying factor: 5000.

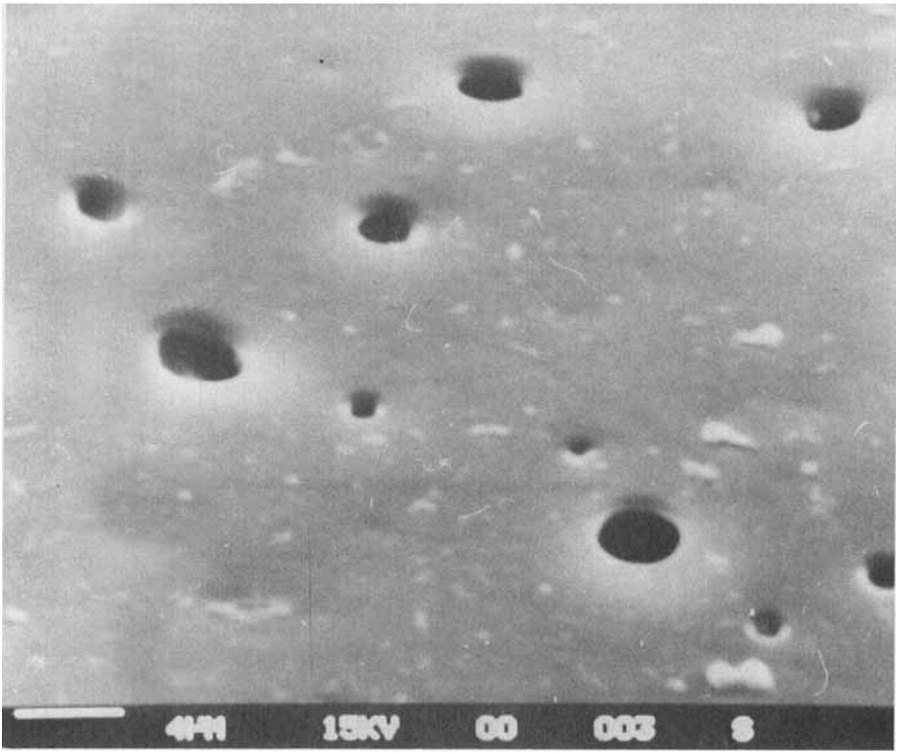

FIG. 7. Scanning electron microscope photograph of the rear side of a microporous membrane cast from Silastic-445 at a medium concentration of MPPA. Magnifying factor: 5000.

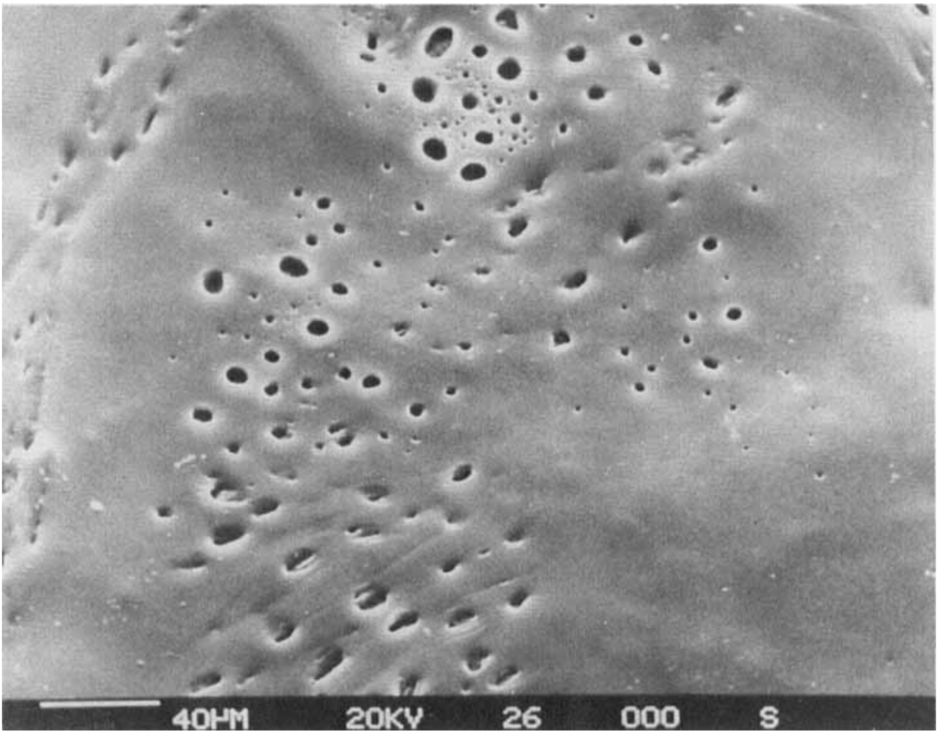

FIG. 8. Scanning electron microscope photograph of the front side of a microporous membrane cast from Silastic-445 at a high concentration of MPPA. Magnifying factor: 500.

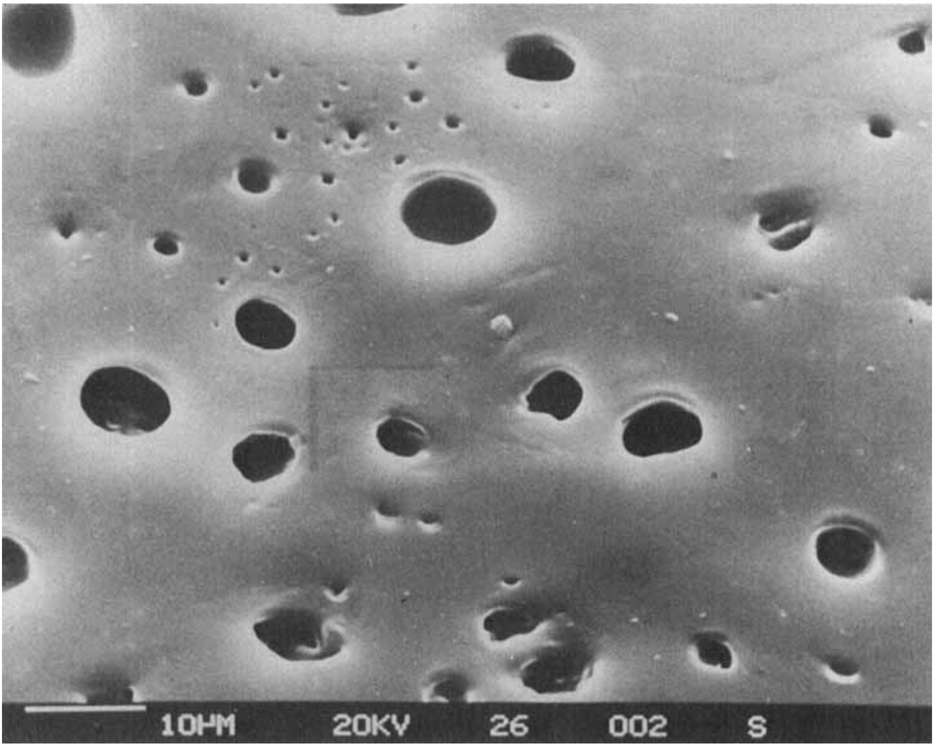

FIG. 9. Scanning electron microscope photograph of the front side of a microporous membrane cast from Silastic-445 at a high concentration of MPPA. Magnifying factor: 2000.

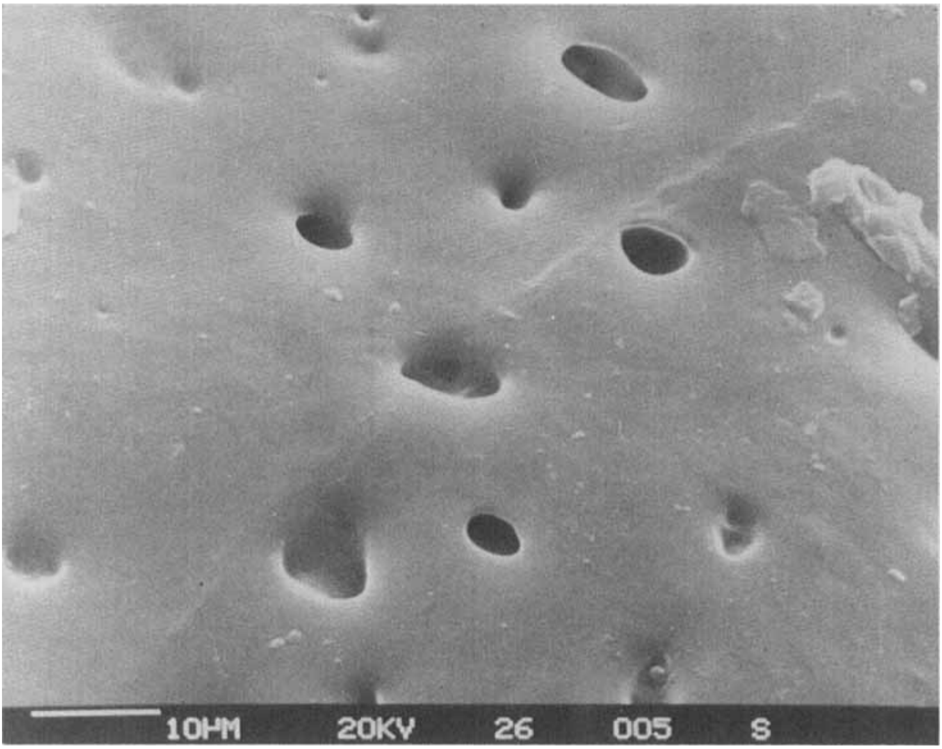

FIG. 10. Scanning electron microscope photograph of the rear side of a microporous membrane cast from Silastic-445 at a high concentration of MPPA. Magnifying factor: 2000.

threefold, the overall pore density in the membranes increases from 4.0 to 10^6 to 4.8×10^6 pores/cm^2.

Microporous membranes fabricated with a high concentration of MPPA (Figs. 8-10) showed nonuniform pore size distributions, some exceeding 7 μm in certain cases (Fig. 9). The properties of all of the membranes prepared with the higher concentrations of MPPA did not comply with the limits established for microporosity, namely a maximum diameter of 5.0 ± 0.5 μm.

In conclusion, the above study clearly indicates that it is with medium concentrations of MPPA that one obtains membranes with uniform micropore distributions, high gas transmission rates, and sufficient mechanical resistance.

Further studies relating to biocompatibility and preparation of membranes from other materials and their characterization are in progress. The results will be reported on in due course.

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