

The resistance towards gas transport of the sublayer of asymmetric PPO hollow fiber membranes determined by plasma-etching

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Abstract

Plasma-etching is a powerful tool in the determination of the resistance of the sublayer of skinned asymmetric hollow fiber membranes of poly(2,6-dimethyl-1,4-phenylene oxide). Using a resistance model and data provided by etched hollow PPO fiber membranes it is possible to predict the ultimate selectivity of the total membrane for helium over nitrogen and oxygen over nitrogen. From this model and from permeability measurements it is shown that the gas resistance of the sublayer of asymmetric membranes with a selective layer has a large effect on the ultimate overall selectivity of the membranes. In order to improve the membrane performance the resistance of the sublayer has to be minimized. Etching experiments were performed on hollow fiber membranes spun from PPO-types with different intrinsic viscosities. The resistance of the sublayer decreased markedly with increasing intrinsic viscosity of the PPO. To a lesser extent the membrane preparation (the length of the air gap) influences the gas resistance of the sublayer.

Keywords: membrane preparation and structure; hollow-fiber membranes; gas and vapor permeation; gas separations; poly(2,6-dimethyl-1,4-phenylene oxide); plasma etching

Introduction

Until recently the production of high flux asymmetric hollow fiber membranes for gas separation with high selectivity in a single step process was not possible on a commercial scale due to the presence of small imperfections in the separating layer. At the Plastics and Rubber Research Institute of TNO [1–3] as well as at the University of Twente [4] spinning procedures have been developed which overcome this problem. TNO has developed asymmetric hollow fiber membranes of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by means of a dry-wet spinning process.

However, in some applications the selectivity of the hollow fiber membranes will be decreased as a consequence of the resistance of the sublayer towards gas transport. The effect of the resistance gets more pronounced on reducing the skin thickness in combination with a high flux. This effect has been described with resistance models by Henis and Tripodi [5] for skinned asymmetric membranes and Pinnau et al. [6] for composite membranes. According to Cuperus, Bargeman and Smolders [7] PPO-membranes of the latter type can be considered as membranes consisting of two distinct layers: the sublayer and the compact top layer, which is gas selective.

If these layers are thought of as two separate resistances in series, a simple equation can be found [6]:

$$R_{\text{total}} = R_1 + R_2 \quad (1)$$

In this equation the resistance R represents the ratio of the layer thickness d of the selective layer (1) or the sublayer (2) and the corresponding permeability P_1 respectively P_2 . Thus eqn. (1) can be rewritten as:

$$\frac{d_{\text{total}}}{P_{\text{total}}} = \frac{d_1}{P_1} + \frac{d_2}{P_2} \quad (2)$$

The selectivity of these two-layered membranes for gas a over gas b ($\alpha^{a/b}$) depends on the permeabilities (P) and thicknesses (d) as follows [6]:

$$\alpha^{a/b} = \frac{d_1/P_1^b + d_2/P_2^b}{d_1/P_1^a + d_2/P_2^a} \quad (3)$$

For the permeabilities and the selectivities limiting values can be found if one of the resistances is much larger than the other one:

$$\frac{d_i}{P_i} \gg \frac{d_j}{P_j} \xrightarrow{(2)} \frac{d_{\text{total}}}{P_{\text{total}}} = \frac{d_i}{P_i} \quad (4)$$

$$\xrightarrow{(3)} \alpha^{a/b} = \frac{d_i/P_i^b}{d_i/P_i^a} = \frac{P_i^a}{P_i^b} \quad (5)$$

If the resistance of the compact top layer dominates, the selectivity and the resistance of the total membrane will equal the intrinsic selectivity of the membrane material (for PPO: $\alpha^{\text{He}/\text{N}_2} = 35$ and $\alpha^{\text{O}_2/\text{N}_2} = 5$) respectively the ratio of the actual compact layer thickness and the actual PPO permeability. In the other case (high sublayer resistance) the total membrane selectivity and the resistance are determined by Poiseuille or Knudsen flows.

In order to improve the performance of the membrane by reducing the resistance of the sublayer, a method has to be found to characterize the gas permeability of the sublayer (P_2). The properties of the sublayer in composite membranes can be determined directly by gas permeability measurements of the support in contrast to skinned asymmetric membranes. In an asymmetric

membrane, like the hollow fiber membranes used in this study, the porous support and the selective top layer are formed simultaneously in a single step. Measurements on a membrane without the gas selective layer, produced by changing the spinning conditions, are questionable since it is likely that the properties of the support of these membranes will differ from those of skinned membranes. Therefore a method for determining the gas resistance of the sublayer of hollow PPO fiber membranes has been adapted and applied to PPO-membranes at TNO.

It was found [8–12] that highly reactive particles from a gas plasma can remove or etch a surface very gradually. Van 't Hoff et al. [8] and Fritsche et al. [10,11] performed etching experiments with oxygen plasma on polyethersulfone gas separation hollow fiber membranes and on asymmetric polysulfone hollow fibers, respectively. They showed that it was possible to determine the sublayer resistance after etching the fibers.

In this paper we show the results of plasma-etching experiments on hollow PPO fiber membranes. Using the resistance model and data provided by etched hollow PPO fiber membranes we show the correlation between the data on the ultimate selectivity of the total membrane for helium over nitrogen and oxygen over nitrogen provided by the model and actual data.

Experimental

Materials

PPO resins were synthesized from 2,6-dimethylphenol with copper (I) chloride/pyridin catalyst [13,14]. From these syntheses we obtained several batches of PPO with different intrinsic viscosities (1.10, 1.15, 1.20, 1.35 dl/g, determined in chloroform at 25 °C). Also PPO resin was supplied by General Electric Company with an intrinsic viscosity of 0.7 dl/g. All chemicals for spinning hollow fibers [trichloroethylene (solvent, Biesterveld), methanol (non-solvent, UCB) and 2-ethyl-1-hexanol (non-solvent, Fluka)] were used as received with the exception of ethanol (nonsolvent, Merck) which was degassed before use. Oxygen (Air Products) with a purity of 99.5%, was used to obtain an etching plasma. For permeability experiments pure gases, nitrogen, oxygen and helium (Air Products) were used.

Apparatus

Hollow fibers were spun by a dry-wet spinning process described by Albers and Greidanus [1] and by Smid, Albers and Kusters [3]. A spinning solution of PPO, trichloroethylene and ethyl-hexanol was spun through a tube-in-orifice-type spinnerette via an air gap in the coagulant methanol. Ethanol was used as bore liquid. Fibers were rinsed in methanol and subsequently dried in air. The outer diameter and the wall thickness of the fibers were 650 and 60 μm , respectively. By changing the length of the airgap it was possible to control

the ultimate thickness of the compact toplayer on the outside of the hollow fibers.

Permeability experiments were carried out on single hollow fibers with pure gases [3]. The fibers were pressurized from the outside. Gas fluxes could be measured by a thermal massflow meter (Brooks 5850 TR). From the results of the permeability experiments an apparent thickness of the selective toplayer can be calculated as shown by Smid, Albers and Kusters [3]. After correction of this value with the gas resistance of the sublayer the actual thickness can be found. For practical reasons we rather use P/d -values instead of resistance values (d/P).

Plasma etching was performed in a tube-shaped plasma-reactor as shown schematically in Fig. 1. The oxygen plasma was formed inductively by means of a 13.56 MHz radio-frequency generator with variable output power (ENI-ACG-3) coupled with an impedance modifying unit (Astech ATH 50) to minimize the amount of reflected power. For etching experiments 20 W output power was used. A two-stage rotation vacuum pump (Balzer DUO 016B) was connected to the plasma reactor by means of a cold trap (Pink type C). Pressure in the reactor was continuously measured by a membrane manometer (MKS Baratron 222B). Oxygen flow could be controlled by a thermal mass flow meter (MKS PR 3000). At operating conditions the pressure varied between 0.09 and 0.15 Torr. A sample for etching experiments consisted of a few fibers of 100 mm length with a total weight of ca. 0.1 g.

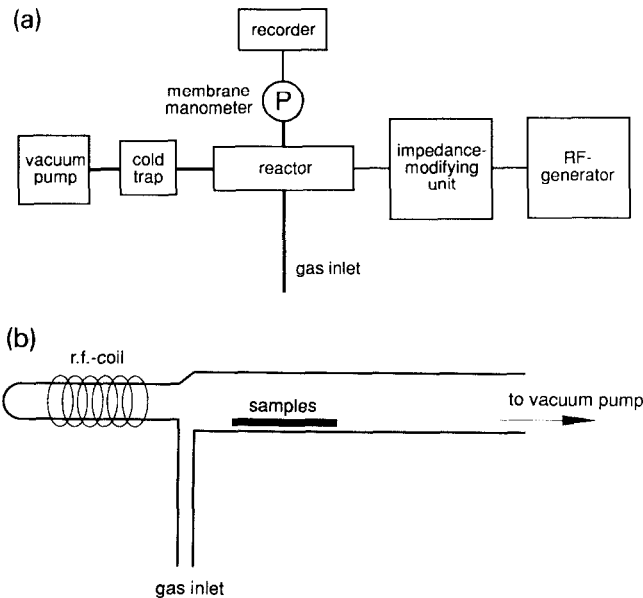


Fig. 1. Schematic drawing of plasma-etching apparatus (a) and plasma reactor (b).

With electronmicroscopy structures of cross-sections and surfaces of the hollow fibers were determined. Samples of these cross-sections were made by swelling hollow fibers in methanol and breaking these fibers in liquid nitrogen. After drying the fibers were coated with gold. X-ray diffraction was performed on hollow PPO fibers and recorded by a Guinier-Johannson camera.

Results and discussion

In Fig. 2 results of etching experiments are shown of hollow fibers which have a compact layer thickness of about $1\ \mu\text{m}$ according to permeability experiments (details of determination of compact layer thickness in [3]). PPO fibers decrease continuously in weight upon etching as can be seen from this figure. After an etching period of ca. 8 min, the loss of weight increases more rapidly due to the transition from the compact toplayer to the porous sublayer.

The etching time corresponding to these transitions is linearly related to the thickness of the compact layer (data obtained with other fibers with different thicknesses of the compact layer). Thus phenomena like chemical reactions or melting of the topmost layer as a consequence of etching by the oxygen plasma can be excluded. Therefore we assume that the intersection point of the two lines in Fig. 2 corresponds with the etching time and the amount of weight loss where the compact toplayer has just vanished.

The gas permeabilities and selectivities of the etched fibers are also monitored (Fig. 3). The selectivities of the fibers for helium over nitrogen decrease rapidly from 33 to 2-3 and the reduced permeability (P/d) of helium increases

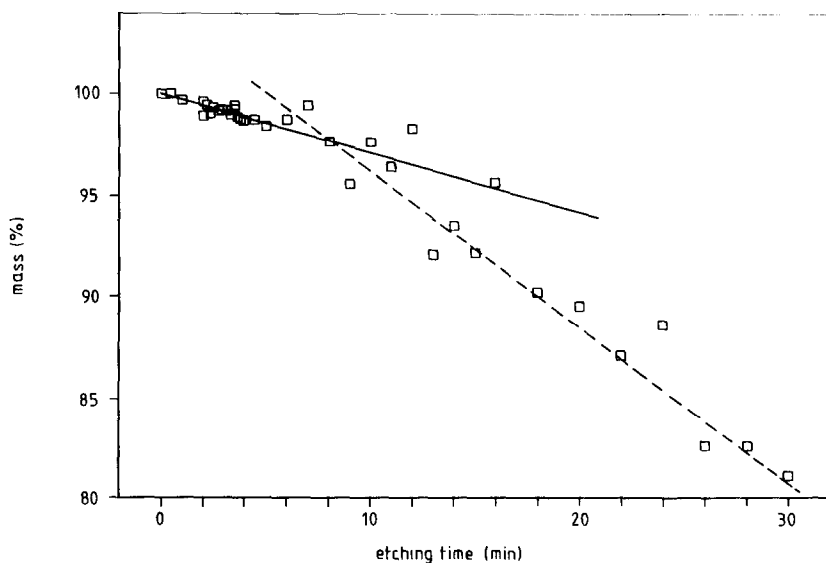


Fig. 2. Weight loss of PPO fibers during etching.

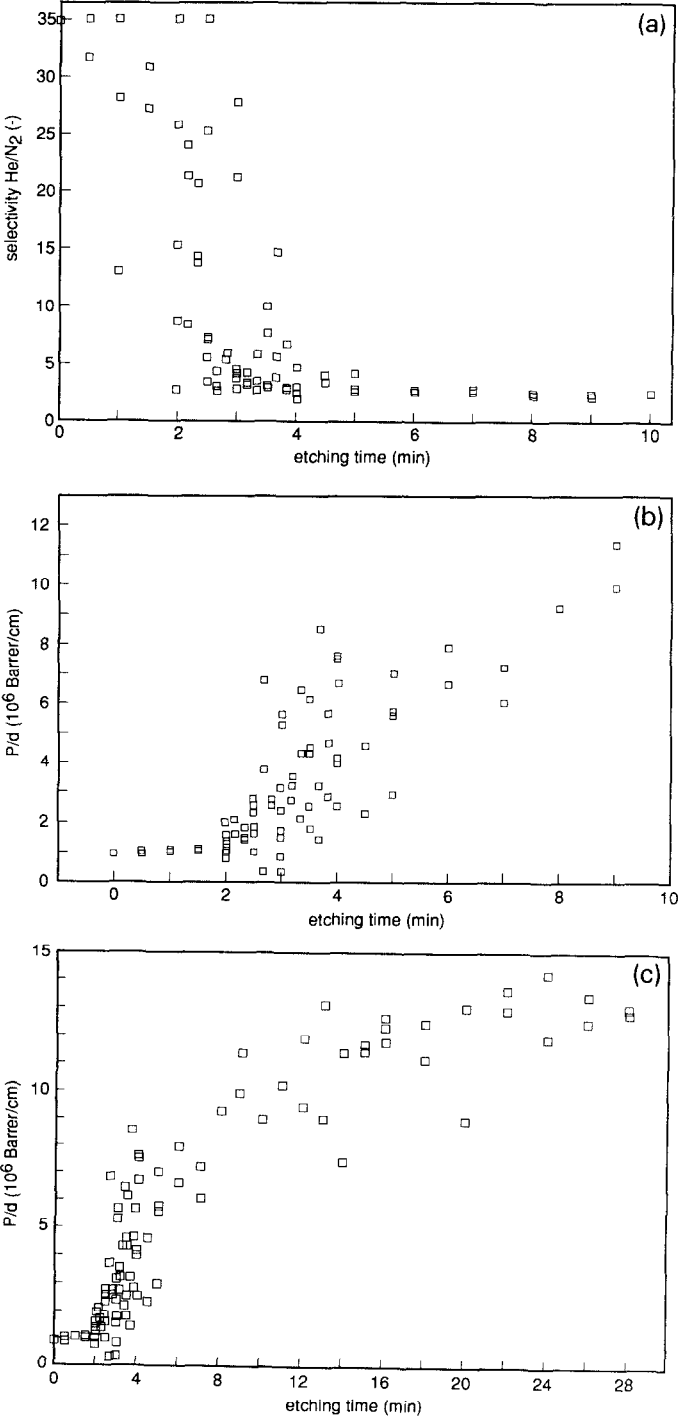


Fig. 3. Selectivity of helium over nitrogen (a) and reduced permeability of helium (P/d) (b and c) as a function of etching time.

upon etching from 0.83×10^6 to 13×10^6 barrer/cm. When the toplayer is completely removed, the reduced permeability reaches a plateau value (Fig. 3(c)). As can be seen from the fluxes and selectivities in Figs. 3(a) and 3(b) the compact toplayer is removed after 2 to 4 min, respectively. However, electronmicrographs (Fig. 4) still show the presence of a compact layer after 4 min of etching (Figure 4(b)), only after prolonged etching periods the toplayer is completely removed (Figs. 4(c) and 4(d)). The latter is in agreement with the results of Fig. 2: only after 8 min of etching the toplayer is completely removed. This indicates that the compact toplayer of the original hollow fibers as shown in electronmicrographs is not entirely homogeneous. As can be seen from the electronmicrographs, the dense layer may consist of two layers: a homogeneous compact layer and a layer, which has pores with dimensions smaller than the resolution of the electronmicroscope (smaller than $0.2 \mu\text{m}$). This corresponds with the etching results of Fritsche et al. [10] on polysulfone fibers. They also suggested that a transitional zone should be present beneath the toplayer.

The plateau of reduced permeabilities reached during etching has a limiting value of 13.2×10^6 barrer/cm for helium (Fig. 3(c)). For oxygen and nitrogen reduced permeabilities of 5.3×10^6 and 5.8×10^6 barrer/cm are found. These reduced permeabilities are assumed to be the reduced permeability of the sublayer (P_2/d_2). The ratios of the reduced permeabilities indicate that Knudsen diffusion will be the main gas transport mechanism through the porous sublayer ($\alpha^{\text{He}/\text{N}_2} = 2.3$, $\alpha^{\text{O}_2/\text{N}_2} = 0.9$). These values have been used in the calculation of the selectivity of the total membrane (eqn. (1)). In the calculations we take the intrinsic permeabilities of PPO for helium, oxygen and nitrogen of 88.1, 13.4 and 2.6 barrer, respectively, as they were measured at 30°C in our laboratory. These values are slightly less in comparison to literature data [15]. This implies that the maximal selectivities of the hollow fiber membranes can be 33.9 for helium over nitrogen and 5.15 for oxygen over nitrogen. The calculated lines are shown in Fig. 5. The calculations are in good agreement with experimental values of the selectivities of skinned hollow fiber membranes. This figure also shows the influence of the sublayer resistance on the selectivity at small thickness of the compact layer: the selectivities are smaller than the intrinsic selectivities of the polymer. If the resistance of the sublayer dominates (the thickness of the compact toplayer approaches zero) the selectivities will be as low as 2.3 and 0.9 for helium over nitrogen and oxygen over nitrogen, respectively. However, if the resistance of the compact toplayer dominates, it is shown that the selectivities approach the intrinsic selectivities.

Etching experiments are also performed on fibers spun from other PPO types. Plateau-values of reduced permeabilities are used in the calculations for the determination of the overall selectivity of the membrane. Sublayers of fibers spun from low molecular-weight PPO-resin (General Electric) have a remarkable high resistance towards gas transport. The reduced permeability of the porous sublayer is as low as 0.2×10^6 barrer/cm for helium. In Fig. 6 the results

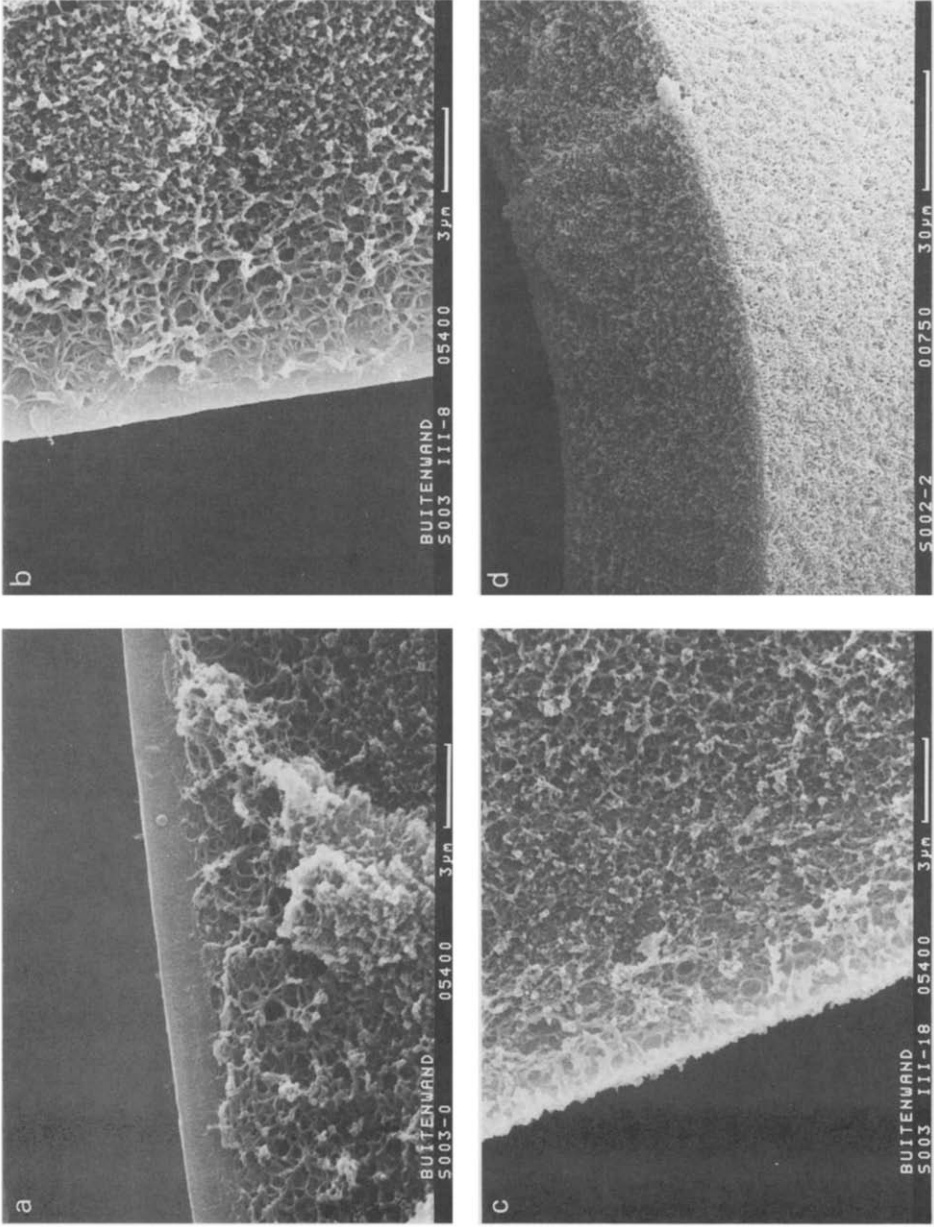


Fig. 4. Scanning electronmicrographs of cross sections of PPO-fibers. (a) original fiber; (b) fiber after 4 min of etching; (c) fiber after 18 min of etching; (d) cross section and part of outer surface of fiber after 18 min of etching.

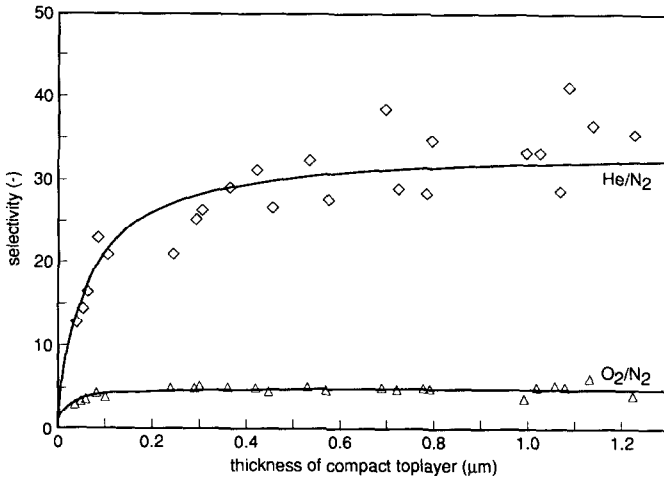


Fig. 5. Calculated (line) and experimental values for selectivities of helium over nitrogen (\square) and oxygen over nitrogen (\triangle) of the total membrane as a function of the toplayer thickness.

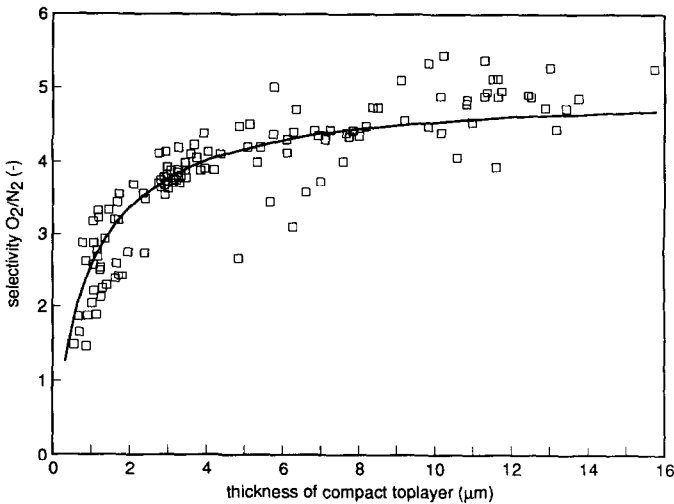


Fig. 6. Calculated (lines) and experimental values for selectivities of oxygen over nitrogen (\square) of the total membrane as a function of the toplayer thickness for low molecular weight PPO.

of the calculations and the experimental selectivity values for oxygen over nitrogen are shown. From this figure it can be seen that only fibers with selective layers which are larger than approximately $4 \mu\text{m}$, have selectivities higher than 4.

In determining and comparing the resistances of different porous sublayers, care must be taken to etch fibers which are spun under the same processing conditions. Smid, Albers and Kusters [3] already showed that an increase in

length of the air gap resulted in an increase of the ultimate apparent compact layer thickness. Etching experiments on several fibers with different compact layer thicknesses reveal a relation between the reduced permeability of the sublayer and the thickness of the compact layer (Fig. 7). This indicates that variation of the air gap length also affects the liquid-liquid demixing behaviour of the solution at the bore side of the extruded polymer solution and thus influences the structure of the sublayer. The differences between the values of the reduced permeabilities in these experiments are much smaller than those found with fibers spun from PPO with different molecular weights (1.5 to 2 fold increase compared to 30 to 1000 fold increase). Also eqn. (1) is rather insensitive for small variations, like those we find in the resistance values of sublayers from fibers with different toplayer thicknesses.

Table 1 shows the measured reduced permeabilities of helium for hollow fibers with approximately the same compact layer thicknesses ($0.2 \mu\text{m}$) pro-

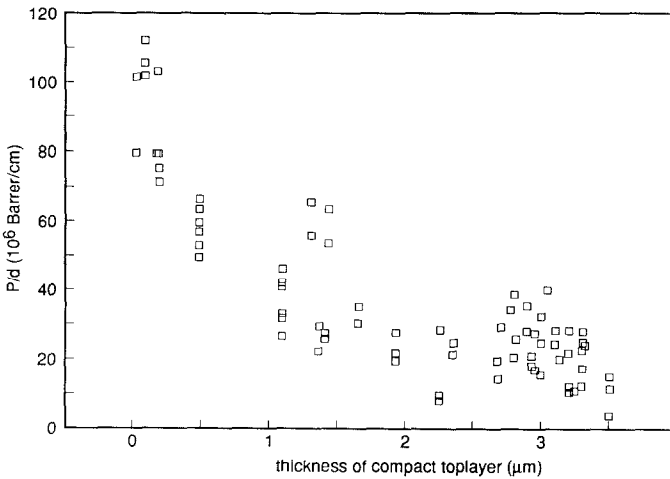


Fig. 7. Reduced permeability of the sublayer for helium as a function of the toplayer thickness.

TABLE 1

Reduced permeability (P/d) of the sublayer of hollow fibers spun from PPO with different intrinsic viscosities [η]

[η] (dl/g)	P/d (10^6 barrer/cm)
0.7	0.2
1.10	5.4
1.15	42.1
1.20	81.5
1.35	148.7

duced from different PPO-types. It can be concluded that increasing the molecular weight of the PPO-resin results in a lower gas resistance of the sublayer. Smid, Albers and Kusters [3] showed that a correlation exists between the selectivity of oxygen over nitrogen and the thickness of the selective toplayer of hollow fiber membranes. The parameters changed when fibers made from PPOs with different intrinsic viscosities (or molecular weights) are used. This can now be explained by the differences in gas transport properties of the sublayer of the hollow fibers from different PPO-types we found using the resistance model.

The explanation of the differences in gas resistance in different molecular weight PPOs may be due to differences in crystallinity or mobility of the polymer chains during the coagulation process.

According to Wijmans et al. [16,17] PPO is a semi-crystalline polymer. For highly crystalline polymers like polypropylene it was found [18] that the degree of crystallinity and the nucleation rate increase as the molecular weight decreases. Wijmans [16] concluded that phase separation in PPO-mixtures is accompanied by nucleation and growth of a crystalline phase. If these nuclei are considered as junctions of a network, it can readily be understood that a large amount of nuclei (in the case of low molecular weight PPO) will render a network with meshes of small size. This kind of a network will have a relative high resistance for gas transport. In the case of high molecular weight PPO relatively few nuclei will render a network with larger meshes, which results in a structure with a low resistance towards gas transport. So in low and high molecular weight PPO differences in crystallinity are expected to be found.

Differential scanning calorimetry (data not shown) and X-ray diffraction of hollow PPO-fibers (Fig. 8) show the crystalline phase to be present. However, no difference can be found between two PPO-types of different molecular weight. In the X-ray diffraction diagram both polymers exhibit a very broad band at approximately 14° (deflection angle 2θ). So with these two techniques it is possible to prove the presence of crystallinity in a qualitative way. The differences in the crystalline structure of the PPO-types will be too small and too subtle to be detected by these methods. Therefore other techniques are needed to determine differences in crystalline structure.

Another reason for the different sublayer resistances may be the difference in the mobility of the polymer molecules during the coagulation process. Lower molecular weight polymers have a shorter relaxation time τ than higher molecular weight polymers, according to the relation [19]:

$$\tau \propto M^{3/2} \quad (6)$$

In this equation M denotes the molecular weight of the polymer. Due to higher mobility a more organized and denser structure may result after the coagulation process. The denser structure of the ultimate sublayer will contain less open pores and have a relatively high resistance towards gas transport. The

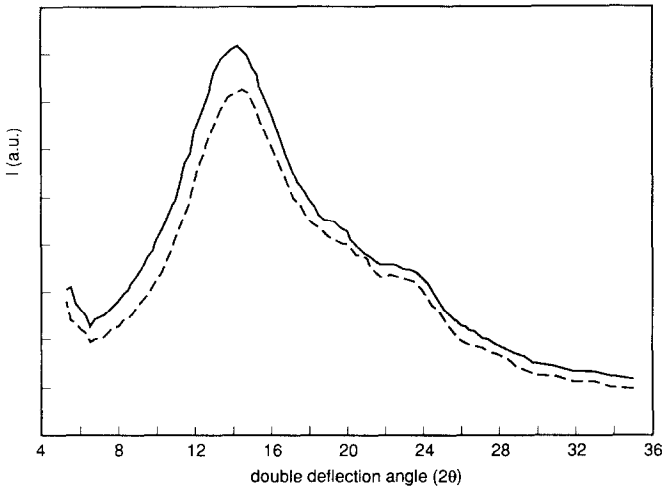


Fig. 8. X-ray diffraction diagrams of PPO fibers with an intrinsic viscosity of 1.3 dl/g (—) and of 0.7 dl/g (-----).

explanation of the differences in sublayer resistance will be studied more extensively in our further research work.

Conclusions

It is clearly shown that plasma-etching is a powerful tool in determining resistances of sublayers of skinned asymmetric hollow PPO fibers towards gas transport. With this technique data are obtained with which it is possible to predict (according to a resistance model) the ultimate selectivities of the hollow fiber membranes. It has been proven that the resistance of the sublayer of skinned asymmetric hollow fiber PPO-membranes has a great influence on the overall membrane properties. By decreasing the sublayer resistance the overall selectivity of membranes with thin selective layers can be improved.

The molecular weight of PPO has a large effect on the resistance of the sublayer: the higher the molecular weight, the lower the gas resistance of the sublayer will be, in agreement with results found by Smid, Albers and Kusters [3]. So far no satisfying explanation for the relation between the intrinsic viscosity and the gas resistance of the sublayer has been found and more research work has to be done. Besides on molecular weight of PPO, the gas resistance of the sublayer also depends (to a lesser extent) on membrane preparation. The resistance of the sublayer and the thickness of the compact layer decrease with decreasing length of the air gap.

From electronmicroscopy and from etching experiments it can be concluded that a gradual transition between the porous sublayer and the compact to-

player must be present in membranes with rather thick compact layers (approximately $1\ \mu\text{m}$).

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