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Scanning Probe Microscopy Techniques in the Investigation of Homogeneous and Heterogeneous Dense Membranes: the Case for Gas Separation Membranes
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5.1
Introduction

Membrane processes are being applied in many fields. It is clear that membranes developed for such a wide variety of processes must necessarily have very different properties and structure. Membranes could be classified according to different aspects [1].

In any case, morphological and structural aspects are crucial as far as they determine the barrier properties of a membrane along with their physicochemical properties. According to their structure membranes can be classified as porous membranes or as nonporous or dense ones. A porous membrane presenting equal pores should be called homoporous; actually all membranes have pores with a more or less wide range, so being heteroporous.

Really, the concept of a pore could be generalized to include all interstices in the materials of a solid film. According to this, strictly speaking all membranes should be porous. Even if we accept that pores are only supra-molecular, more or less interconnected paths, with an estimable contribution to the transport through the membrane, many membranes usually considered as dense, as for example gas separation or reverse osmosis membranes, should be reinterpreted as porous as far as microvoids in amorphous or semicrystalline polymeric films play a relevant role in permeability.

In any case, what can be understood as dense membranes depends on the scale to which they are studied. In dense membranes, the performance (permeability, selectivity) is determined by the intrinsic properties of the material by solution–diffusion through the molecular interstices in the membrane material. When this is not the main mechanism, the membranes can be called porous. In this case, the selectivity is mainly determined by the dimension of the pores. Actually it can also
play a key role in selectivity through its charge and dielectric constant when the solute is charged. When this is not the case the material also has very important effects through phenomena such as adsorption and chemical stability under the conditions of actual application and membrane cleaning [2].

The processes where porous membranes find their main applications are pressure-driven ones, such as microfiltration, ultrafiltration and nanofiltration. These processes are also especially interesting due to their wide range of practical applications. They can be used for the processing of fine particles, colloids and biological materials such as protein precipitates and microorganisms [3]. Membranes used are commonly polymeric materials but innovative development has been made in the fields of ceramic and inorganic membranes.

However, membranes can be symmetric or asymmetric. Many porous or dense membranes are asymmetric and have one or several more porous supporting layers and a thin skin layer which, in fact, gives selectivity. If these two layers are made of different materials, the membrane is a composite one. On some occasions, dense membranes have inclusions of other materials; these are, of course, also composite membranes. In the case of gas separation membranes it has became usual to include inorganic charges in a polymeric membrane to get what is called a mixed matrix composite membrane.

The prediction of the process performances of these membranes for industrially relevant separations ultimately rests on the development and application of effective procedures for membrane characterization.

Most manufacturers of porous membranes describe their products by giving a single pore size or a molecular weight cut-off value. These data are usually obtained by measuring the rejection of macromolecules or particles of increasing hydrodynamic diameter or molecular weight. Of course, such a single value does not determine totally their structure nor their separation properties. In any case, the molecular weight cut-off can be accepted as a useful datum only for preliminary selection. However, all membranes must be assumed to contain size-distributed pores.

There are several independent methods that can be used to study pore statistics [2, 4–7]. The major ones are summarily presented below [8].

1. Electron microscopy uses several available electronic microscopy techniques to view the top or cross-sections of membranes: scanning electron microscopy (SEM), transmission electron microscopy (TEM), field effect scanning electron microscopy (FESEM), etc. The corresponding images are analyzed to obtain pore size distributions [9] (see Chapter 3).

2. Scanning probe microscopy (SPM) and specifically atomic force microscopy (AFM) are techniques allowing a study of the surfaces of nonconducting materials, down to the scale of nanometers [10]. The main advantage of such techniques is that no previous preparation of the sample is needed [9]. Although it is a relatively novel technique, application to membranes, both biological and synthetic, is growing rapidly [11, 12] (see Chapter 6).

3. Bubble pressure methods [13] are based on the measurement of the pressure necessary to force a fluid to pass through the pores previously filled with
another fluid. These include both gas–liquid and liquid–liquid displacement techniques [14–18]. In the pure bubble point method, air is pushed until its first appearance on the permeate side of a previously swollen membrane. This method has been frequently used for an estimation of a representative pore size of many commercial membranes.

4. Mercury porosimetry is a method based on the same principles as the bubble pressure method; but now mercury (a nonwetting fluid) is used to fill a dry membrane [19].

5. Adsorption–desorption methods [20] allow analysis of pore size distribution. The technique is based on the Kelvin equation, which relates the reduced vapor pressure of a liquid with a curved interface to the equilibrium vapor pressure of the same liquid in bulk with a plane liquid–vapor interface [21]. The BET adsorption theory is frequently applied to gas adsorption in order to obtain specific surface areas.

6. Permporometry is based on the controlled blocking of pores by condensation of the vapor present as a component of a gas mixture, with the simultaneous measurement of the flux of the noncondensable gas in the mixture [22]. If the Kelvin equation is used, the pore size distribution is obtained.

7. Thermoporometry, first suggested by Brun et al. [23], is based on the fact that the solidification point of the vapor condensed in the pores is a function of the interface curvature. By using a differential scanning calorimeter (DSC), the phase transition can be easily monitored and the pore size distribution calculated.

8. The solute retention test, where rejection is measured under more or less standardized conditions for various solutes of increasing molecular weights or hydrodynamic sizes, allows an evaluation of the pore size distribution [24, 25].

Other techniques can also be used for determining pores and pore sizes in filters such as, for example, NMR measurements [26], wide angle X-ray diffraction [27], small angle X-ray scattering [28] and electrical conductance [29]. These are methods that have been used to get pore sizes of different membranes.

When dealing with the free volume or interstices in dense membranes, small angle X-ray spectroscopy (SAXS) is very helpful, along with positron annihilation lifetime spectroscopy (PALS) [30], or even ellipsometry [31, 32], which measures density locally giving a first insight on the space free volume distribution in depth.

Of course there are many other experimental facilities that can give important physical and chemical parameters, other than pore size distributions, of porous or dense materials, such as electron spectroscopy for chemical analysis (ESCA), Fourier transform infrared spectroscopy (FTIR) and contact angle determinations. Also thermal or thermomechanical analysis, including differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) customarily used to characterize polymers in materials science, can be very valuable when applied to dense or porous membranes.

A description of these techniques is not our objective here. It is clear, nevertheless, that they can be placed in two main groups: some of these methods (the ones developed for the characterization of general porous materials)
directly obtain morphological properties, while others give parameters related to membrane permeation (those designed specifically to characterize membrane materials) [33].

Appropriate elucidation of structure is not only relevant to describe sieving effects but also to study the interactions of the membrane material with the feed to be treated, as far as the corresponding interfaces are placed inside the pores as well as on the membrane external surface. Thus, electrically determined membrane properties act on the solutes inside the pores and transport is affected by these properties (zeta potential, surface charges, etc.) in such a way that makes necessary a detailed knowledge of the geometry of both the inner and external surfaces of the membrane to adequately correlate interactions with their effects on flux (see Chapter 9).

Actually most of the techniques outlined above can also be useful to characterize dense membranes. In effect, solid dense membranes are usually fixed on a porous support whose structure can penetrate into the dense layer, leading to defects in the dense material and corrections to the expected flow. Even if these defects are not present, transport through the support material can play a significant role in process features.

Those techniques not referring specifically to porous morphology are especially relevant when concerning dense membranes. For example microscopy, including SEM, TEM, FESEM and especially SPM, can give information on the characteristics of nonporous surfaces of dense membranes and thus can be of great help.

Among the dense membranes, those designed to perform gas separations are very important. In effect, there is a big market for gas separation through membranes. Of course, the material structure and, thus, synthesis processes must be considerably improved to reach optimization of selectivity and permeability for target gases. Long-term research has been dedicated to this aim. The fractional free volume in the most restrictive layer, usually that just on the active surface layer, plays a key role in the selectivity and permeability of dense membranes in gas separation. As a consequence it is very important to characterise the membrane surface.

Our objective here is to describe how techniques of microscopy (namely scanning probe microscopy; SPM) can help in the investigation of homogeneous and heterogeneous dense membranes. In order to show their potentialities, we focus specifically on gas separation membranes.

5.2 Microscopic Techniques

Visual inspection of microscopical structure is an invaluable tool for a deep knowledge of filters. This is why the visualizing techniques were very early used to characterize them. Nevertheless, as the developed filters included relevant structures with submicron sizes, optical microscopy was no longer useful to achieve a
real picture of the membrane topography, given that the resolution is limited by
the light diffraction pattern. Only the development of non-optical microscopic
techniques made it possible to solve this problem. Originally, electron microscopy
[34], and afterwards scanning probe microscopy [10], were shown to be priceless
tools for the characterization of membranes, so that we can now have information
of membrane surfaces covering the full range of membranes.

5.2 Microscopic Techniques

5.2.1 Electron Microscopy: SEM and TEM

When high-energy electrons collide with a solid, the interactions between the solid
material and the electron beam can be used to identify the specimen and the
elements present in it, but also to characterize physically the solid surfaces and
bulk, including the holes, pores or inclusions appearing through it.

Transmission electron microscopy (TEM) operates by flooding the sample with
an electron beam, most commonly at 100–200 keV and detecting the image generated
by both elastically and inelastically scattered electrons passing through the
sample. TEM operates in the magnification range from $600 \times$ to $10^6 \times$.

Similarly, a fine beam of medium-energy electrons (5–50 keV) causes several
interactions with the material, secondary electrons being used in the SEM tech-
nique. SEM equipment is able to achieve magnifications ranging from $20 \times$ to
$10^5 \times$, giving images marked by a great depth of field and thus leading to con-
siderable information about the surface texture of the target.

The main problems and difficulties of the microscopic observation by both TEM
and SEM are how to prepare a membrane sample without any artefact. The first
step of the preparation is a careful drying of the sample, and in order to avoid
collapse of the original structure, the freeze-dry technique using liquid nitrogen or
the critical-point drying method with carbon dioxide is usually employed.

In order to observe cross-sections by SEM, the dried membrane must first be
fractured at the liquid nitrogen temperature and then fixed perpendicularly onto
the sample holder. Usually, samples are afterwards covered by a thin metallic layer
(normally a gold film of some hundreds of angstroms), increasing the production
of secondary electrons and therefore improving the image contrast [35]. For TEM
observation, a more complicated procedure is required. The dried sample is
usually firstly embedded and then cut by using a microtome. Of course the em-
bedding medium has to be adequate in order to avoid any influence on the
membrane. The section must be thin enough for electrons to penetrate, that is,
less than 50 nm. If only the surface is being analyzed, a replica technique can be
used by coating the membrane with a carbon film and then removing the mem-
brane material (by dissolving it for example) and analyzing this replica [36].

When high electron beam energy is applied, the maximum resolution of TEM is
$\sim 0.3–0.5$ nm, while SEM has 10 times greater resolution. In these conditions, the
sample surface can be seriously damaged, especially when dealing with polymeric
membranes, which makes observation difficult. In the early 1980s field emission scanning electron microscopy (FESEM) was developed and used to observe the surface pores of ultrafiltration membranes [37]. Nowadays FESEM achieves very high resolution (to 0.7 nm), even at low beam energy, with accelerating voltages in the range 1.5–4.0 kV.

5.2.2 Scanning Probe Microscopy: STM and AFM

Atomic force microscopy (AFM) covers a range of recently developed techniques that can be used to characterize membranes. Actually it presents very high possibilities of development and application in the field of microscopic observation and characterization of various surfaces. A very small tip scans the surface and moves vertically according to its interaction with the sample, similar to the technique used in scanning tunneling microscopy (STM).

The two techniques that can be called scanning probe microscopy differ in the method they use to detect interactions. In STM the tip is so close to the sample (both being electrically conducting) that it allows a current to flow by tunnel effect and the sample or tip moves to keep this current constant. In AFM the tip is placed on a cantilever whose deflection can be detected by the reflection of a laser beam appropriately focused. This allows the analysis of nonconducting materials, which makes the method more convenient to study membrane materials [38, 39].

Several operation procedures can be used in AFM:

1. Contact mode AFM. This measures the sample topography by sliding the probe tip across the sample surface. The tip–sample distance is maintained within the repulsive range of the atomic forces.

2. Noncontact mode AFM. The topography of the sample is measured by sensing the Van der Waals attractive forces between the surface and the probe tip held above the surface. Of course, worse resolution than contact mode is achieved. Nevertheless, the risk of sample damage is avoided or minimized.

3. Tapping or intermittent contact mode AFM. This is a variation of the contact mode and operationally it is similar to noncontact mode; thus it features the best characteristics of both methods. The cantilever is oscillated at its resonant frequency with high amplitude (over 100 nm) allowing it to touch the sample during the oscillation. The topographical information is obtained from the register of the vertical displacements of the set-point needed to keep the oscillation amplitude constant. This method maintains the high resolutions achieved in contact mode, but minimizes surface damage, as far as it eliminates the lateral friction forces.

These previously commented techniques give an account of the sample topography. Other information on the surface can be acquired by AFM, such as for example heterogeneities that can be detected attending to differences in adhesion
and in elasticity or stiffness. Techniques that spot these differences are:

1. Phase contrast. In the tapping mode technique the tip of the probe is oscillating near the surface of the sample at a given frequency and amplitude. When the tip approaches the surface there is a shift in the phase of the oscillating cantilever. If in this situation there is a variation in the interaction, when scanning the surface, the corresponding phase shift changes in accordance. This modification in the interaction, and thus in the phase shift, can be caused by surface topographic accidents and by the appearance of interaction forces, that could be for example magnetic or electric. They can also be caused by a change in the surface material due, in this case, to the viscoelastic properties of the surface.

2. Force modulation. In this technique the cantilever is forced to oscillate at a very low frequency (far below the cantilever natural frequency) when it is close to the surface. In this way the amplitude of the oscillation decreases when the constant energy supplied has to be spent in overcoming the strong interaction appearing when the surface is somehow sticky, while it gives big amplitudes when the surface is hard enough.

3. Lateral force microscopy. In this case, the frictional force between the probe tip and the sample surface is analyzed. The sample is swept in such a way that the cantilever tends to bend, with a this torsion force which is proportional to the friction force. Of course this frictional force depends on the material and reveals easily the inhomogeneities on the membrane surface.

Other properties of the surfaces can be analyzed by measuring different forces between sample and tip. Magnetic and electric force microscopy (MFM, EFM) both measure magnetic (or electric) force gradient distribution above the sample surface. Surface potential microscopy measures differences in local surface potential across the sample surface. Finally, electrochemical microscopy measures the surface structure and properties of conducting materials immersed in electrolyte solutions with or without potential control.

In many of these techniques, an appropriate treatment of the measured forces is necessary to eliminate the contribution of the topographical images. This is necessary to minimize or to eliminate the influence of the pure topographical information, to isolate the information concerning the specific interaction studied. This method consists of registering the topographical information and reproducing the scan at a constant distance on the surface, now revealing only the deflections caused by the interaction being studied.

5.2.3

**Computerized Image Analysis**

Image analysis can be carried out by means of a plethora of software packages, some of which are supplied by the main optical or electronic microscopies manufacturers (Jeol, Leica, Karl Zeiss, Nikkon, etc.) as a complement to their devices.
In all cases each photograph is first digitized by assigning to each pixel a gray level ranging from 0 (black) to 255 (white). Then, a clearfield equalization is made to each image field to eliminate parasite changes in gray levels due to uneven illumination. Obviously, a perfect clearfield equalization should require a blank image with a perfect flat sample of the same material equally treated and acquired in the same way. In fact this is impossible and even inconvenient, as far as uneven illumination can be due to the roughness of the sample itself. What can be done is to use what is called pseudoclearfield equalization by dividing the original image into a convenient number of rectangles. Then we can assign to all pixels the intensity such that 95% of the original pixels have a lower intensity. Finally these rectangles are placed together by linear interpolation from rectangle to rectangle and substracted from the original picture.

Once illumination effects are eliminated, the image gray spectrum is spanned to get the maximum contrast and definition. Then the images are redefined according to an assigned gray threshold level under which every pixel is assigned to 1 and the rest to 0. The resulting binary picture is improved by scrapping isolated pixels, in such a way that all the remaining 1 s in the matrix are assumed to belong to a pore, an inclusion or a segregated phase of the material. Finally the borders are smoothed in order to reduce the influence of the finite size of pixels and low definition.

Of course a correct selection of threshold gray level is fundamental to performing a correct analysis of accurate assigned pores. Customarily the gray spectrum is analyzed and the threshold placed centered in the peak to peak valley of the almost bimodal distributions obtained. Unfortunately sometimes the spectra are so flat that this technique is only of relative help to make a correct threshold election [40]. In any case, eye inspection facilitates the process of selection of several reasonable threshold candidates whose outcomes are conveniently averaged.

5.2.4
Roughness and Fractal Dimension

Average roughness ($R_q$) can be directly obtained from AFM images for different explored areas using the definition expressed by the following equation:

$$R_q = \sqrt{\frac{1}{n} \sum_{i=0}^{n} (Z_i - Z_m)^2} \quad (5.1)$$

where $Z_m$ is the mean value of the tip height in each point of the image ($Z_i$) over a reference baseline ($Z$) [41].

The roughness versus scanned area pattern is characteristic of a given material and defines a fractal dimension, $d_f$, which is evaluated as: $d_f = 3 - \alpha$ where $\alpha$ is the so-called roughness exponent that can be calculated as the slope of roughness versus scan size in a double log plot [42].
This fractal dimension experimentally gives a good representation of how roughness increases with scan size, with accurate fittings to experimental data [43]. Thus, a value of fractal dimension close to 2.0 means that the membrane has a reasonably flat surface; while, if $d_f$ is close to 3.0, the membrane surface has a 3D-like interface.

5.3 Gas Separation Membranes

In the competition with other more traditional processes of gas separation, such as cryogenic distillation or pressure swing adsorption, polymeric membranes have the advantage of their simplicity, continuous working ability, low energy consumption and low capital costs [44].

A high selectivity leads to a high purity of products and allows a reduction in the number of operation steps. A high permeability involves a high process velocity and a lower membrane area. Nevertheless, high selectivity is normally obtained with low permeability and vice versa [45]. Of course, it should be convenient to reach simultaneously high permeabilities and selectivities or at least to increase one of these parameters without decreasing the other.

Permeability of the $i$-th gas can be obtained as the product of its diffusivity ($D_i$) and its solubility ($S_i$):

$$P_i = D_i S_i$$

(5.2)

with selectivity for a given pair of gases:

$$\alpha_{ij} = \frac{P_i}{P_j}$$

(5.3)

Unfortunately, the Robeson bound [45] gives an upper limit for the selectivity versus permeability correlation that can be reached by increasing in chain stiffness and/or fractional free volume of a polymeric material. This limit is based on empirical data and seems to underestimate slightly the predictions of a relatively simple model by Freeman [46, 47].

The main physicochemical characteristics that rule gas permeability and thus selectivity of polymers are:

- The intersegmental spacing and the corresponding polymer free volume.
- The mobility of the polymer chains that can be correlated with the glass transition temperature, $T_g$.
- The interaction between the polymer and the penetrant gas or its solubility [48].

It seems clear that there is a direct correlation between gas diffusivity in the polymer and its free volume [49]. In turn, solubility should increase with the inner surface of the voids where the gas can enter. Thus it seems that selectivity should be caused by differences in the free volume accessible to each gas along
with the differences of gas-surface interactions. Furthermore the restricting
fraction of free volume should be very relevant in building up selectivity. Thus,
the size and characteristics of the narrower necks connecting bigger voids are very
important.

In summary, both selectivity and permeability characteristics can be interpreted
in terms of a series of parameters that are substantially determined or basically
controlled by the characteristics of the free volume of the polymer [50].

Attending to the membrane manufacture procedures, these aspects should be
more restrictive at the membrane surface, where free volume should have an in-
fluence in the roughness of the resulting surface of the membrane. We give two
examples below on how an analysis of the resulting fractal dimension to increase
gas permeability-selectivity performances.

Another possible way to improve the performance of a membrane relies on
increasing flux for a given permeability and selectivity by simply reducing the
thickness of the active layer. An example on how AFM can help in this research
program is worthy of comment here. This is the procedure to make Matrimid
asymmetric membranes.

Finally, other possible way to produce useful membranes is to mix a certain
material (usually a polymer with good mechanical and chemical properties)
with another material (an activated carbon for example) with better selectivity-
permeability performances but which is not advisable to use alone in the actual
gas environment for a given application or which is difficult to obtain in a resistant
film layer. This constitutes what is called a mixed matrix composite membrane
(MMCM).

For a system where the filler is very close to a disposition of dispersed spheres
and there are no significant changes in permeability caused by the interaction of
the filler with the continuous polymeric phase, the theory of Maxwell can be ap-
plied to give:

\[
P_{i,\text{mem}} = P_{i,c} \left[ \frac{P_{i,d} + 2P_{i,c} - 2\phi(P_{i,c} - P_{i,d})}{P_{i,d} + 2P_{i,c} + \phi(P_{i,c} - P_{i,d})} \right] \tag{5.4}
\]

for the permeability of the membrane (MMCM) for the \(i\)-th gas and with \(d\)
and \(c\) subindexes referring to disperse (filler) and continuous (polymer) phases
[51–53]. This equation is usually expected to hold for low volume fractions of the
filler [54].

The possible effects of the interaction of the filler with the continuous phase
where it is inserted can produce an interfacial layer in between them that, depending
on their compactness, can have different effects [55], as shown in Figure 5.1.

The good dispersion, agglomeration and the amount of filler included in the
continuous phase as well as the quality of the interfaces between the two phases
forming MMCM can be analyzed by using scanning probe microscopy. An ex-
ample concerning two kinds of activated carbon in an acrylonitrile butadiene
styrene (ABS) matrix is explained in the next section.
5.4 Case Studies

5.4.1 Phase Segregated Membranes

The electronic interactions of CO$_2$ with the oxygen in the ethylene groups in polyethylene glycols (PEG) increase the solubility of this gas in the polymeric matrix and thus should lead to an improved transport and better permeability and selectivity of CO$_2$. In order to explore this possibility, several polymers were tested. They were obtained by a two-steps polyimidation of 3,3',4,4'-biphenyltetracarboxyl (BPDA) or 3,3',4,4'-benzophenonetetracarboxyl (BKDA) dianhydride with mixtures of different diamines. The diamines in these mixtures were an aromatic one, benzidine (BNZ), oxodiamiline (ODA) or phenyldiamine (PPD), and an aliphatic one with PEG. Several proportions of aromatic to aliphatic diamines have been tested. The films were thermally dehydrated at 120 °C and the corresponding complete imidation was tested by FT-IR.

The resulting polymer was solved in dimethylacetamide (DMAc) and evaporated at 60 °C during 5 h. Finally the obtained membranes were heated from 160 °C to 265 °C under a N$_2$ atmosphere.

In all cases the resulting permeability and selectivity were very interesting [56, 57]. As an example the permeability and selectivity of two of these membranes are shown in Figure 5.2. The notable increase in permeability and selectivity, when the membrane was thermally treated at temperatures below degradation, should be explained in terms of the changes in the membrane morphology.
Figure 5.2 Robeson diagram showing CO$_2$/N$_2$ selectivity versus CO$_2$ permeability for the membranes BPDA-PEG2000-ODA 2/1 and BPDA-PEG2000-BNZ 2/1 after different temperatures of treatment. An insert showing their CO$_2$ permeability as a function of temperature is also included.

Figure 5.3 AFM topographic tapping mode pictures of the BPDA-PEG2000-BNZ 2/1 membrane after treatment at different temperatures.
In order to investigate the corresponding changes in the membrane material after thermal treatement of these membranes, AFM pictures were analyzed. Figure 5.3 shows an example of AFM pictures. These images were obtained for membranes treated at different temperatures and using the tapping mode. The corresponding fractal dimension is shown as a function of the treatment temperature in Figure 5.4. From these results it seems clear that the membranes are becoming more and more flat when heated.

A certain phase segregation is seen to appear by SAXS \[58, 59\]. An example is shown in Figure 5.5, where the mean distance from phase to phase is shown versus the treatment temperature. Note that the corresponding phase segregation should start at temperatures only slightly over the imidation one. The phase segregation is also seen, for example, in the TEM image shown in Figure 5.6.

5.4.2 Solvent Evaporation

It has been shown that the introduction of bulky groups in the chains of glassy polymers makes their structure stiffer and hinders an efficient packing of chains \[60, 61\]. This should lead to an increase in free volume. An example of such a kind of polymer is 6FDA-6FpDA, polymerized from 2,2-bis(4-aminophenyl) hexafluoropolyldione and 2,2 bis-(3,4 dicarboxyphenyl) hexafluoropropylidine dianhydride \[62\].
Fluorinated polyimides are particularly interesting for gas separation because they have good mechanical, thermal and transport properties [63]. They also have a certain resistance to plasticization [64].

In most cases it has been assumed that the solvent used in the casting does not influence the resulting structure of the membrane once it has been evacuated. Nevertheless some studies have been done on this dependency [65, 66] without conclusive explanation for the differences in permeation found.

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**Figure 5.5** SAXS results showing the phase spacing for the BPDA-PEG2000-ODA 2/1 membrane as a function of the temperature of treatment. The range of imidation and the starting of phase separation are also shown.

**Figure 5.6** TEM picture of the BPDA-PEG2000-ODA 2/1 membrane showing that at this temperature PEG is totally segregated.
The surface of the membranes made with different solvents and/or at different evaporation temperatures (for DMAC) show different conformations. Figure 5.7 shows examples of these different conformations for different solvents. Note that, when the solvent is good enough, the surface of the membrane is much flatter: while for not so good solvents the surface shows a granular structure.

Differences in selectivity and permeability have also been detected on 6FDA-6FpDA membranes, depending on the solvent used in their manufacture. Moreover, the morphology of the membrane, both on the surface and in the bulk, along with permeability and selectivity, could be correlated with the solvent characteristics.

The quality of a solvent–polymer system can be correlated with their Hildebrand solubility parameters ($\delta$) in such a way that, when these parameters are similar: $|\delta_s - \delta_p| \leq 2.5 \text{ (cal/cm}^3)^{1/2}$, the solubility is acceptable (where $\delta_s$ and $\delta_p$ are the Hildebrand solubility parameters for the solvent and the polymer, respectively). The above criterion comes from the approximate Flory–Huggins theory.

Figure 5.8 plots the fractal dimension versus $\delta_s$ for the solvents used, as obtained in the literature [43, 67, 68]. A parabolic plot should be obtained in this kind of plot [68], with a minimum in fractal dimension (flat membrane surface). Here, this minimum appears at $10.2 \text{ (cal/cm}^3)^{1/2}$ when 6FDA-6FpDA dissolves best.
The minimum in fractal dimension is mainly due to the polar contribution of the solubility Hildebrand parameter. This can be proved by the reproducibility of the minimum when the polar solubility parameter of Hansen is used, while no correlation between fractal dimension and the dispersive or hydrogen bond Hansen parameters can be found [69]. Moreover, a similar tendency, but oppositely now showing a maximum, can hold for the glass transition temperature of the resulting membrane [67], as shown in Figure 5.9 with a very similar extremal Hildebrand parameter. The maximum glass transition temperature, or minimum fractal dimension, appears at a solvent Hildebrand parameter that very finely estimates that of the polymer.

The Flory–Huggins theory can be improved to incorporate new terms. For example, the Prigogine–Flory–Patterson theory introduces an entropic contribution due to free volume effects in order to obtain more realistic results [70]. This contribution does not modify the solubility criterion as stated above. When the Flory interaction parameter ($\chi$) is considered to have both an enthalpic component $\chi^H$ and an entropic (or residual) component $\chi^S$, such a Flory parameter [71] appears as:

$$\chi = \chi^S + \chi^H = 0.34 + \frac{V_s}{kT} \left( \delta_s - \delta_p \right)^2$$  \((5.5)\)

This dimensionless interaction parameter characterizes the interaction energy per solvent molecule normalized in terms of $kT$. Assuming that the molar volume of the solvent is almost independent of temperature, like the Hildebrand’s parameters of solubility for both solvent and polymer, Equation (5.5) can be used to take into account the influence of the temperature of membrane fabrication.

In order to study in a more quantitative way how a change in the solvent can increase permeability and selectivity, the distance from the point in a selectivity

Figure 5.8 Fractal dimension versus the solvent solubility parameter for 6FDA-6FpDA membranes manufactured with different solvents or evaporated at different temperatures (for DMAc) below the solvent boiling point, $\Delta T$. 

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versus permeability plot to the Robeson trade-off line, $\Delta_R$, can be used ($\Delta_R < 0$ if the point is below the Robeson bound and $\Delta_R > 0$ if the point is above it) [67]. In these terms, it can be shown that this distance to the Robeson’s curve is a decreasing function of the solvent–polymer interaction energy, as shown in
5.4.3
Asymmetric Polymeric Membranes

The more important factors from an industrial point of view are a high flux or productivity and a high selectivity or separation effectiveness. It is here that asymmetric membranes find more application, due to their high flux. When the same material forms two layers differing in their structure, with a thin active dense skin layer associated with another layer that acts as a mechanical support and has no significant resistance to mass flux, the resulting membranes are called integral.

In our case, these membranes were made of the same material and prepared by phase inversion process [72, 73]. The dense selective skin layer was possible because of the evaporation of solvent during the initial period and the macroporous layer sticking to the skin layer was formed due to the exchange between the solvent and nonsolvent systems inside the precipitation bath [74].

The polymeric material used to prepare integral asymmetric gas separation membranes was Matrimid 5218. This is a commercial polyimide with good properties for gas separation. A mixture of tetrahydrofuran (THF) and γ-butil-lactone (GBL) was used as solvent, while n-butanol (n-BuOH) was used as nonsolvent. The precipitation media was a bath with ethanol and water. Taking into account the corresponding ternary phase diagram, the compositions selected were 14% of Matrimid and 10% or 12% of n-BuOH in a 50:50 mixture of THF/GBL. Films were cast on a leveled glass plate and the solvent was left to evaporate at ambient temperature during a range from 2 s to 40 s.

In order to avoid or to minimize the influence of micropores appearing on the surface of the dense layer, the membranes were recovered by a thin layer of
silicone rubber. This was chosen because it has a high permeability with a relatively low selectivity for all gases. The membrane was submerged in a solution prepared with 2% silicone in iso-octane during some seconds.

The structural characterization of these materials is difficult. The main factor here should be the thickness of the several dense or porous layers. In effect, the width of the dense skin layer determines the flux. Because of this, it is interesting to obtain thin membranes [75–78], with good mechanical, thermal and chemical resistances [79–81]. Actually, the borders within the several layers of the membrane are not easy to detect as far as they correspond to the same material.

In this sense we put special emphasis on the study of AFM and SEM pictures. Figure 5.11 shows the support and active layers as obtained by tapping mode AFM. The borders between layers are better revealed by phase contrast and force modulation techniques, as shown in Figure 5.12. The corresponding thicknesses for the Matrimid dense layer are shown in Figure 5.13 as a function of the time of evaporation used in order to eliminate the solvent once phase inversion took place.

Figure 5.13 also shows the corresponding thickness for the Matrimid dense layer as obtained from SEM. The thickness obtained by assuming that only the dense active layer of Matrimid has a significant resistance to the flux of gas according to

$$\delta_m' = \frac{P_m \Delta p}{J} \quad (5.6)$$

are also shown in Figure 5.13 [72, 73]. If the two thin layers of silicone rubber deposited on the active layer and on the porous layer are taken into account, the
width of the active layer of dense Matrimid could be evaluated by

$$\delta_m = \frac{\delta_m'}{1 + \frac{P_m}{P_S}} - 2\delta_s$$  \hspace{1cm} (5.7)

where $\delta_s$ (thickness of each of the two films of silicone rubber) is found to be $0.48 \pm 0.12 \mu m$ as measured by AFM and SEM (note that $\delta_s$ does not depend on the evaporation time, nor on the composition of the initial polymer solution, but rather on the method of silicone deposition, which is the same for all cases). This procedure leads to values for the thickness of the Matrimid dense layer that, as shown in Figure 5.14, are in good accordance with those directly measured by AFM. The values for $P_m$ and $P_S$ are taken from the literature [82, 83].

### 5.4.4 Mixed Matrix Membranes

Activated carbons (with high permeability and selectivity but with very inconvenient mechanic properties when used alone) are proposed as inorganic fillers in order to profit from their different adsorption capacities for polar and unsaturated compounds against nonpolar and saturated chemicals. Some characteristics of the used activated carbons are shown in Table 5.1. ABS has been selected as the polymeric matrix thus far because it is a copolymer that combines the good selectivity of glassy polymers with the high permeability of rubbery polymers [84, 85].

Both sides of the membranes have been studied by AFM and areas from $50 \times 50 \mu m$ to $0.5 \times 0.5 \mu m$ have been scanned. The obtained roughness are always higher for the upper side than for the down side. Moreover, $R_q$ of both sides of the

![Figure 5.13 Thickness of the active layer of Matrimid membranes 14/10 and 14/12 as a function of the evaporation time obtained by different methods.](image-url)
membrane increase with the content of active carbon when big areas are scanned. For scanned areas below $2.5 \times 2.5 \mu m^2$, roughness becomes independent of the AC content, which seems to confirm that there is always a layer of polymer over the activated carbon particles. This is also confirmed by phase contrast AFM, which shows that no heterogeneous viscoelasticity can be detected on the membrane surfaces. The constant roughnesses so reached are: 6.40 nm for the upper side and 3.50 nm for the under side of membranes containing AC2; and 4.89 nm for the upper side and 3.65 nm for the under side of membranes containing AC1.

The different roughness for both sides of each membrane can be attributed to the presence of pores ranging from 40 nm to 150 nm that should, probably, be due to the evacuation of solvent and appear more frequently, as can be observed in

![Figure 5.14](image)

**Figure 5.14** Active layer thickness obtained by taking into account the silicone layers as a function of the corresponding thickness as measured by AFM for the 14/10 Matrimid membrane.

### Table 5.1 Some characteristics of the activated carbons used.

<table>
<thead>
<tr>
<th></th>
<th>AC1</th>
<th>AC2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_w ) (m²/g)</td>
<td>3272</td>
<td>818</td>
</tr>
<tr>
<td>( V_m ) (cm³(STP)/g)</td>
<td>752</td>
<td>188</td>
</tr>
<tr>
<td>( \rho_f ) (g/cm³)</td>
<td>0.28</td>
<td>0.42</td>
</tr>
<tr>
<td>( d_p ) (Å)</td>
<td>Bimodal</td>
<td>Bimodal</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>22.4</td>
<td>70.0</td>
</tr>
<tr>
<td>( d ) (μm)</td>
<td>0.90 ± 0.08</td>
<td>4.5 ± 2.8</td>
</tr>
</tbody>
</table>

Some characteristics of the activated carbons used.
Figure 5.15, in the side open to air during casting. The surface density of these pores is 4.64 pores/μm² in the upper side and 1.92 pores/μm² in the under side for membranes containing AC2 and 7.52 pores/μm² and 2.20 pores/μm² respectively for membranes containing AC1. These pores appear more for membranes containing AC1 because AC1 particles have more porous volume (higher BET area, lower apparent density, as can be seen in Table 5.1). They are purely superficial as far as otherwise permeability should be much higher than actually found and selectivity much lower. Roughness also depends on the size of activated carbon particles, as far as AC1 has a mean diameter of 0.9 μm whereas AC2 has a mean diameter of 4.4 μm.

Transverse sections show carbon particles and agglomerates from 1 μm to 30 μm for AC1 membranes and 3 μm to 20 μm for AC2 membranes, when big scanned areas are studied. These sizes should correspond to aggregates up to 30 particles of AC1 and five particles of AC2. These sizes are within the optical microscopy range and can actually be seen by optical microscopy.

In higher resolution images, corresponding to small scanned areas, much smaller particles are revealed: ranging from 60 nm to 750 nm (with an average of 140 nm) for membranes containing AC1 and from 60 nm and 900 nm (with an average of 300 nm) for those containing AC2. It is worth noting that also these small activated carbon particles are bigger for AC2 than for AC1, as is the case with those shown in Table 5.1.

The biggest agglomerates detected are visualized directly in topography due to the process of fracture, while the small particles are detectable by using the phase contrast technique. Examples of the corresponding AFM pictures are shown in Figures 5.16 and 5.17. Higher carbon densities are found for AC2 containing membranes.
All transverse sections always show a good adherence and contact between the polymer continuous matrix and the activated carbon particles. No changes are seen in the viscoelastic properties of the polymeric phases in contact with carbon disperse phase.

Permeability and selectivity clearly increase with the content of active carbon, as shown in Figure 5.18. According to the analysis of Moore and Koros [55], such
A simultaneous increase in permeability and selectivity should correspond to an absence of modifications of the polymer properties in the interface with the inorganic filler, with no clogging of transport path though the filler particles and with a good adhesion of filler to polymer. This good adhesion agrees with the absence of voids around particle fillers seen in SEM and AFM pictures; and it allows an application of the Maxwell theory.

Acknowledgments

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Figure 5.18 Robeson chart for the CO\textsubscript{2}/CH\textsubscript{4} gases and the MMCM membranes obtained from ABS including AC1 and AC2 active carbon as filler (2–10% of AC1; 20–40% of AC2) showing the best fitting Maxwell predictions for the pure active carbons.
References


References