# The development of polymer membranes and modules for air separation

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**Abstract.** Technology of hollow fiber membrane and modules for air separation was developed. Hollow fibers from the polyphenylene oxide (PPO) having a diameter of 500 um were obtained. The permeability of the fibers by oxygen was up to 250 Ba, while the separation factor by $O_2/N_2$ was 4.3. The membrane module has been made by using these fibers and tested for permeability of individual gases.

## 1. Introduction

Membrane technology is the most rational method for producing gaseous nitrogen with a purity up to 99.5%. Plants based on this technology are produced worldwide. The performance of these plants can be up to 5000 Nm3 / h[1].

Henis and Tripodi [2] proposed to produce high-performance composite membrane covering a thin selective layer on a porous substrate. The properties of this membrane as well as other commercially available, permitted to develop the series of modules and industrial units for air separations.

In this paper the development of polymer membranes, accompanied by membrane modules, construction and their separation properties are being analyzed and discussed.

## 2. The analyzes and determination of the required geometric and operational characteristics

Initially, it was necessary to determine the separation surface of membrane module. For this purpose it was necessary to determine the geometrical parameters of the membrane and its packing density.

Membranes packing density ($m^2_{membrane\ surface}/m^3_{module\ volume}$) on the one hand should not be too low to present a so called "plug" mode in interfibrillar space. On the other hand a too tight packing leads to the formation of "dead" zones. In both cases, the separation performance decreases. Optimum packing density is stated by Li and al. in the range of 40-45% [3].

In order to optimize values of pressure losses the geometrical parameters of hollow fibers was chosen to be 500x350 microns.

**Table 1.** The input parameters and the results of calculation based on Davis Sandall method [4,5].

| Initial parameters | |
|---|---|
| Separation surface | 7,5 $m^2$ |
| Feed air pressure | 6bar |
| Feed air flow rate | 7.5 $nm^3$/h |
| Retantat flow rate | 3 $nm^3$/h |

| | |
|---|---|
| Residual oxygen concentration in the product nitrogen | 5% |
| Calculation results | |
| Desired membrane permeability to oxygen in the module | 0.32 $nm^3/(m^2 \cdot h \cdot bar)$ |
| Separation factor forO2/N2 | 3.92 |

In order to determine the required permeability of the polymer was necessary to determine the thickness of the selective layer. The thickness of the layer in the commercial polymeric (gas separation) membranes varies usually from 0.1 to 0.5 um[5–7].The dependence of the membrane permeability and the selective layer thickness has an inverse relationship. For selective layer thickness of 0.1-0.5 um required permeability values are of 11.4-57.1.

## 3. Selection of the polymeric material

The choice of the gas separation membrane such as the $O_2$ permeability coefficient accompanied be $O_2/N_2$ separation factor the attention was focused on permeability characteristics. Mechanical strength and operational characteristics are also the important parameters to be analyzed.

Despite the large number of polymeric materials developed for gas separation processes, the number of polymers used in industrial applications is quite limited. Results of the analysis of existing polymer materials are shown below in table 2.

**Table 2.** Existing membrane polymer materials

| Polymer type | Internal structure | Glass temperature, $^\circ$C | $O_2$permeability, Ba | $O_2/N_2$separation factor | Reference |
|---|---|---|---|---|---|
| Cellulose acetate (CA) | Glassy polymer | 187 | 1.3 | 5.0 | [8] |
| Polysulfone (PS) | Amorphous polymer | 190 | 1.0 | 7.5 | [9],[10] |
| Polyetherimide (PEI) | Glassy polymer | 216 | 1.1 | 7.6 | [5] |
| Polycarbonate (PC) | Glassy polymer | 150 | 1.5 | 4.8 | [11] |
| Polyimides (PI) | Glassy polymer | >240 | 1.1 | 7.2 | [12] |
| Polyphenylene oxide (PPO) | Glassy polymer | 218 | 15 | 4.5 | [13] |

Poly(phenylene oxide) became the best candidate suitable under requirements. The polymer has a permeability of about 15 Barrer, while the selectivity of O2/N2 is 4.5-4.6[13]. In this case, the thickness of the selective layer should be no more than 0.13 um.

## 4. Fabrication of hollow fibers

So called "dry-wet spinning" method (fig. 1)was used to obtain the hollow fiber membranes with a pronounced anisotropy (asymmetry).For this aim as the first step the state of PPO solutions was studied.
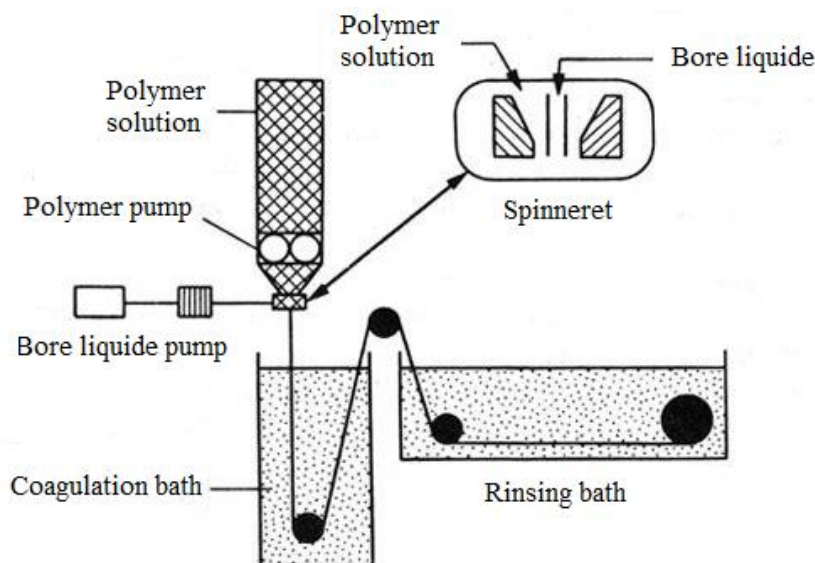
**Figure 1.** Apparatus for forming a hollow fiber gas separation.

Spinning process involves several stages:

1. The diffusion of internal precipitant molecules into the concentrated forming polymer solution. At the same time polymer coagulates (precipitates from solution) to form a solid phase.

2. A cross-diffusion of solvent molecules from the polymer solution into the internal nonsolvent. This speeds up the process of coagulation of the polymer and the formation of the porous structure of the fiber body.

3. Evaporation of the solvent molecules to the outer surface of the fiber into the air. The concentration of polymer on the outer surface of the fiber is increased and the formation of dense (selective) polymer layer is formed.

The polymer concentration in the spinning solution is important, since it affects the strength of the spinning solution exiting from spinneret. It should be sufficient to withstand the weight suspended in the air or immersed in the nonsolvent fiber. Furthermore, there are literature data that the selectivity of the membranes of the PPO by oxygen/nitrogen is higher, the higher the concentration of the initial spinning solution. However, a high concentration of PPO (18-20 wt.%) brought a great technological challenges.

Moreover, during forming select the optimal fiber spinning solution feed rate to a spinneret. The feed rate of bore-liquid into the fiber and the rate of filament winding onto a bobbin also controlled.

Quality control of the fibers was carried out by visual inspection of the surface and shape of fibers. With the help of micrographs of the fiber sections was evaluated their internal structure. Photomicrographs were made using a scanning electron microscope Phenom manufactured by FEI Company at maximum magnification 24000x.

As a result thin dense (selective) layer on the outer fiber surface was obtained (fig. 2).
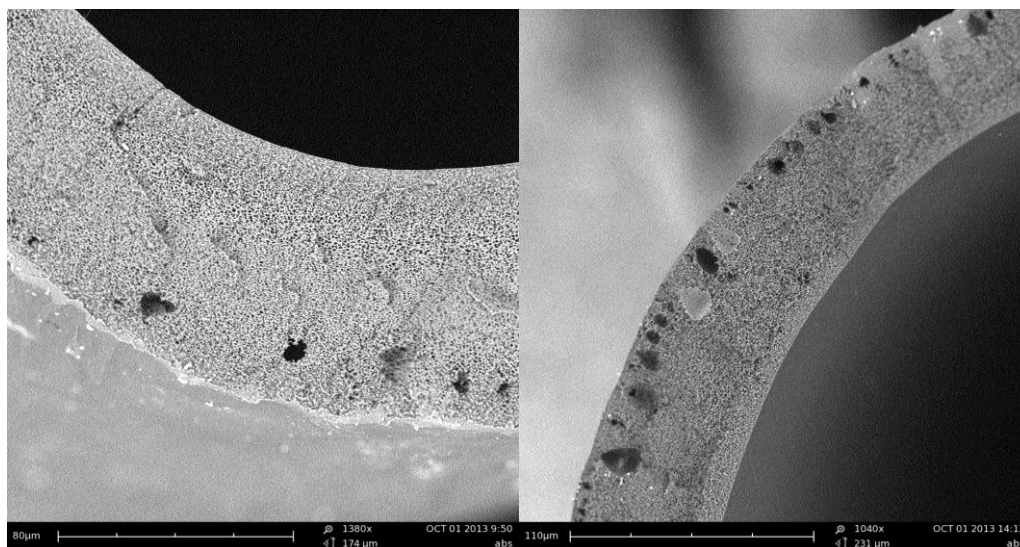
**Figure 2.** Micrographs of fibers sections

Fabricated fibers were selectively tested on individual gases (oxygen and nitrogen) permeability values. Average permeability of the fiber was 200-250 Ba, while the average selectivity by$O_2/N_2$ was 4.2. Defects in the surface of the fibers in the form of "furrows" hade no influence on the selectivity of the membranes.

The outer diameter of the resulting fiber was of 480 to 580 um and the thickness of the dense layer was of 0.1-0.2 um.

## 5. Fabrication of membrane module

Hollow fiber membrane module production procedure was carried out in several stages:

1) Module shell preparation;

2) Hollow fiber bundle preparation;

3) Compound tube sheets casting and ends cutting.

Aluminum was chosen as the material oamodule vessel. Fixing the end caps was accomplished by quickly removing clamps. (fig. 3)
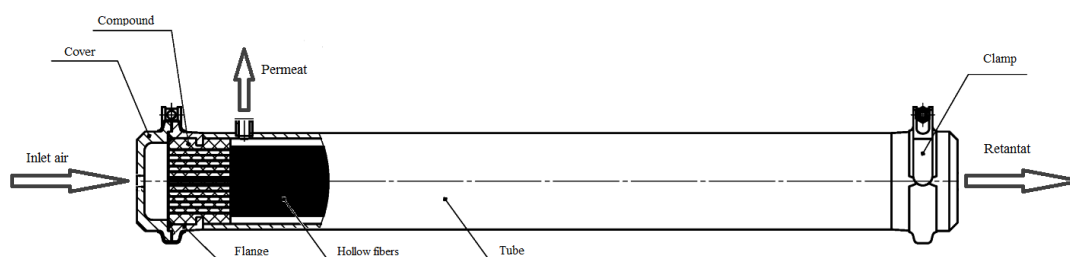


**Figure 3.** Hollow fiber module for air separation

For forming a common bundle of fibers used several bundles with fewer fibers. Each of these bundles was visually looked around for any visible defects. For each bundle were selected the few fibers randomly and tested for permeability to oxygen and nitrogen. Total number of fibers in the bundle was approximately 6,200pcs., and total separation surface was –4.1 m$^2$.

As the compound used industrially manufactured in Russia epoxydiane resin grade ED-20. After curing, the resulting epoxy matrix with fibers cut off at the ends so that the fiber lumen was open. For cutting use high cutting diamond blade. During the cut of epoxy matrix ends need be sure that there is no closing fiber lumens.

Fabricated module has been tested for both pure gases nitrogen and oxygen. The following data were obtained: oxygen permeability – 0.84 nm$^3$/(h·bar·module);separation factor of O2/N2 - 4.34.

## Conclusion

The technology of hollow fiber membranes manufacturing for the separation of air was presented in this paper. Hollow fiber membranes with outer diameter from 480 to 580 μm were obtained. The permeability of the fibers by $O_2$ was 200-250 Ba, the selectivity for $O_2/N_2$ was 4.2-4.5. The membrane air separation module has been made and tested for permeability for individual gases. Permeability of this module was 0.84 nm$^3$/(h·bar), while the selectivity was 4.34.

## References

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