THE CORRELATION OF GAS SEPARATION PROPERTIES OF NONPOROUS POLYMERIC MEMRBANES WITH ITS TOPOGRAPHY

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Introduction

The creation of high-performance membranes for gas separation is closely associated with different physical, chemical and material science problems [1]. Fundamental research of a structure and membrane functional properties is needed for the solution of those problems.

Now there are a variety of methods for studying polymeric membranes including both physical research and techniques based on a membrane behavior in different conditions and environments [2, 3]. Each of the methods with a variety of advantages and drawbacks has the specific application.

An important task is research the effect of surface topography of polymeric membranes on their gas transport properties, since one of the first stages in gas separation is a contact of gas mixture with a membrane surface.

A membrane surface morphology can be assessed by an atomic force microscopy (AFM) [4-6]. This method is suitable for an investigation of polymeric membranes, not only because of high lateral and vertical resolutions, but also its ability of gaining quantitative three-dimensional information about surface topography, a roughness, a height and a tilt angle of topographic structures without destruction of a soft polymer surface. It is worth noting is that it is necessary to emphasize characteristic parameters of different polymer surfaces during the AFM analysis. For example, for porous membranes, such parameters are porosity and a pore size distribution, and for non-porous membranes, such parameters are a surface structure and its roughness.

However, AFM imaging results alone are not enough to assess the impact of morphological features of polymeric membranes on their transport properties. For studying non-porous polymeric membranes, AFM imaging is useful to combine with a Daynes-Barrer method [7, 8].

In this paper, the AFM combined with the Daynes-Barrer method has been applied to investigate the non-porous polymeric membranes based on polysulfone (PS), which have been casted on substrates with a different roughness.

Experiments

The samples of the polymeric membranes based on polyamide were prepared as follows. The 25 wt. % solution of polyamide in dimethylformamide (DMF) was prepared and applied by curtain coating on glass substrates with a different roughness. One substrate was a standard glass plate, and the other was a glass plate treated with a finely dispersed abrasive. The formation of the polymeric membranes on the substrates was due to evaporation of the solvent under equilibrium conditions at 60 °C for 24 hours. The obtained samples were detached from the substrates in distilled water.

The investigation of the membrane surface morphologies was carried out using the AFM method by a scanning probe microscope SPM-9700 (Shimadzu, Japan). The maximum scanning field was 30 μm. The scans were data arrays with a dimension of 256 × 256 pixels. For checking purposes reproducibility, AFM scanning was carried out on different sites of the studied surfaces.

Before AFM scanning, fragments of the polymer samples were fixed to metal sample discs using adhesive carbon tabs (SPI Supplies Division of Structure Probe Inc., USA) and were cleaned of dust with ethanol.

Since polymeric membranes have a loosely-coupled surface structure, AFM scanning was performed using a tapping mode by silicon vibrating cantilevers POINTPROBE FMR-20 (Nano World Innovative Technologies, USA) with a stiffness coefficient of 1.3 N/m and

a typical tip radius of no more than 8 nm (guaranteed - no more than 12 nm), a tip height was from 10 to 15 microns. The experiments were carried out under ambient conditions. Automatic correction of linear noise was applied during scanning.

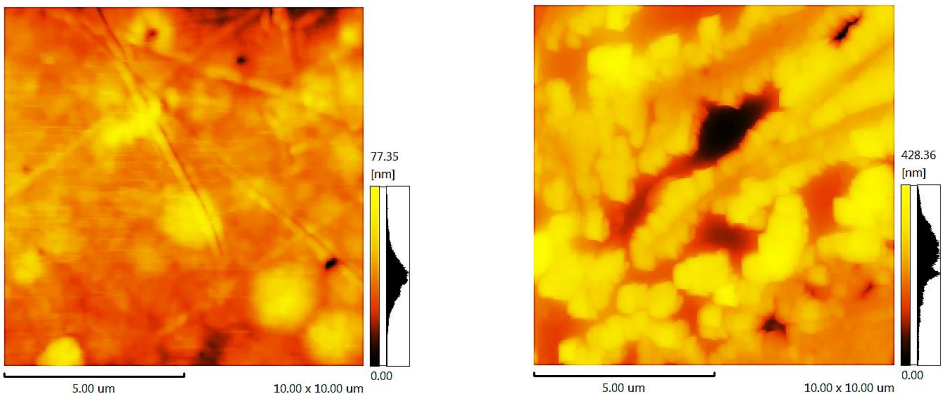
Digital imaging of the measurement results consisted in representation of topographic maps (heights are reflected by colors) and three-dimensional images. Processing of the obtained AFM images and their analysis were performed by a software SPM Manager ver. 4.02 (Shimadzu, Japan).

Gas transport properties of the polyamide membranes were determined by the Daynes-Barrer method in a constant-volume variable-pressure apparatus for gas permeability measurements at an operating pressure of 0.11 MPa. The permeate pressure variation was recorded with a sampling rate of 10 ms. Analyzed gases were helium (He) and methane (CH_4). Each single-gas test was repeated at least three times.

Physicomechanical properties of the membranes (namely, values of a breaking stress (σ) and elasticity (ε)) were determined on a universal test machine Zwick Z005 (Zwick Roell, Germany) at a pulling speed of 50 mm/min.

Results and discussion

According to the scanning results, an arithmetic average roughness height (R_a) and a mean roughness depth (R_z) were obtained. A base length (a length of a line used for unevennesses selection) was 10 μm (Table 1). These data indicate that the surface topography of the obtained membranes is directly proportional to the surface roughness of the substrates. At that, the surface character remains constant (Figure 1).



a) *b)*

Figure 1. The AFM images of the polyamide membranes casted on: a) the standard glass plate; b) the glass plate treated with an abrasive

The comparative analysis of the AFM results and the gas transport properties (Table 1) shows that the permeability coefficient (P) of the «rough» sample is almost 7 times more than one of the «smooth» sample, and the selectivity (α) of both sample remains constant. The growth of the permeability coefficient can be explained by the fact that a real working area (and, as a consequence, a contact area of a membrane with gas mixture) increases with increasing roughness of a membrane surface. The consistency of the membranes selectivity is confirmed by the fact that selective properties of non-porous polymeric membranes depend only on physicochemical properties of a polymer.

Table 1: Parameters of the polyamide membranes

Substrate	R_a, nm	R_z, nm	P, Barrer		α	σ, MPa	ε, %
			He	CH_4			
«Smooth»	7.07 ± 0.01	34.4 ± 0.01	4 ± 0.009	1 ± 0.007	4 ± 0.007	32.28	1.91
«Rough»	52.81 ± 0.02	207.1 ± 0.02	26.5 ± 0.14	6.8 ± 0.07	3.9 ± 0.005	30.03	1.74

In addition, it is worth noting is that the comparative analysis of the AFM results with the physicomechanical parameters shows that the breaking stress and the elasticity slightly decrease with increasing the roughness (Table 1).

Thus, it is possible to control a permeability coefficient of non-porous polymeric membranes without change of selectivity and physicomechanical properties by varying their surface roughness.

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