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Study of the surface structure of membranes and correlation analysis with the conformational state of the polymer

George Bibileishvili*, Liana Ebanoidze, Nana Gogesashvili, Mzia Kezherashvili, Liana Kuparadze, Manana Mamulashvili

*Academic Doctor of Chemical and Biological Engineering - e-mail 75bibileishvili@mail.com ORCID https://orcid.org/0009-0003-7712-2436

Engineering Institute of Membrane Technologies Georgian Technical University

Abstract

The paper presents a topographic study of the surface relief of the solidified phase of polymer composite membranes using scanning probe microscopy. The study was conducted using a high-resolution scanning probe and tunneling microscope, Certus Standart V, equipped with an NSG20-type cantilever, operating in non-contact mode. Tips with of radius of probe of 10 nm, 5 nm, 3 nm, 2 nm, and 1 nm were used, enabling nanoscale structural analysis.

Reducing the radius of the probe tip resulted in a consistent increase in spatial resolution, making it possible to perform detailed nanoscale structural characterization and to identify structural elements of different sizes and shapes. A correlation was identified between the conformational state of the polymer and the structural characteristics of the solidified phase. It was found that decreasing radius of probe enhances spatial resolution, which allows for more precise identification of nanostructural elements and inhomogeneities (heterogeneity).

Keywords: membrane, structure, morphology, relief, roughness, conformation

1. Introduction

Polysulfone and polyethersulfone membranes are widely used for the separation, purification, and concentration of substances. Owing to their high chemical and thermal stability, mechanical strength, and resistance to aggressive environments, these membranes play an important role in water treatment, pharmaceutical manufacturing, biotechnological processes, and the food industry [1-2].

The selectivity, specific performance, and fouling resistance of membranes depend on their structural and morphological characteristics, which are in turn determined by surface topography, pore size, and relief surface elevations and valleys (roughness) .

The conformational state of macromolecules (helical, extended, or aggregated forms) has a significant impact on the spatial organization of the polymer matrix (hard regions), including the three-dimensional arrangement of polymer macromolecules, their interconnection between crystalline and amorphous regions, and the resulting morphology (pore size, distribution, forme, shape relief surface elevations and valleys). In-depth (a comprehensive) analysis of the relationship between polymer conformation and surface morphological parameters remains an unsolved scientific challenge [3-6].

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A complete assessment of the structural and morphological characteristics of polyethersulfone membranes can be achieved using Scanning Probe Microscopy (SPM), which provides high-resolution imaging at the nanometric and subnanometric levels and delivers detailed information about the topography, morphology, and physical and mechanical properties of the membrane surface [7-12].

The aim of this research is to analyze the surface-relief topography of the solidified phase of polymer compositions of membranes using a scanning probe and tunneling microscope - Certus Standard V, equipped with an NSG20-type cantilever with tip radii of 10 nm, 5 nm, 3 nm, 2 nm, and 1 nm, and to correlate the conformational state of the polymer with the structure of its solidified phase

2. Research object

The object of research is selected as a polyethersulfone membrane.

2.1. Research materials and methods

Polymer compositions were prepared using a polymer (Polyethersulfone, PES), a solvent (Dimethylformamide, DMF), and organic additives (Polyethylene glycol, PEG), which ensured solution homogeneity, appropriate viscosity, and the required concentration.

Asymmetric, porous polyethersulfone (PES) membranes with a dense selective layer were fabricated by the wet phase inversion method (Non-solvent Induced Phase Separation, NIPS), which is based on the phase separation of a polymer solution due to diffusional exchange between solvent and non-solvent [13].

3. Experiment

The membrane structure was investigated using a Certus standard V scanning probe and tunneling microscope using an NSG20 type cantilever. Scanning was performed over an area of 13.047μm×13.002μm≈169.6μm^2 in non-contact mode. Tips with radius of probe of 10 nm, 5 nm, 3 nm, 2 nm, and 1 nm were used, whereby the spatial resolution varied and different structural elements of the membrane were identified.

Before measurement, the membrane prepared by the phase inversion technique was washed with deionized water, dried at 4°C, and mounted on a solid support.

During the scanning process, dynamic changes in surface forces and electrical signals were recorded by moving the probe cantilever tip over the membrane surface. After signal processing, the screen displayed 2D (flat geometry, two dimensions - length and width) or 3D (spatial

geometry, three dimensions - length, width, and depth) images of the surface high-resolution. A detailed analysis of the porous microstructure of the membrane was performed by scanning. The results of the study are presented in Tables 1, 2, 3 and 4 and illustrated in Figures 1, 2, 3, 4, 5 and 6.

Table 1. Characteristics of measurements using with radius of probes 10 nm, 5 nm, 3 nm, 2 nm, and 1 nm

Parameter	Characteristic		
	Distortion type	Roughness, Sa_{meas},	Cause of loss
10 nm	Expressive convolution	Strong topographic smoothing	Significant loss of nanorelief
5 nm	Moderate convolution	Is partially is decreasing	Moderate loss of terrain
3 nm	Weak Convolution	Good compliance	Little loss of relief
2 nm	Very weak convolution	Maximum Compatibility	Minimal loss
1 nm	Minimal convolution	Almost real terrain	Practically lossless

Table 2. Comparison of probes

Probe radius, nm	Distortion	Expansion
10 nm	Strong	Low
5 nm	Moderate	Average
3 nm	Weak	High
2 nm	Very weak	Very high
1 nm	Minimum	Maximum

Table 3. Values of the radius of gyration (Rg) and the measured average roughness (Sa_{meas},) using with radius of probe 10 nm, 5 nm, 3 nm, 2 nm, and 1 nm

№	Radius of inertia Rg, nm	Roughness (True) Sa, nm	Average roughness (measured) depending on the radius of probe used, Sa_{meas}, nm				
			10 nm	5 nm	3 nm	2 nm	1 nm
1	3	3.32	1.59	2.03	2.35	2.57	2.88
2	4	3.13	1.67	2.09	2.37	2.55	2.80
3	5	2.43	1.40	1.72	1.92	2.05	2.22
4	6	2.06	1.26	1.52	1.68	1.78	1.91
5	7	1.83	1.17	1.40	1.53	1.61	1.71
6	8	1.51	1.01	1.18	1.29	1.35	1.42

Table 3. Values of radius of gyration (Rg), measured average roughness (Sa_{meas}), and loss (absolute and relative) accuracy when using 10 nm, 5 nm, 3 nm, 2 nm, and 1 nm radius of probes

№	Radius of inertia Rg, nm	Roughness (True) Sa, nm	Probe radius, R_t, nm	Average Roughness (measured), Sa_{meas}, nm	Loss accuracy	
					Absolute loss, nm	Relative loss, %
1	3	3.32	10	1.59	≈1.73	≈52.1
2	4	3.13		1.67	≈1.46	≈46.6
3	5	2.43		1.40	≈1.03	≈42.4
4	6	2.06		1.26	≈0.80	≈38.8
5	7	1.83		1.17	≈0.66	≈31.1
6	8	1.51		1.01	≈0.50	≈33.1
1	3	3.32	5	2.03	≈1.29	≈38.9
2	4	3.13		2.09	≈1.04	≈33.2

3	5	2.43		1.72	≈0.71	≈29.2
4	6	2.06		1.52	≈0.54	≈26.2
5	7	1.83		1.40	≈0.43	≈23.5
6	8	1.51		1.18	≈0.33	≈21.9
1	3	3.32	3	2.35	≈0.97	≈29.2
2	4	3.13		2.37	≈0.76	≈24.3
3	5	2.43		1.92	≈0.51	≈21.0
4	6	2.06		1.68	≈0.38	≈18.4
5	7	1.83		1.53	≈0.30	≈16.4
6	8	1.51		1.29	≈0.22	≈14.16
1	3	3.32	2	2.57	≈0.75	≈22.6
2	4	3.13		2.55	≈0.58	≈18,5
3	5	2.43		2.05	≈0.38	≈15.6
4	6	2.06		1.78	≈0.28	≈13.6
5	7	1.83		1.61	≈0.22	≈12.0
6	8	1.51		1.35	≈0.16	≈10.6
1	3	3.32	1	2.88	≈0.44	≈13.3
2	4	3.13		2.80	≈0.33	≈10.5
3	5	2.43		2.22	≈0.21	≈8.6
4	6	2.06		1.91	≈0.15	≈7.3
5	7	1.83		1.71	≈0.12	≈6.6
6	8	1.51		1.42	≈0.09	≈6.0

4. Judging and Concluding the Research Results

The analysis showed that when using a 10 nm radius of probe, the smoothness of the surface relief is clearly visible in high-resolution 2D and 3D images (Figure 1), due to the convolution

(curvature, distortion) effect, which is due to the imperfect geometry of the probe tip used (the probe tip is not thin/sharp enough). The arithmetic mean (R_a) and root mean square (R_q,) values of surface roughness are relatively low - approximately 35-45% less than in the data obtained with a 1 nm radius of probe, which significantly limits the resolution of pores with diameters less than 30 nm. As a result of the convolution effect, the elevations of the polymer matrix are artificially enlarged, and the contrast of the image is reduced. The morphological picture of the surface is quite uniform. However, it still cannot fully reflect the microstructural differences caused by polymer conformation. At this level of resolution, it is impossible to accurately differentiate between both extended coil and collapsed globule conformations.

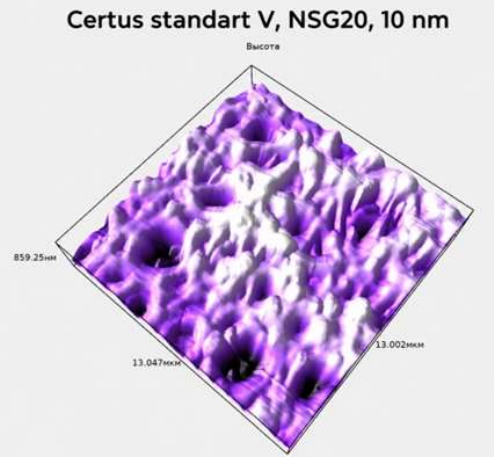

Figure 1. 3D image of the membrane surface obtained using Scanning probe microscope a 10 nm radius of probe

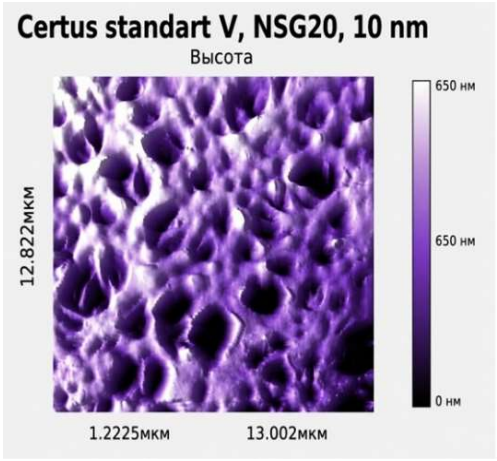

Figure 2. 2D image of the membrane surface obtained with Scanning probe microscope a 10 nm radius of probe

Reducing the probe tip radius to 5 nm revealed an improvement in lateral resolution, which provided relatively clear and detailed visualization of pores with sizes ranging from 15–60 nm. Under these conditions, a 15-2% increase in surface roughness (R_a, and R_q) parameters was observed compared to the data obtained with a 10 nm radius of probe, indicating a more accurate reflection of the surface topography. The pore distribution has become adequate and more consistent. However, structures smaller than 10 nm are still subject to partial convolution effects, which in this case is also explained by the geometric limitations of the probe. At this level of resolution, morphological differences due to the conformational state of the polymer are relatively clearly visible. In particular, samples with an expanded coil polymer globule conformation, obtained from a good solvent (χ<0.5, good solvent), are dominated by a structured system of medium-sized (25-50 nm) pores and increased roughness. In contrast, in the case of a compact conformation (χ> 0.5, poor solvent), the polymer chains are more tightly packed, which contributes to the formation of a denser structure, where small pores (<25 nm) predominate (sponge-like morphology).

By reducing the radius of probe to 3 nm, a significant improvement in surface relief detail at the micro- and nano-level is observed in the 2D image (Figure 2.), along with its clarity. The

roughness (R_a, and R_q) parameters increased by 25-45% compared to the 10 nm radius of probe, and proper identification of small pores with a diameter of 10-20 nm began. The morphological picture acquired a more pronounced asymmetric/gradient spatial organization (a more regular and ordered arrangement of pores and layers in space), which is typical for polymer membranes obtained by phase inversion. Here, a correlation with the polymer conformation was clearly revealed: the extended coil conformation of the macromolecules led to the formation of an open bi- or trimodal porous structure with well-developed nanofibrillar matrix elements and maximum pore size (R_{max}) values. In contrast, the partially collapsed globule promoted the formation of a denser layer - with a predominance of pores smaller than 15 nm and a 20-30% reduction in roughness.

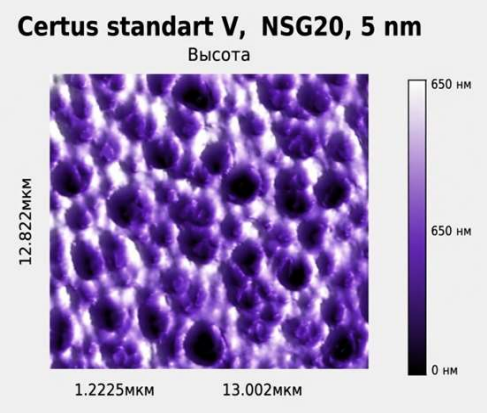

Figure 3. 2D image of the membrane surface obtained using Scanning probe microscope a 5 nm radius of probe

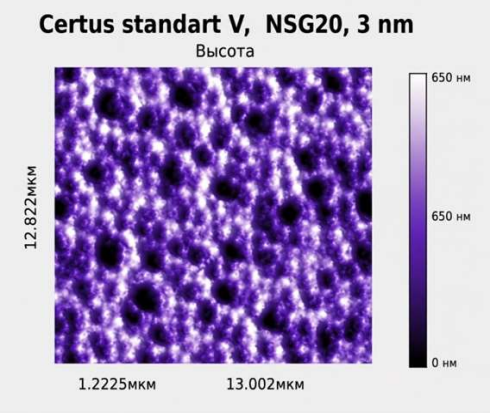

Figure 4. 2D image of the membrane surface obtained with Scanning probe microscope a 3 nm radius of probe

Comparative analysis of 2D images (Figure 3.) showed that the use of high-precision probes with a radius of 1-2 nm resulted in maximum surface detailing. Pores with a diameter of less than 10 nm and the smallest nanostructured elements of the polymer matrix were accurately and reliably distinguished (identified). The roughness parameters (R_a, R_q and R_{max}) reached their maximum values, and the pore distribution became more uniform and differentiated. It is at this level of resolution that the dependence of the membrane structure on the conformational state of the polymer becomes apparent, namely:

- In the case of the extended coil conformation of the polymer, a morphology with a wide pore distribution (from less than 10 nm to 60 nm) and maximum values of all thickness parameters roughness;
- Under the conditions of the compact conformation of the collapsed globule of the polymer, a denser and more uniform surface was formed, which is distinguished by a decrease in the number of pores less than 10 nm, a shift in the pore size distribution to the region less than 20 nm, as well as a 35–50% decrease in the roughness parameters (R_a, and R_q,) compared to the expanded conformation. These changes indicate rapid globular aggregation of polymer chains.

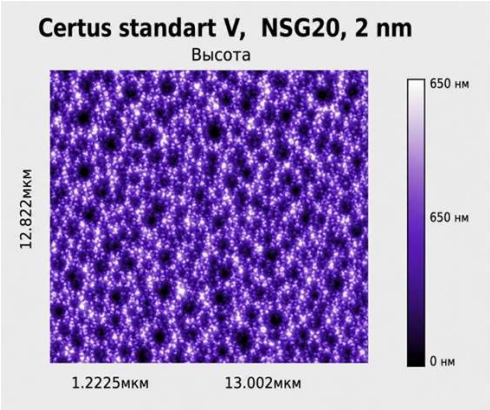

Figure 5. 2D image of the membrane surface obtained using Scanning probe microscope a 2 nm radius of probe

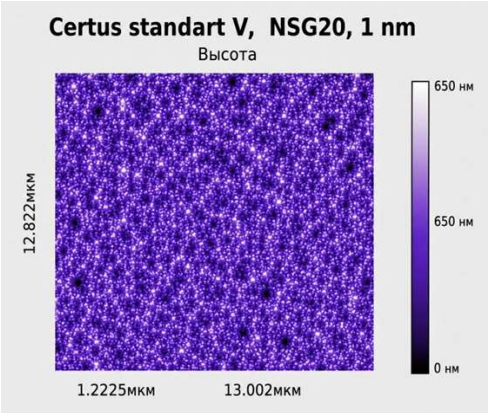

Figure 6. 2D image of the membrane surface obtained with Scanning probe microscope a 1 nm radius of probe

Thus, reducing the probe tip radius results in a substantial improvement in the spatial resolution of 2D and 3D images. A probe with a radius of 10 nm resulted in convolutional smoothing and a reduction in the roughness parameters, which limits the accurate identification of sub-nanometer (<30 nm) pores. Reducing the radius of probe to 3 nm, and especially to 1 nm, revealed the nanostructural features of the surface, maximum detailing of the roughness parameters (R_a, R_q, R_{max}), and a clear differentiation of the polymer conformational states (extended coil and collapsed globule) at the morphological level.

References

1. Rahma Tamime, Yvan Wyart, Laure Siozade, Isabelle Baudin, Carole Deumie, Karl Glucina, Philippe Moulin. Membrane Characterization by Microscopic and Scattering Methods: Multiscale Structure. Membranes 2011, 1, pp. 91-97. doi:10.3390/membranes1020091;
2. N. Ochoa, P. Prádanos, L. Palacio, C. Pagliero, J. Marchese, A. Hernández. Pore size distributions based on AFM imaging and retention of multidisperse polymer solutes: Characterisation of polyethersulfone UF membranes with dopes containing different PVP. Journal of Membrane Science, V.187, №1–2, 2001, pp.227-237.
3. G.Bibileishvili, M.Kezherashvili, N.Gogesashvili, L.Kuparadze, L.Ebanoidze, Z.Javashvili. Effect of the Temperature of the Non-Solvent on the Morphology of the Polymeric Membrane. European Journal of Scientific Research (EJSR), V.161, №1, 2022. pp.5-15. ISSN: 1450-216X/1450-202X;

4. Bibileishvili G.V., Gogesashvili N.N., Mamulashvili M.A., Javashvili Z.D. Study of the Effect of Polimer Additive on the Structure of Membranes Obtaind from Aliphatic Amides. Georgian Engineering News, V.93, №2, 2021. pp.107-109. ISSN: 1512-0287. https://doi.org/10.36073/1512-0287;
5. Bibileishvili G.V., Gogesashvili N.N., Gogiberidze I.B. Study of Issues of Structural Organization of Polymer in Acceptable Compositions of Microfiltration Membranes. Georgian Engineering News, V.98, №2, 2023. pp.55. ISSN: 1512-0287. https://doi.org/10.36073/1512-0287;
6. Bibileishvili G.V., Gogesashvili N.N., Kezherashvili M.G., Kakabadze E.G. Influence of Membrane Structure Forming Polymer Additive on Quantitative Characteristics of Porosity. Georgian Engineering News, V.95, №1, 2022. pp.130-131. ISSN: 1512-0287. https://doi.org/10.36073/1512-0287;
7. G.Bibileishvili, M.Kezherashvili, Z.Javashvili, Kh.Zakroshvili. Influence of the Composition of the Molding Solution on the Structure and Porosity of the Membrane. Georgia Chemical Journal, V.18, №1, 2018. pp.126-128. ISSN: 1512-0686;
8. G.Bibileishvili, M.Kezherashvili, Z.Javashvili. Structural and Topographical Survey of Polymeric Materials for the Creation of Industrial Composite Membranes. Georgian Chemical Journal, V.17, №1, 2017. pp.174-176. ISSN: 1512-0686;
9. G.Bibileishvili, M.Kezherashvili, Z.Javashvili, M.Madzgarashvili. Study of Surface Roughness of Modified and Unmodified Membranes. Georgia Chemical Journal, V.18, №1, 2018. pp.124-125. ISSN: 1512-0686;
10. G.Bibileishvili, M.Kezherashvili, N.Gogesashvili, N.Mumladze, E.Kakabadze, L.Ebanoidze, T.Butkhuzi, Z.Javashvili. Processing of Methods for Topographical and Structural Studies of a Polymeric Membrane Using an Electronic Scanning Probe Microscope. Georgia Chemical Journal, V.18, №1, 2018. pp.133-135. ISSN: 1512-0686;
11. Bibileishvili G.V., Kezherashvili M.G., Mamulashvili M.A. Effect of Different Solvents and Fore-Forming Agents on Morphology and Performance of Polyethersulphone Membrans. Oxidation Communication, V.47, №3, 2024. pp.534–542. ISSN: 0209-4541. https://scibulcom.net/en/journal/0209-4541/issue/2024-47-3/ https://scibulcom.net/en/article/ZrGfjjEAHMz45dN7qeWe;
12. Bibileishvili G.V., Gogesashvili N.N., Ebanoidze L.O., Kezherashvili M.G. Reasearch of the Influence of Organic Additives on the Structure of Polysulfone Membranes. Georgian Engineering News, V.93, №2, 2021. pp.110-112. ISSN: 1512-0287. https://doi.org/10.36073/1512-0287;
13. Bibileishvili, G.V., Kujawsk, M.W., Gogesashvili, N.N., Kezherashvili, M.G., Javashvili, Z.D., Ebanoidze, L.O., Kakabadze, E.D. Study of the Effect of Varying Amounts of Polyvinylpyralidone and LiCl on the Structure and Properties of Polyehersulphone Membranes. Oxidation Communications, V.48, №3, 2025. pp.992–999. ISSN: 0209-4541

https://scibulcom.net/en/journal/0209-4541/issue/2025-48-3/
https://scibulcom.net/en/article/0209-4541_2025_48_3_992-999;

მემბრანების ზედაპირის სტრუქტურის კვლევა სხვადასხვა სივრცითი გარჩევადობის პირობებში და კონფორმაციული მდგომარეობათან კორელაციური ანალიზი

გიორგი ბიბილეიშვილი*, ლიანა ებანოიძე, ნანა გოგესაშვილი, მზია კეჟერაშვილი, ლიანა ყუფარაძე, მანანა მამულაშვილი

*ქიმური და ბიოლოგიური ინჟინერიის აკადემიური დოქტორი, მთავარი მეცნიერი - e-mail 75bibileishvili@mail.com ORCID https://orcid.org/0009-0003-7712-2436

საქართველოს ტექნიკური უნივერსიტეტის მემბრანული ტექნოლოგიების საინჟინრო ინსტიტუტი

აბსტრაქტი

ნაშრომში წარმოდგენილია პოლიმერული კომპოზიციების გამყარებული ფაზის - მემბრანების ზედაპირის რელიეფის ტოპოგრაფიული კვლევა მასკანირებული ზონდური მიკროსკოპიის გამოყენებით. კვლევა ჩატარებულია მაღალი რეზოლუციის მასკანირებულ ზონდურ და ტუნელურ მიკროსკოპზე - Certus standart V, NSG20 ტიპის კანტილევერით, უკონტაქტო რეჟიმის პირობებში და ზონდის ნემსის რადიუსით 10 ნმ, 5 ნმ, 3 ნმ, 2 ნმ და 1 ნმ, რამაც უზრუნველყო სტრუქტურული ანალიზის წარმოება ნანომასშტაბიან დონეზე. ზონდის ნემსის რადიუსის შემცირებამ უზრუნველყო სივრცითი გარჩევადობის თანმიმდევრული ზრდა, შესაძლებელი გახადა ნანომასშტაბიან დონეზე სტრუქტურული ანალიზის ჩატარება და განსხვავებული მასშტაბის (ზომის ან ფორმის) სტრუქტურული ელემენტების იდენტიფიკაცია. გამოვლენილია კორელაციური კავშირი პოლიმერის კონფორმაციულ მდგომარეობასა და გამყარებული ფაზის სტრუქტურულ მახასიათებლებს შორის. დადგინდა, რომ ზონდის ნემსის რადიუსის შემცირება ზრდის შესაძლებელ სივრცით გარჩევადობას, რაც ნანოსტრუქტურული ელემენტებისა და არაერთგვაროვნებების (ჰეტეროგენულობების) დეტალური იდენტიფიკაციის საშუალებას იძლევა.

საკვანძო სიტყვები: მემბრანა, სტრუქტურა, მორფოლოგია, რელიეფი, სიმქისე, კონფორმაცია