



Using modern statistical methods to predict peak data for pore size values

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Summary

In this paper, a simple mathematical model is presented based on the changes in the pore size values of new membranes obtained from different concentrations of polymer systems PMIA/DMF/LiCl/PEG. Using modern statistical methods of organizing and planning experiments, a two-factor mathematical design is developed to predict the morphology of the membranes. The phase binodal diagrams of the PMIA/DMF/LiCl/PEG casting solutions were also studied. The physicochemical characteristics and surface morphology of the obtained new membranes were characterized using scanning probe microscopy.

Keywords: PMIA, membrane, phase inversion, binodal, planning.

Phase inversion processes, in which a liquid polymer film is transformed into a solid matrix, are widely used technologies for the preparation of polymer membranes [1,2,3,4,5]. The study of the relationship between the variable parameters of the inversion process and the final structure of the membranes remains a major challenge in the membrane technology process. In recent years, modeling efforts have been made to predict the final morphology of membranes by taking into account such factors as the composition of the casting solution, precipitation temperature, pressure, and separation rate [6,7,8,9,10]. Mathematical modeling allows us to investigate the relationship between the experimentally obtained pore size values and the phase inversion

conditions of membranes made from polymer compositions of different compositions. Subsequently, to predict the pore size and structure of the membranes.

Polyphenylene isophthalamide (PMIA) was used for the experiments. Different amounts of dried PMIA (PMIA content from 7% to 11% by weight) were placed in a 100 ml flask in a 5% solution of LiCl in DMF and the dissolution process was carried out by heating to 55°C with constant stirring with a magnetic stirrer. Polyethylene glycol (PEG was taken as 25% of the polymer mass) casting solutions were obtained in a similar manner. Table 1 shows the composition of the additive casting solutions.

PMIA	DMF	PEG
7	91,2	1,8
8	90	2
9	88,5	2,25
10	87,5	2,5

Table 1. Composition of polymer compositions containing PEG.

A binodal diagram was drawn for the resulting additive systems, which is presented in Figure 1.

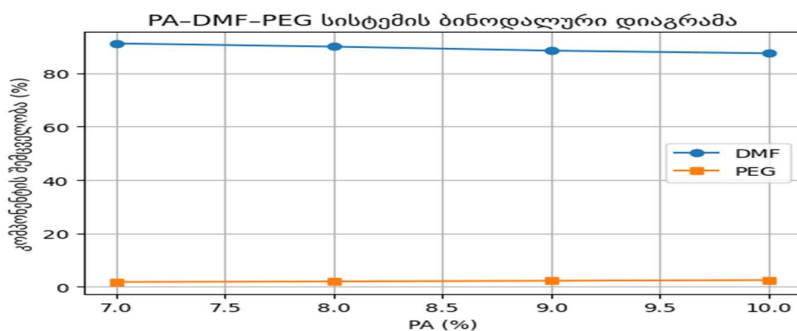


Figure 1. Binodal diagram of the PMIA/DMF/PEG system.

The figure shows that with increasing PMIA concentration, the DMF content decreases, while that of PEG gradually increases, indicating the tendency of the system to phase separation. The binodal curve shows the interaction of the components and changes in phase stability with increasing PMIA concentration. The resulting uniform, homogeneous, PMIA/DMF/ LiCl and PMIA/DMF/ LiCl/ PEG casting compositions were, after filtration and vacuum deaeration, applied to a polished glass plate (76mmx26mmx1mm) placed on a laboratory filler with the help of a stainless steel blade.

The precipitation procedures were carried out in a distilled water coagulation bath at 60°C. The obtained samples were washed with 60°C water for 6 hours and kept in the washing bath until the water-soluble substances were removed. The compositions of PMIA-compositions of different concentrations and the characteristics of the precipitated new membranes are given in the table.

PMIA, mass %	DMF mass %	PEG, mass %	membranes	The size of the pore, D μm	Bubble point pressure, Bar	Membrane porosity
7	93	-	P1	0,81	1	18 \pm 2
8	92	-	P2	0,59	1,36	20 \pm 3
9	91	-	P3	0,49	1,65	24 \pm 1
10	90	-	P4	0,42	1,92	29 \pm 2
7	91,2	1,8	P5	0,37	2,2	31 \pm 3
8	90	2	P6	0,34	2,35	42 \pm 1
9	88,5	2,25	P7	0,33	2,4	54 \pm 4
10	87,5	2,5	P8	0,31	2,6	70 \pm 3

Table 2. Characteristics of polymer compositions and obtained membranes

Table 2 shows that with increasing PMIA concentration, the pore size decreases. In particular, the pore size of the P1 membrane was 0.81 μm , while the pore size of the P4 sample became 0.42 μm , almost twice reduced. Then, in the samples obtained with the addition of PEG (25% of the polymer mass), the pore size gradually decreases again, and the pore size value of the P10 sample becomes 0.31 μm . The difference between the pore size values of the P7 and P10 samples is 0.5 μm . The membrane tests have determined the following performances. The results are given in Table 3.

Obtained membrane	Productivity l/m ² h, 0,1mPa
P1	800
P2	678
P3	528
P4	430
P5	396
P6	289
P7	205
P8	180

Table 3. Productivity of the obtained membranes

It has been established that increasing the PMIA concentration from 7% to 11% decreases the membrane performance, but improves the surface morphology and porosity of the membranes (Figures 3 and 4). The performances of membranes P7 and P8 obtained from dilute polymer solutions are relatively high, but due to the heterogeneity of the polymer framework, structural disorder, and globular formations, the number of pores is relatively small, which is also confirmed by micrographic images (Figures 2 and 3). The decrease in the performance of membranes obtained with the addition of polyethylene glycol (400) for samples P5, P6, P7 and P8 is due to the ability of PEG to increase the viscosity of the casting solutions, slow down the phase inversion process, narrow and form new pores, suppress the formation of macrocavities and increase the porosity of the membranes (Table 2). These factors explain the minimum value of the performance of the P8 membrane and the improved surface morphology (Figure 4).

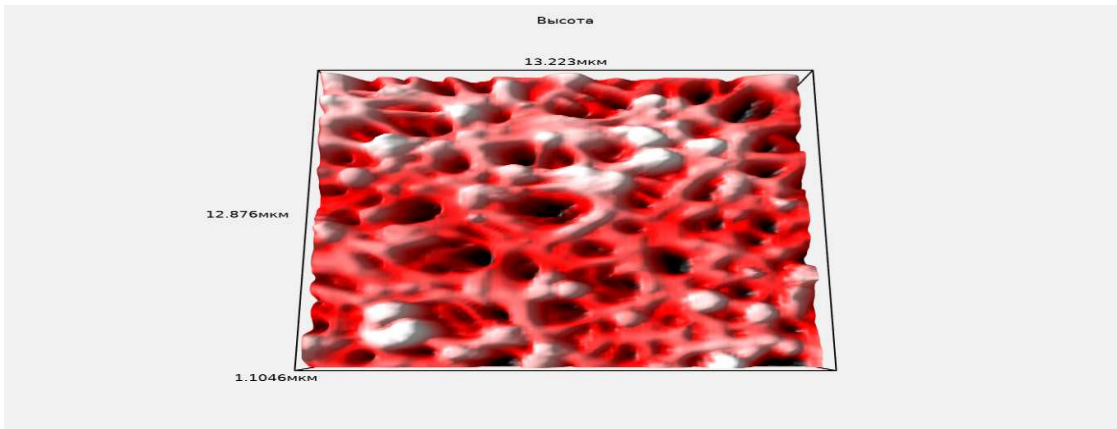


Figure 2. Micrograph of N2 membrane

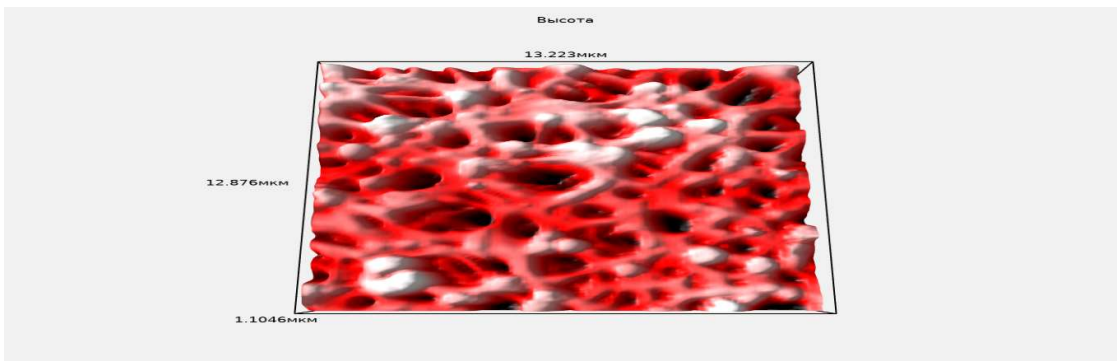


Figure 2. Micrograph of N3 membrane

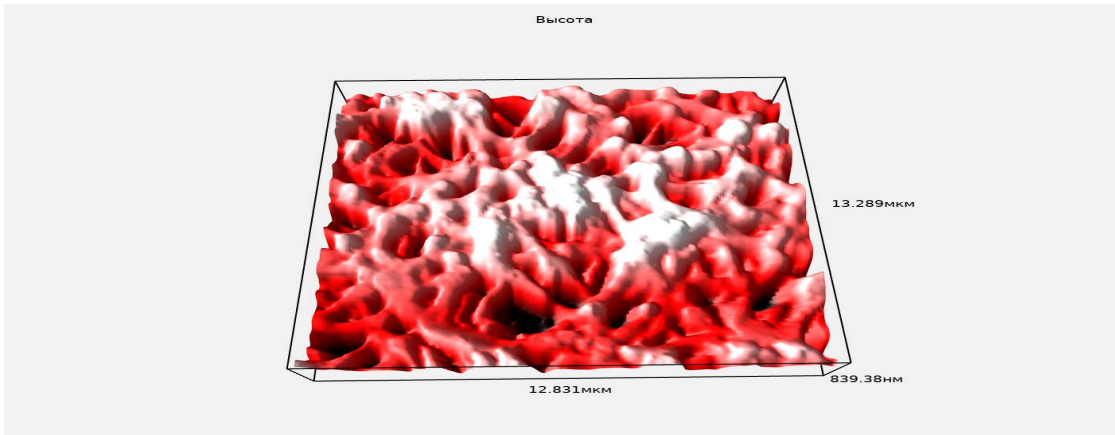


Figure 3. Micrograph of N4 membrane

Of the regression coefficients of the following linear equation was sought.

$$= b_0^1 + b_1^1 x_1 + b_2^1 x_1 \quad (1)$$

In the phase inversion experiments, the x_1 factor is a solution with different percentages, namely, 7% and 10%, and the x_2 factor is an additive with different percentages, namely, 0% and 25%. The pressure is denoted by y . The results of our experiments are given in the table (Table 1) as follows:

N	x_1	x_2	y
1	7	0	1
2	7	25	2,2
3	10	0	1,9
4	10	25	2,6

The center of the rectangle 0 is chosen as the origin of coordinates, whose coordinates are (1,5;12,5). First, changes were made to the upper and lower levels of both factors with the results obtained by trial and error for all their possible $N=2^2=4$ combinations. For this, appropriate key points were created: 1 ($x_1^{(1)}; x_2^{(1)}$), 2 ($x_1^{(2)}; x_2^{(2)}$), 3 ($x_1^{(3)}; x_2^{(3)}$), 4 ($x_1^{(4)}; x_2^{(4)}$), from the trial data (Table 3) $x_1^{(1)} = 7, x_1^{(2)} = 7, x_1^{(3)} = 10, x_1^{(4)} = 10, x_2^{(1)} = 0, x_2^{(2)} = 25, x_2^{(3)} = 0, x_2^{(4)} = 25$. These changes are graphically presented in Figure 4.

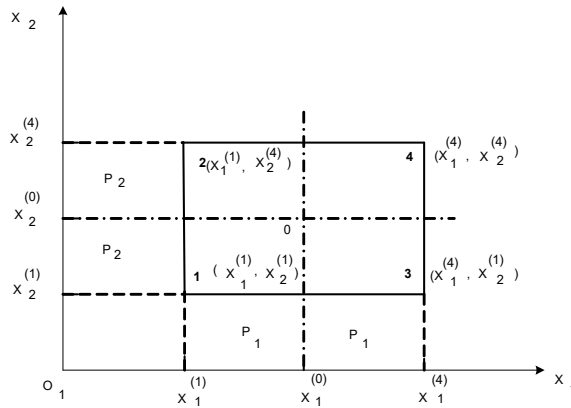


Figure 4. Calculation scheme.

The following sequence of steps has been performed: transition to dimensionless coded variables, first the coordinate origin was moved from point 0 to point 0₁ with the following coordinate transformation (Figure 1):

$$(x_1^{0_1}, x_2^{0_1}) \quad \text{ს} \quad x_1^{0_1} = x_1^0 + \frac{x_1^{(4)} - x_1^{(1)}}{2} = 7 + \frac{10-7}{2} = 8,5 \quad , \quad x_2^{0_1} = 0 + \frac{x_2^{(4)} - x_2^{(1)}}{2} = \frac{25-0}{2} =$$

$$12,5 \quad \text{and on the following scale: } \tilde{x}_1 = \frac{x_1 - x_1^0}{P_1} \quad \text{და} \quad \tilde{x}_2 = \frac{x_2 - x_2^0}{P_2} \quad , \quad \text{სადაც} \quad P_1 = \frac{x_1^{(4)} - x_1^{(1)}}{2} = \frac{10-7}{2} = 1,5; \quad P_2 = \frac{x_2^{(4)} - x_2^{(1)}}{2} = \frac{25-0}{2} = 12,5.$$

In this case, the square is obtained, in the new coordinate system (\tilde{x}_1, \tilde{x}_2) (coded coordinate system). In this system, the coordinates of the corner points of the square are: 1(-1,-1), 2(-1,+1), 3(+1,-1), 4(+1,+1): A linear regression equation in coded variables will generally have the form: $\check{y} = b_0 + b_1 \tilde{x}_1 + b_2 \tilde{x}_2$ (2) $\text{ს} \quad b_0 = \frac{\sum_{u=1}^4 \tilde{x}_{0u} y_u}{4} = \frac{y_1 + y_2 + y_3 + y_4}{4} = \frac{1+2,2+1,9+2,6}{4} = \frac{7,7}{4} = 1,925, \quad b_1 = \frac{\sum_{u=1}^4 \tilde{x}_{1u} y_u}{4} = \frac{-y_1 - y_2 + y_3 + y_4}{4} = \frac{-1-2,2+1,9+2,6}{4} = \frac{1,3}{4} = 0,325 \quad , \quad b_2 = \frac{\sum_{u=1}^4 \tilde{x}_{2u} y_u}{4} = \frac{-y_1 + y_2 - y_3 + y_4}{4} = \frac{1+2,2-1,9+2,6}{4} = \frac{1,9}{4} = 0,475$ The appropriate response values are calculated using the formula:

$$\check{Y}_N = b_0 + b_1 \tilde{x}_1^N + b_2 \tilde{x}_2^N = 1,925 + 0,325 \tilde{x}_1^N + 0,475 \tilde{x}_2^N \quad \text{ს} \quad N=1,2,3,4. \quad (3)$$

$\check{Y}_1 = 1,125; \check{Y}_2 = 2,075; \check{Y}_3 = 1,775; \check{Y}_4 = 2,725$ The difference between the experimental results and the theoretically obtained results is 12.5%.

To illustrate the method, the transition was made to the response report of a 9% solution. In this case, the planning center $(x_1^0, x_2^0) = (8,5; 12,5)$ is the same as it was before, only this time it will change $P_1 = \frac{x_1 - x_1^0}{2} = \frac{9-8,5}{2} = 0,25$, Therefore coefficient changes by 0,25 before \tilde{x}_1 .

P_2 remains the same that is \tilde{x}_2 remains the same. By inserting these quantities, we obtain the following regression equation: $\check{y} = 1,925 + 0,325 \tilde{x}_1 + 0,475 \tilde{x}_2 = 1,925 + 0,25 \times 0,325 + 0,475 = 1,925 + 0,08125 + 0,475 = 2,48125$. The result obtained by experiment is $y = 2,4$. $y - \check{y} = -0,08125$, difference between theoretical and experimental data is up to $\approx 9\%$.

It has been established that the use of modern statistical methods for organizing and planning experiments for membranes obtained from PMIA/DMF/LiCl/PEG solutions with concentrations ranging from 7% to 11% allows predicting the results of pressures with sufficient accuracy for peak pore size data of samples precipitated from any concentration of the casting solution without conducting experiments.

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თანამედროვე სტატისტიკური მეთოდების გამოყენება ფორის ზომების მნიშვნელობების პიკური მონაცემების პროგნოზირებისათვის

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ნაშრომში განსხვავებული კონცენტრაციის პოლიმერული სისტემებიდან PMIA/DMF/LiCl/PEG მიღებული ახალი მემბრანების ფორის ზომის მნიშვნელობების ცვლილებების საფუძველზე მოცემულია მარტივი მათემატიკური მოდელი. ექსპერიმენტების ორგანიზებისა და დაგეგმვის თანამედროვე სტატისტიკური მეთოდების გამოყენებით შედგენილია ორფაქტორიანი მათემატიკური გეგმარება მემბრანების მორფოლოგიის პროგნოზირებისათვის. შესწავლილია ასევე დასასხმელი ხსნარების PMIA/DMF/LiCl/PEG ფაზური ბინოდალური დიაგრამები. განსზღვრულია მიღებული ახალი მემბრანების ფიზიკურ-ქიმიური მახასიათებლები და ზედაპირული მორფოლოგია მასკანირებელი ზონდური მიკროსკოპის გამოყენებით.

საკვანძო სიტყვები: PMIA, მემბრანა, ფაზური ინვერსია, ბინოდალი, დაგეგმარება.