

Effect of the Temperature of the Non-Solvent on the Morphology of the Polymeric Membrane

George Bibileishvili

*Engineering Institute of Membrane Technology of Georgian Technical University
Tbilisi, Georgia*

Mzia Kezherashvili

*Coressponding author: Engineering Institute of Membrane Technology of Georgian Technical
University, Tbilisi, Georgia*
E-mail: kezherashvilimzia@gmail.com.
Tel: +995-593741384

Nana Gogesashvili

*Engineering Institute of Membrane Technology of Georgian Technical University
Tbilisi, Georgia*

Liana Kuparadze

*Engineering Institute of Membrane Technology of Georgian Technical University
Tbilisi, Georgia*

Liana Ebanoidze

*Engineering Institute of Membrane Technology of Georgian Technical University
Tbilisi, Georgia*

Zaza Javashvili

*Engineering Institute of Membrane Technology of Georgian Technical University
Tbilisi, Georgia*

Abstract

The effect of the temperature of the non-solvent on the morphology, pore size, the frequency of its distribution and high productivity membranes obtained on the basis of Poly [N, N'-(1,3-phenylene) isophthalamide] (PMIA) and polyethylene glycol (PEG) by wet method of phase inversion has been studied.

As a result of the research it was found that at the process of the phase inversion by variation of the temperature of the non-solvent the regulation of its viscosity and of the diffusion coefficient of solvent-non-solvent alloying the prediction of the morphology and structure of the film. It was established that at high temperature of solving of the polymeric composition in the solution such distribution of particle size and polydispersion index is attained which causes obtaining of the membranes with high frequency of pore distribution and of high productivity. The structure and morphology of the membranes was studied by scanning probe microscope. The monitoring of the distribution of the particles size and concentration in the polymeric composition was carried out by the analyzer for determination of nanoparticles size, mass and z-potential.

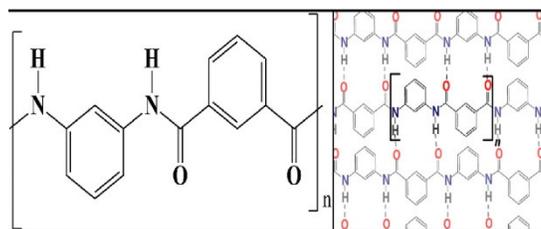
Keywords: polymer membranes, coagulation temperature, microfiltration, polymeric composition, nanomaterials.

1. Introduction

Because of the deficit of fresh water caused by rapid growth of population as well as by ecological problems and climate worsening the requirement on new innovative technologies increases which are connected with the purification, disinfection and regeneration of natural waters and sewage of various origin by membrane processes [1,2]. In comparison with other traditional methods, such as biological purification, adsorption, oxidation, the processes of membrane separation reveal the high power efficiency, low operating costs and, what is more important, they do not act negatively on the environment [3]. Micro-, ultra- and nano filtration and inverse osmosis is considered as the promising alternative which may solve successfully the topical problem of purification of natural waters and sewage, contaminated by different degree [4]. There are basic polymers for obtaining of micro- and ultrafiltration membranes: polysulfide (PS), poly(ether)sulfone (PES), polypropylene (PP), cellulose esters, polycarbonate (PC), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyvinylchloride (PVC), polybenzimidazole (PBI). In spite of a lot of the polymers and of the large option of the methods for preparation of the membranes from them, the search of the polymeric materials characterized by new, improved physical-chemical properties, is necessary for increase of membrane productivity, hydrophilic, thermal- and chemical stability, service life, temperature range and for extension of the areal of their use [5,6].

The goal of the presented paper involves the prediction of morphology and structure of the membrane in the process of obtaining of microfiltration membranes in coagulation bath by variation of non-solvent temperature, viscosity and by regulation of the diffusion coefficients of solvent-non-solvent on the basis of Poly [N, N'-(1,3-phenylene) isophthalamide] (PMIA) and polyethylene glycol (PEG). PMIA presents the synthetic polymer of aromatic polyamide group in which amide groups and the net of hydrogen bonds determine its high thermal stability (melting point $>371^{\circ}\text{C}$), chemical inertness against aggressive areas, mechanical characteristics and ability of film formation [7,8].

Figure 1: Chemical structure of PMIA.



Because of these facts the membranes, prepared on the basis of PMIA, are characterized by good physical-chemical characteristics. Amide bonds in PMIA provide the high surface free energy, which determines the hydrophilic of prepared membranes and high filtration properties [9,10].

There are researches in scientific literature where the preparation of the membranes of various type on the basis of PMIA were studied. In the work of Chun-E Lina, Jun Wang the preparation of ultrafiltration membrane is presented in which dimethylacetamide /dimethylformamide/glycerine was used for alloying PMIA [11]. Ren Huang obtained polyamide nano filtration asymmetric membrane by phase inversion by which the separation of Cr(VI) and chromium-containing paints is possible from the sewage [12]. Company Wang prepared nano filtration membranes by dry and wet methods where acetone and polyvinylpyrrolidone were used for polymer alloying [8]. The effect of non-soluble additives on polymer morphology and on separation efficiency was studied. In the work of Ian composition membrane PMIA/CO was prepared and studied which reveals the potential of water purification [13].

There are a number of factors in the process of membrane preparation by inversion which effect on the processes of mixing and precipitation of solvent-polymer-non-solvent: constitution of polymer composition, polymer concentration, various organic and inorganic compounds, solvent, non-solvent, composition of coagulation bath and temperature [14,15]. In the non-solvent induced phase method the selection of mentioned parameters determines the mechanism of phase separation, which, finally, defines the morphology of prepared membranes, pore sizes, frequency of their distribution (porosity) and specific productivity [16,17].

For optimization of the main characteristics of microfiltration membranes our investigation involves the selection of the main polymer, lies between the technology of membrane preparation and the control of its morphology.

We use the empirical way of research for revealing of the conditions where by variation of non-solvent temperature the regulation of diffusion coefficient of solvent-non-solvent allows the prediction of the morphology and structure of membrane film.

2. Experimental

2.1. Materials

Poly[N,N'-(1,3-phenylene)isophthalamide] was delivered by the Company DuPont (USA). Its chemical structure is presented in Figure 1. Its drying was carried out at 100⁰C over 12 hours. Polyethylene glycol (M_w=400), Lithium chloride -LiCl was delivered by the Company DuPont (USA). N, N'-dimethylformamide (DMF>99%) was delivered by BASF (Germany). Distilled water was used as a non-solvent in coagulation bath, electric conductivity of which comprised 5.2x10⁻⁴cm/m.

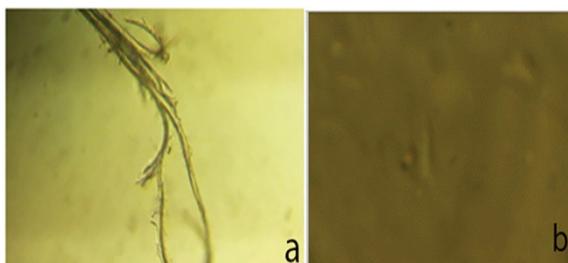
2.2. Preparation of the Composition for Membrane Dispensing

To obtain the membrane dispensed composition Poly [N, N'-(1,3-phenylene)isophthalamide] (PMIA) (9wt%), Polyethylene glycol (PEG-400) (25wt%), Lithium chloride (LiCl- (4wt%) and DMF (62wt%) are placed in 100 ml reaction flask, heated, in the conditions of constant mixing by magnetic mixer, at the temperatures of 25⁰ C 40⁰C, 55⁰C, 70⁰C.

2.3. Monitoring of Polymer Solving in Composition for Membrane Preparation

Monitoring of the process of PMIA solving was carried out by polarization-interference microscope (Biolar, Poland), with magnifying range 350-400 and equipped by mounted digital chamber with definition of 10.7 pixel which magnifies the image by a factor of 1.5-3. Mixing of the composition was continued till the total solving of the polymer up to total disappearance of the particles (Figure 2) and to obtaining of transparent homogenous solution.

Figure 2: Micro photographic image of the Poly [N, N'-(1,3-phenylene) isophthalamide] compositions before (a) and after (b) solving.



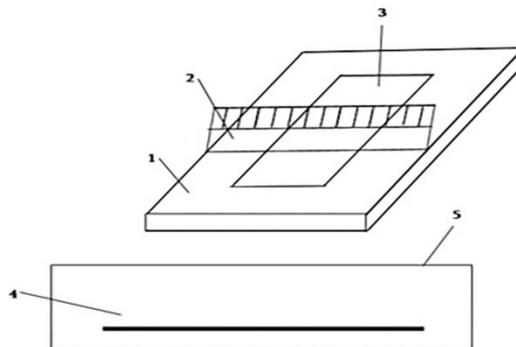
2.4. Determination of the Parameters of Solving of Polymeric Composition

For membrane preparation at 25⁰C, 40⁰C, 55⁰C, 70⁰C the parameters of polymer solving in the composition particle size, concentration and polydispersion index (PDI) were determined by analyzer (Zetasizer Nano Zen3690, Malvern Instruments, U.K). The solutions, prepared for every temperature were treated in ultrasonic apparatus (Unitra-Unima, UM-4, Olsztyn, Poland), (50 Hz) in water bath over 1 hour for increase of particle stability. Particle size, concentration and PDI were determined in the solutions of the following concentration: 100g/l, 25g/l, 10g/l and 5g/l.

2.5. Preparation of Test Samples of Plate Membrane

Dispensing compositions of obtained homogenous, transparent membranes are kept at 25⁰C for removal of air bubbles. Removal of suspended particles is carried out in the centrifuge (Centrifuge MPW-210, MPW Med Instruments, Poland). The solution is dispensed to polished glassy plate (0.076m × 0.026m × 0.001m), fixed on the filler, in the form of the layer of 0.1-0.2mm thickness, the correction of which is carried out by the stainless steel knife.

Figure 3: Principal scheme of the filler for membrane manufacturing: (1) polymeric composition, (2) stainless steel knife, (3) filler, (4) coagulation bath, (5) coagulant



The filler is placed in aqueous coagulation bath at the following temperatures: 25⁰C, 40⁰C, 55⁰C. As a result of coagulation the solid films are obtained (Membrane code: M10, M25, M40, M55) in accordance with the temperature. Obtained membranes are washed by water (60⁰C), kept in the washing bath for removal of soluble compounds. Monitoring of membrane washing was carried out in washing bath by measuring of the amount of Li⁺ and Cl⁻ ions, passed from membrane film to water, and of pH by means of ion meter (U-60, Belarus). Monitoring was continued as long as the water neutral reaction was fixed.

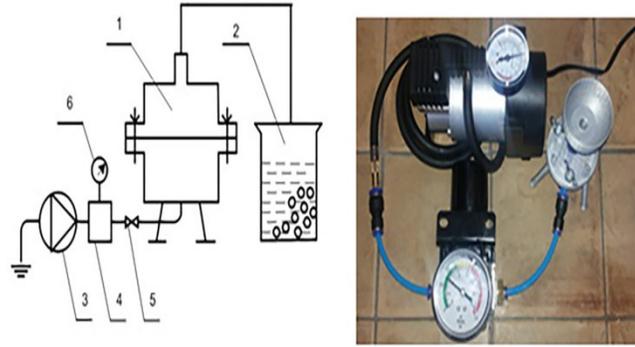
2.6. Characterization of Membrane Structure and Morphology

Membrane structure and morphology was studied by scanning probe microscope (SPM, Certus Standard V, Nano Can Technologies, Ltd, Russia). Relief of membrane surface, elevations and hollows, amount of pores per unit of area and pore sizes were determined by cantilever of NSG 20 type by needle radius of 10 nm, 5nm and 1nm. To study membrane relief and topography the scanning area comprised 20-20 μm, for pore size of 1μm-1μm and for porosity: 5μm-5μm. Universal software NSpec allows to treat the obtained data and to visualize as 2D and 3D images.

2.7. The Size of the Membrane Pores

Size of membrane pores was determined by the method of formation of bubble point in the Experimental Design Department of the Institute on the manufactured laboratory plant (MTSI-BP-4).

Figure 4: Principal scheme of the plant MTSI-BP-4: (1) cell, (2) bubble point fixing dish, (3) gas pump, (4) gas pressure regulator, (5) catch, (6) pressure gauge and laboratory plant.



Plastic details of the plant were fabricated by AutoCad2019 program at 3D printer (ULTIMAKER-2, Germany)) and connecting details-from the stainless steel (class 316). Pore size was defined by formula:

$$D_{max.} = \frac{0,81}{P} \quad (1)$$

where D_{max} is diameter of the pore, P -pressure, at which the bubble point formed.

2. 8. Performance Characterization

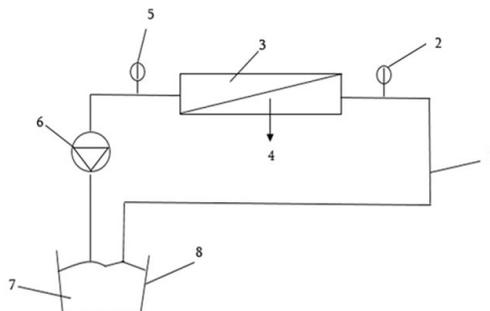
The membrane performances can be evaluated by their productivity (rate). Parameters like flux (J), can be calculated as:

$$J = \frac{V}{St} \quad (2)$$

Where, (V) is the total weight of the permeate passing through the membrane (L), (S) is effective membrane area and (t) is sampling time (h). Efficient area of the membrane comprised $0.00027m^2$. Filtrate purity was checked at turbidity measurer (Turb555IR, Germany).

Experiments for determination of specific productivity were carried out in the Experimental Design Department of the Institute on the manufactured laboratory plant (MTSI-JM-5).

Figure 5: Principal scheme of the device MTSI-JM-5 for determination productivity of the membrane: (1) circulatory contour, (2) manometer, (3) membrane pressure cell, (4) filtrate, (5) manometer, (6) pump, (7) processing fluid, (8) water tank.



3. Results and Discussion

3.1. Characterization of Polymeric Composition

At monitoring of solving in the process of preparation of dispensed membrane polymeric composition at the temperature at 25⁰C, 40⁰C, 55⁰C, 70⁰C after checking by polarization–interference optical microscope the solutions were studied by dynamic method of the light scattering.

Polymeric composition presents polydispersiti system, the particles size of which depends on the temperature of solution preparation, solvent nature and concentration. At mentioned temperatures, as a result of solving of membrane dispensed polymeric composition, the nanoparticle size particles were prepared and pure water flux of the membranes, obtained from this solution, are presented in Table 1.

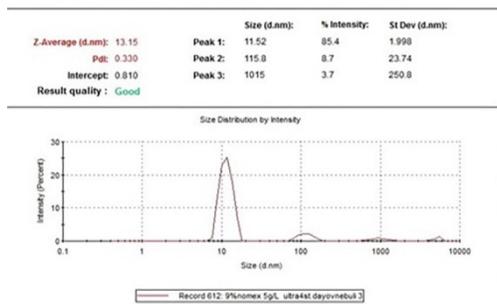
Table 1: Constitution of polymeric composition at solving at temperatures of 25⁰C, 40⁰C, 55⁰C, 70⁰C and water flux of membranes obtained at coagulant temperature of 20⁰C.

Temperature of preparation of polymer composition T ⁰ C	Z-Average (d nm)	PDI	coagulant temperature T ⁰ C	water flux L/m ² h
25	67.45	1	20	1200
40	57.12	0.9	20	1877
55	24.68	0.5	20	2188
70	13.15	0.33	20	2510

** Effect of coagulation bath was studied at 70⁰C for prepared composition.

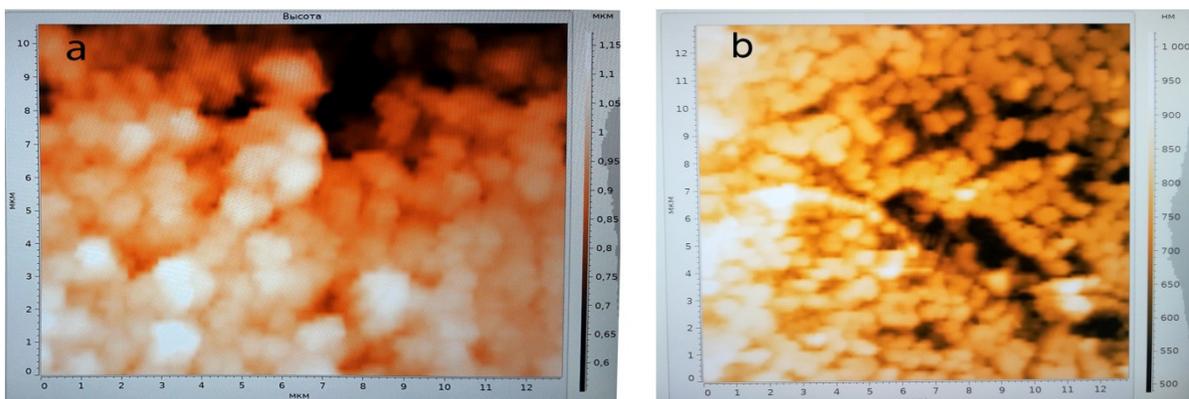
From the data of Table 1 it is evident that in the solutions particle size, PDI and the values of unit area filtration productivity of the membranes, prepared from the mentioned solutions, depend on the solving temperature: by increase of the solving temperature of polymeric composition the polydispersiti index reduces from 1 to 0.33, size of macromolecules from 67.45 nm to 13.15nm. Unit area filtration productivity of the membrane, obtained from the solution at 70⁰C exceeds the same values for membranes prepared at the temperatures of 25⁰C, 40⁰C, 55⁰C and comprises 2510 L/m²h. Size of nanoparticle of polymeric composition, prepared at 70⁰C, is given at Figure 6.

Figure 6: Size of nanoparticles of polymeric composition, prepared at 70⁰C, in accordance with intensity, defined by analyzer Nano Zen3690.



Membrane films, obtained by polymeric composition, solved at 25⁰C, 40⁰C, 55⁰C, 70⁰C, was studied by scanning probe microscope. On the Figure 7 the micrographic image of the surfaces of the membrane, obtained from the composition, prepared at 25⁰C and 70⁰C, are expressed. The surface of both samples presents the foam-like matrix. The formation of light color on the picture are interpreted as the surface and of dark color as the pores.

Figure 7: Micro photographic 2D images from scanning probe microscope for membrane surfaces: obtained (a) at 25⁰C and (b) at 70⁰C from prepared composition at 20⁰C of coagulation temperature



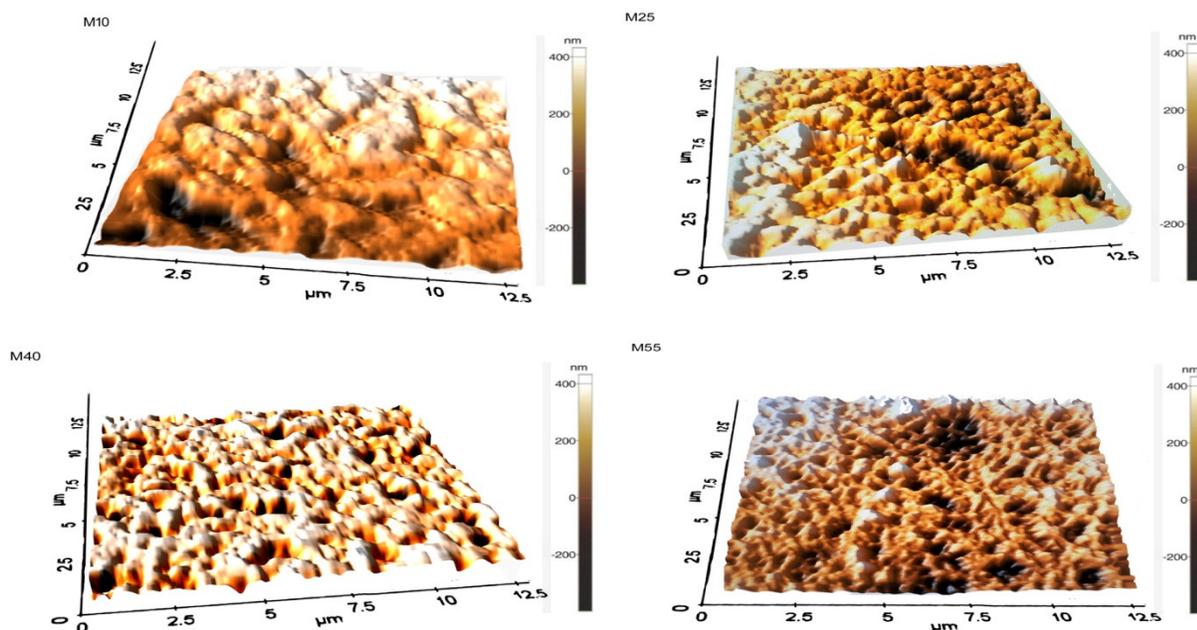
At sample **a** surface dark and light sections are non-uniformly distributed, light color dominates which is indicative of the small amount of the pores at the surface. Dark and light colors at the surface of sample **b** are uniformly distributed which is indicative of homogeneity and porosity of membrane surface. In polymeric composition, prepared at high temperature, reduction of particle size and PDI is caused by structural variations in the solution through the effect of 70⁰C temperature, which reduces the size of micro gel particles (disperse phase of the solution aggregated as macromolecules) and increases their amount in unit volume. Small sizes of micro gel particles and their distribution in the solution provided the large areas of pore formation (Figure 7, b) as well as high porosity which determines relatively high specific productivity of the membrane, obtained from the solution, prepared at high temperatures of solving.

3.2. Effect of Coagulation Temperature on Membrane Morphology

From 3D micrograph (Figure 8) of scanning probe microscope it is evident that topographic images of M10, M25, M40 and M55 membrane surfaces, obtained in coagulation bath at the temperatures of 10°C, 25°C, 40°C and 55°C, are distinguished. Sample surfaces are characterized by typical structure: “ridge and valley”. On membrane surface the light peaks (ridge) and dark peaks (valley) are distributed uniformly. Surface relief varies in accordance with coagulation temperature. At the surface of M25, M40 (Figure 8) membranes symmetry elements of the peaks increase and at the surface of M55 membrane light and dark peaks are distributed symmetrically at all area.

To obtain the membrane on the basis of PMIA, selected system: solvent-non-solvent is characterized by high mutual solubility: DMF/water comprises is 31.14. At the beginning of the process of phase inversion the system polymer-solvent is thermodynamically stable by the contact of which the variation of the stability is induced. By this variation between the liquid phase of small polymer content and liquid phase-rich by polymer, the equilibrium is established which depends on diffusion interchange between solvent-DMF and non-solvent-water (kinetically aspect) [18,19]. As a result of double-sided diffusion, the line of diffusion front goes after polymer coagulation front the, velocities of their motion depend on temperature, molecule size and viscosity of external medium, in which mentioned molecules diffuse (by Stokes-Einstein formula). At high temperatures at the boundary of the contact: coagulant-aqueous polymer-solvent the convectional streams are formed the efficiency of which is associated with solvent. Therefore, water molecules diffuse rapidly in the polymer solution. Ratio of non-solvent inflow is high in comparison with solvent drain [20]. Because of diffusion high velocity the process of phase separation and precipitation is accelerated, formation and duplication of structure of light pores is formed in great quantities (Figure 8, M55, Table 2).

Figure 8: SEM micrographic 3D image of PMIA membrane. Obtained at 10°C (M10), 25°C (M25), 40°C (M40), 55°C (M55) temperatures of coagulant



At coagulant low temperature DMF passes more rapidly to coagulation bath than the water diffuses in polymer solution. Therefore, the diffusion proceeds by low velocity which determines the hindrance of phase inversion [21]. Since the coagulation possibility of water is reduced, therefore, the solidification process is relatively slow, primary nucleus are formed in great quantities the great number of which causes depression of micro cavities. Therefore, obtained membrane is characterized by a small number of the pores (Figure 8, M25, Table 2).

3.3. Control of Regulation of Pore Sizes and Amount

Pore sizes and porosity of the membranes, obtained at coagulation temperature of 10⁰C, 25⁰C, 40⁰C and 55⁰C, are given in Table 2. As is evident, by increase of coagulant temperature the sizes of membrane pores enhance from 0.22 μm , to 0.38 μm and porosity – from 36.12% to 68.45%.

Table 2: Average diameter and porosity of PMIA membranes, obtained at the following temperatures of coagulant: 10⁰C, 25⁰C, 40⁰C and 55⁰C.

membrane code	M10	M25	M40	M55
diameter of the pore d, μm	0, 22	0, 28	0, 34	0,38
porosity %	36.12+0,47	22.34+0,28	48.23+0.38	68.45+0.18

Data of the table 2 and the micrographic images (Figure 8) of the membrane confirm the regulating effect of coagulant temperature in increase of porosity of obtained membranes. Because of low velocity of diffusion at low temperature in coagulation bath and slow process of precipitation the consistent structure membrane with less porosity is formed which is confirmed by obtained micrographic image of the membrane (Figure 8, M10) on which the pores are located irregularly.

This fact is consistent with the microphotograph of membrane surface (Figure 8, M55) in which pore dislocation is regular and their amount is considerably increased.

3.4. Unit Area Filtration Productivity of Obtained Membranes

The results of the testing of the membranes obtained in coagulation bath at various coagulant temperatures are presented in Table 3.

Table 3: The flux of the membrane samples obtained at the following temperatures of coagulant: 10⁰C (M10), 25⁰C(M25), 40⁰C(M40) and 55⁰C(M55).

Membrane Code	M10	M25	M40	M55
flux of pure water $L/m^2 h$ 0.1 MPa	640	2400	2777	3600

By increase of coagulant temperature in coagulation bath the membrane productivity enhances for water. For the membrane obtained at coagulant temperature 55⁰C the pure water flux is higher than the same value at 10⁰C, 25⁰C and 40⁰C, which is confirmed by membrane morphology (Figure 8, M55, Table 2). From these data it is evident that the membrane has a great number of the pores and narrow areal of distribution by pore sizes.

4. Conclusions

As a result of empirical research the conditions were revealed in which in the process of phase inversion the regulation of its viscosity and diffusion coefficient of solvent/non-solvent by variation of coagulant temperature allows the prediction of morphology and structure of membrane film.

It was established that by increase of the temperature of solving of polymeric composition such distribution of polydispersity index, nanoparticle size and concentration is attained which determines the increase of productivity of obtained membranes.

As a result of the research it was established that by increase of coagulant temperature in the process of phase inversion, by regulation of its viscosity and diffusion coefficient of solvent/non-solvent, the increase of pores, porosity and productivity of obtained membranes was attained.

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