

## **Determination of the Polymeric Membranes Pore Size Distribution by the Method of Capillary Flow Porometry**

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(Presented by Academy Member Ramaz Katsarava)

**An accurate determination of membrane pore size and pore size distribution is important for media used in filtration and separation processes. Ultrafiltration membranes were produced from the solutions of various concentrations of polysulfone and polyoxadiazole (solvent N-methylpyrrolidone). Membrane films were produced from the polymer homogeneous solutions by the phase inversion method with the use of Automatic Coating Machine (Memcast<sup>TM</sup>, Porometer NV). We varied the parameters, namely: cast thickness, casting speed, time of waiting. As a result, we produced the polymeric membranes of various thickness and porosity. Membrane pore sizes were determined with the use of the POROLUX<sup>TM</sup> 500 (Porometer NV), an instrument based on capillary flow porometry measuring pore size distribution and gas permeability. By means of the Porometer we measured the following properties of the membrane synthesized by us: the smallest, mean and bubble point pore sizes, air permeability, hydraulic flow, classification of pores according to sizes. For the samples where the POROLUX<sup>TM</sup> showed very small flow at the end pressure of 35 bar we used also the alternative method of Liquid Liquid Porometry (LLP). We researched the properties of the synthesized membrane such as trapping of the dispersed colloids and microorganisms containing in water and matching the optimal dimensions of the membrane pores. The obtained data is important for matching of the appropriate membrane for filtration process and for further research and modification of membranes. © 2020 Bull. Georg. Natl. Acad. Sci.**

Ultrafiltration membranes, capillary flow porometry, pore sizes distribution

At the beginning of the 21<sup>st</sup> century the mankind is faced with the global problem of provision of population with high quality food, water, energetic resources, protection of the environment, secondary use of raw materials and food supply, etc. In solving these problems the membrane

technologies play an important role [1-3]. Membrane technologies (microfiltration, electro-dialysis, ultrafiltration, reverse osmosis) allow to effect separation, concentration of liquid mixtures and their purification on the molecular level as well as separation of the valuable components and

secondary utilization of wastes. Membrane separation technology is used in production of food and pharmaceuticals, waste water treatment (waste water recycling, desalination, micro pollutants and organics removals, etc.) [4-6]. The membranes can act as barriers to a whole range of particles, both organic and inorganic, including bacteria, pollens, spores, pathogens and pesticides and even high molecular weight solutes, colloidal suspensions, and viruses.

To solve the above problems and tasks it is very important to create and research new, thermo- and chemically stable membranes, determine their parameters and thoroughly research filtration processes for forecasting the industrial processes. For the purpose of production of such membranes, it is required to match polymeric material containing various functional substitutes. Use of the membrane production methods will be based on the regular researches of "structure-feature" relation. Production of the new membranes with the predetermined structure and porosity is required for growing of permeability and selectiveness [7-10].

Nowadays the following techniques of measuring the pores dimensions are known:

- **(Mercury) Intrusion Porosimetry.** The pressurized mercury is forced into the cavities of the porous material. The penetration pressure allows to calculate the pore dimensions. Pore size range: 900  $\mu\text{m}$  – 3.6 nm.

- **Physisorption.** An inert gas ( $\text{N}_2$ ) kept at liquid  $\text{N}_2$  temperature is adsorbed on the surface of a porous solid material. This allows to calculate the surface area and dimensions of the pores of the material. Pore size range: 0.35 – 200 nm.

- **Capillary Flow Porometry.** An inert gas is used to displace wetting liquid from pores and gas flow rate is normally measured using flow meters. Pore size range: 300  $\mu\text{m}$  – 15 nm. Only measures through pores. Measured diameter of pore is the size at the most constricted part of the pore or pore throat.

- **Liquid-liquid Porometry.** The wetting liquid is displaced from pores by another liquid having higher density. The very low liquid flow rates are measured using a liquid flow meter or a microbalance. Pore size range: 0.5  $\mu\text{m}$  – 2 nm.

To research the pore dimensions of the membranes synthesized by us, their sorting out according to pore dimensions and gas permeability method of Capillary Flow Porometry (CFP) was used [11-13]. The method depends upon the capillary rise created by surface tension. This pressure (P) required for displacement of liquid from the pores is inversely related to the pores diameter (D) [11]. Dependence of these two values is expressed by Young–Laplace equation (1):

$$P = \frac{4 * \gamma \cos \theta}{D},$$

where  $\gamma$  is the liquid surface tension,  $\theta$  is fluid-membrane contact angle. When fluid wets surface,  $\theta=0$  and  $\cos \theta=1$ .

Diameter (D) corresponds to the most constricted part of the pores in the membranes (pore throat). The pressure at which the first flow occurs corresponds to the diameter of the largest most constricted pore, the so-called First Bubble point (FBP). The method of capillary flow porometry (CFP) allows to obtain the data of the smallest, mean pores and to classify the pores according to their dimensions.

During the pressure scan the pores with the same diameter but longer pore path can not be emptied at the pressure corresponding to their diameter (if the scan is too fast, there is not enough time to allow the gas to displace the wetting liquid through the pore length). Therefore the longer pores will be detected at higher pressures (later in time) and report smaller diameters than they actually possess. A more accurate measurement of the pore sizes is possible with the so-called pressure/step stability method. A data point is recorded when the defined stability algorithms are met for both pressure and flow. The porometer detects when a

pore empties at a certain pressure and waits until all pores of the same diameter are completely emptied before accepting the data point.

Two approaches of CFP method are as follows: the pressure/step stability method is often used in scientific research: pressure used for displacing the liquid from the pores is stabilized during some period of time and the corresponding data point is recorded when the defined stability algorithms are met for both pressure and flow. This method allows to take into consideration structural peculiarities of pores in case of equal diameter, but different shape and length. We pass to the next data point when the same diameter pores are empty (test liquid is displaced).

In the pressure scan method, gas is supplied continuously, without intermediate stabilization and the data points are recorded uninterruptedly. This method is used for rapid data recording, for example, for determination of the quality of a membrane filter and for testing the same porosity samples. If the materials structure is complicated and the pores are of different shapes and tortuosity, this method causes measurement inaccuracy; because of passing a longer trajectory, the pressure will be higher than required for displacing the liquid from the same diameter pores with gas flow. The data are received at higher pressure and correspond to smaller diameter pores [14-16].

In theory, many different wetting liquids can be used. In order to obtain good wetting of the sample, the wetting liquid should have the following physical properties: zero contact angle, low surface tension, low vapor pressure. Wetting liquids also should be chemically inert and should not causing swelling of the sample.

Thus, capillary flow porometry (CFP) method is a precise technique for measuring the membrane pores for a researcher intending to match a membrane for specific purpose and for further researches. In this work the pressure/step stability method is used for research of the properties of the pores in the membranes synthesized by us.

## Materials, Research Objects and Methods

Production of the membranes and determination of their properties were done in the Membrane Technologies Research Laboratory at the Agrarian and Membrane Technologies Institute, Batumi State University. Pilot cell and plant designed for research of macro- and ultrafiltration process were produced in the mechanic workshop of the Institute.

The material under research includes ultrafiltration membranes synthesized by us from thermally and chemically stable polymers, namely, polyoxadiazole and polysulfone, as well as N-methylpyrrolidone for preparation of polymer casting solution. N-methylpyrrolidone (NMP, 99%) dissolves these polymers well and mixes with water unlimitedly. We preliminarily dried the polymer at 100-110°C temperature up to constant weight, and dewatered the solvent by evaporation.

**Production of polymeric ultrafiltration membranes.** Based on the preliminary researches, we chose polyoxadiazole (POD), polysulfone (PSF), as raw materials for ultrafiltration membrane and N-methylpyrrolidone ( $T_{\text{boil.}} = 202^{\circ}\text{C}$ ) as a solvent for preparation of polymer casting solution. We loaded the polymer into a hermetically closed vessel and periodically mixed up to complete dissolution.

For research purposes we prepared a membrane casting solution with various concentrations of polymer (18%, 20% and 22%). We produced membrane films from polymers homogeneous solutions by the phase inversion method with the use of Automatic Coating Machine (Memcast™, Porometer NV).

After casting the membrane we waited for 20-30 seconds and then dipped the membrane film into coagulation bath (water temperature in the bath – 12-20°C). After 15-20 minutes we washed the produced membrane with running water and stored it in the distilled water before using. In the course of the experiments we varied the parameters, namely: cast thickness 200-250 μm, casting speed 1-2, time of waiting. As a result, we produced the

polymeric membranes samples: various thickness polymeric membranes of various porosity.

Membrane capacity ( $Q$ ) was calculated by the formula [17]:

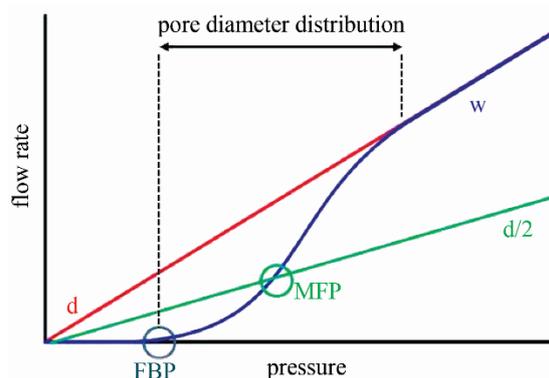
$$Q = \frac{V}{St},$$

where  $Q$  is the membrane capacity ( $l/m^2h$ );  $V$  is pure water volume ( $l$ );  $S$  is average space of membrane ( $m^2$ );  $t$  is filtration time ( $h$ ). Initial capacity was investigated in the pilot plant. Indications were taken in 10 minutes from starting of filtration at 0.15mPa.

The membrane pores sizes were determined with the use of the POROLUX™ 500 (Porometer nv), an instrument based on Capillary Flow Porometry to measure pore size distribution and gas permeability.

In case of capillary porometry, determination of the open-ended pores in the material investigated was provided by the pressure scan method: scanning of the material with gradually rising pressure and ejection of the test fluid from pores by compressed air (ASTM F-316 standard).

By means of porometer we measured the following properties of the membrane synthesized by us: the smallest, mean and bubble point pore sizes, air permeability, hydraulic flow, classification of pores according to sizes. The sample is submersed in Porefil™ (surface tension  $\gamma=16$  dynes/cm), the wetting liquid that fills all pores. The wetted sample is placed in a sample holder and is subjected to increasing pressure. When the gas pressure becomes larger than the capillary force that holds the liquid in the largest pores, the wetting liquid is pushed out. Further increase of pressure results in the opening of more pores and further increase of flow through smaller pores until all the pores are emptied. Wet run: the monitoring of the gas pressure applied and the resulting flow of gas when liquid is being expelled. Dry run: same test but without liquid in the pores (this is the gas permeability of the sample). Pore size distribution calculated by comparing the flows on the “wet” with the “dry” run.



**Fig. 1.** Exemplary measuring curves and resulting parameters in CFP ( $d$ =dry curve,  $w$ =wet curve,  $d/2$ = half-dry curve, FBP=largest pore, MFP=mean flow pore).

For the samples, where the POROLUX™ showed very small flow at the end pressure of 35 bar, we used an alternative method of Liquid-liquid Porometry (LLP) [18,19].

The measurement consists in the impregnation of the porous sample with a wetting fluid but, unlike CFP, the displacement of the wetting fluid is carried out by using a second fluid immiscible with the first one (called displacement fluid) at increasing pressure. As the displacement fluid we used water saturated with isobutanol. The samples for measurement were prepared by the following method: we put (water) wet samples in pure isobutanol to exchange the water. The samples in isobutanol were heated up to 35°C for about 3h. The samples were subsequently measured on the POROLIQU™ 1000 (Porometer NV).

The obtained data is important in finding the right membrane for the concrete filtration process, as well as for further research and modification of membrane.

Membrane porosity ( $P_t$ ) determines its permeability and selectiveness. Membrane value is determined with the formula [20]:

$$P_t = \frac{W_w - W_d}{\rho_w \times V},$$

where  $\rho_w$  is water density at room temperature ( $kg/m^3$ );  $V$  is membrane volume ( $m^3$ );  $W_w$ ,  $W_d$  are membrane mass in wetted and dry state respectively.

**Table. Maximum, minimum and mean pore size diameters for different membrane samples (Ft-fluoroplastic; POD-polyoxadiazole, PSf- polysulfone)**

Sample	Smallest pore size (um)	Main pore size (um)	Bubble point pore size (um)	Smallest pore pressure (bar)	Main flow pressure (bar)	Bubble point pressure (bar)	Bubble point Flow (l/min)	Pressure (bar)	Run time (min)	wetting liquid
Ft	0.652	4.485	10.65	0.980	0.142	0.060	0.293	0-1	3:17	porefil
Ft	1.498	4.418	9.416	0.427	0.1449	0.067	0.238	0-3	9:43	porefil
PSf	0.109	0.112	0.224	5.851	5.705	2.850	0.001	0-6	20:04	porefil
PSf	0.145	0.148	0.358	4.408	4.309	1.788	0.013	0-5.5	17:43	porefil
PSf	0.160	0.169	0.354	4.000	3.776	1.807	0.035	0-4	12:53	porefil
POD	0.152	0.155	0.213	4.200	4.119	3.000	0.020	0-5	16:39	porefil
POD	0.168	0.176	0.581	3.800	3.625	1.100	0,003	0-5	16:19	porefil
POD*	0.005	0.006	0.010	14.9	13.3	7.9	0.012	8-15	89:18	water-izobutanol
POD*	0.027	0.032	0.043	2.95	2.44	1.82	0.003	1-3	67:32	water-izobutanol

\* Membrane pores sizes were determined with the use of the POROLIQ 1000AQ (test liquid – isobutanol – water).

## Results and Discussions

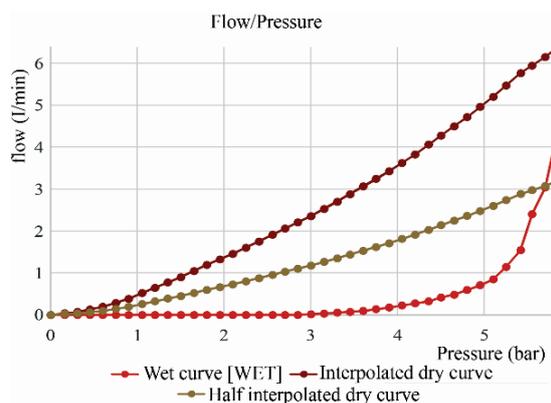
We measured dimensions of the pores of various membranes produced by us using the POROLUX™ 500 porometer. The results are demonstrated in the Table, where bubble point pore size corresponds to the maximum pore diameter, the smallest pore size – to the pressure where the dry curve meets the wet curve, the Main flow diameter- to the pressure where the wet and the half dry curve (obtained by dividing the flow of the dry curve by 2) meet. Half of the flow is through pores larger than the diameter.

Due to changes of the membranes synthesis parameters (casting knife with coating thickness 200 um and 250 um, casting rate, lag time, etc.) the values measured in the various membranes change within the following range:

Polysulfone membrane – minimum pore size is 0.07-0.267 um; main pore size is 0.08-0.597 um, maximum pore size is 0.149-4.004 um;

Polyoxadiazole membrane – minimum pore size is 0.005-0.2528 um; main pore size is 0.1554-0.574 um; maximum pore size is 0.2133-5.86 um.

Below we show the curve demonstrating the results of the analysis:



**Fig. 2.** Flow(ml/min) – pressure (bar) curve. Polysulfone membrane.

**Measurement of flux and rejection.** From the produced membrane samples we selected polyoxadiazole and polysulfone membranes and investigated their capacity indexes and selectivity through the device designed in the Institute. Fluoroplastic (pores size 4.48 um) was also used as a support layer for polyoxadiazole and polysulfone membranes.

We researched selectivity of the chosen membranes. We performed the experiments with drinking water, sea water filtration and established the membranes ability to retain 88-90% of the particles suspended in water.

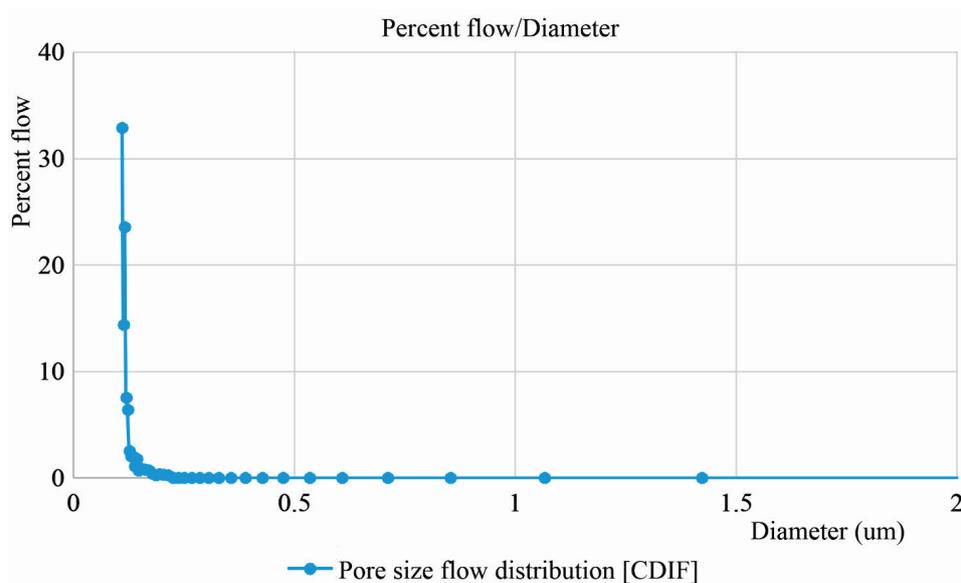


Fig. 3. Flow(%) – diameter (um) curve. Polysulfone membrane.

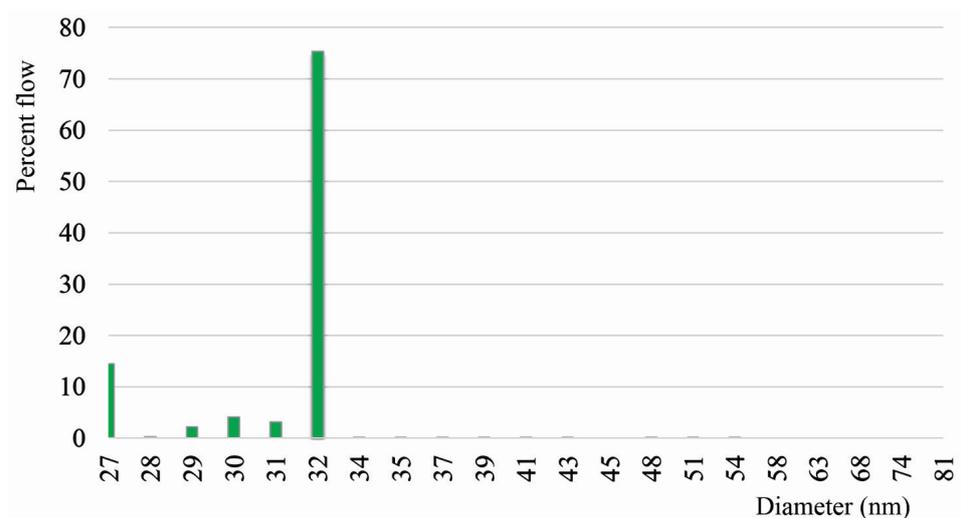


Fig. 4. Pore size (nm) flow distribution. POD\* membrane.

Membranes' ability to disinfect water was proved: the microbiological analyses results showed that after filtration coli-index corresponds to the permitted norm (E-coli <3).

## Conclusion

- Ultrafiltration membranes are produced using polysulfone and polyoxadiazole polymeric materials;
- Their properties, namely membrane thickness, porosity, pore sizes, productivity are researched;

- Selectivity of the chosen membranes is investigated. The membranes' ability to retain the suspended particles in water, as well as possibility of microbiological disinfection of water using the membranes are established.

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## ფიზიკური ქიმია

# პოლიმერული მემბრანების ფორების ზომების განაწილების განსაზღვრა კაპილარული ნაკადის ფორომეტრიის მეთოდის გამოყენებით

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(წარმოდგენილია აკადემიის წევრის რ. ქაცარავას მიერ)

მემბრანების ფორების ზომების და ფორების ზომების განაწილების ზუსტი განსაზღვრა მნიშვნელოვანია ფილტრაციულ და სეპარაციულ პროცესებში. ულტრაფილტრაციული მემბრანები მიღებულია სხვადასხვა კონცენტრაციის პოლისულფონის და პოლიოქსადიაზოლის ხსნარებიდან (გამხსნელი N-მეთილპიროლიდონი). მემბრანის ფორები მიღებულია პოლიმერის ჰომოგენული ხსნარიდან ე.წ. ფაზათა ინვერსიის მეთოდით და ფორების ჩამოსხმელი ავტომატური მოწყობილობის გამოყენებით (Memcast™, Porometer NV). პარამეტრების, კერძოდ დასხმის სისქის, დასხმის სიჩქარის, დაყოვნების დროის ცვლილებით ჩვენ მივიღეთ სხვადასხვა სისქის და ფორების პოლიმერული მემბრანები. მემბრანის ფორების ზომები განსაზღვრულია ფორომეტრის POROLUX™ 500 (Porometer NV) გამოყენებით, ხელსაწყოზე, რომელზეც ფორების ზომების და აირგამტარობის განსაზღვრა ემყარება კაპილარული ფორომეტრიის (CFP) მეთოდს. ფორომეტრის გამოყენებით განსაზღვრეთ ჩვენ მიერ სინთეზირებული მემბრანების შემდეგი თვისებები: უმცირესი, საშუალო და უდიდესი ფორის ზომები (bubble point pore sizes), აირის გამტარობა, ჰიდრაულიკური ნაკადი, ფორების ზომების მიხედვით განაწილება. ნიმუშებისთვის, სადაც ფორომეტრმა აჩვენა მცირე ნაკადი, ჩვენ გამოვიყენეთ სითხე-სითხის ფორომეტრიის მეთოდი (LLP). ჩვენ აგრეთვე გამოვიკვლიეთ სინთეზირებული მემბრანების უნარი შეაკავოს წყალში დისპერსირებული კოლოიდები და მიკროორგანიზმები და შევარჩიეთ მემბრანები ოპტიმალური ფორების ზომებით. მიღებული მონაცემები მნიშვნელოვანია ფილტრაციული პროცესებისთვის მემბრანების შესარჩევად, აგრეთვე შემდგომი კვლევებისა და მემბრანების მოდიფიცირებისათვის.

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