

INFLUENCE OF POLYMER MOLAR MASS ON THE PROPERTIES MEMBRANES WHIT GRAPHENE OXIDE

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Abstract: The aim of the study was to assess the influence of the polymer molar mass on the properties of polymeric membranes produced with the addition of carbon nanostructures (commercial graphene oxide, GO). The membrane support layer was made from polysulfone (PSU) dissolved in dimethylformamide (DMF). The polymer matrix was formed from polyvinylidene fluoride (PVDF) dissolved in dimethylacetamide (DMAC). PVDF, serving as the base polymer, was purchased in two different physical forms, i.e. granules with a molar mass of 530,000 g/mol and powder with a molar mass of 534,000 g/mol. The membranes were prepared via wet phase inversion, with or without the addition of GO to volume of the polymer matrix. The experiments helped to determine the thickness, tensile strength and contact angle of the produced membranes. Hydrodynamic studies allowed calculating the volumetric permeation flux and total resistance of both the reference membranes and the membranes containing GO was evaluated using a laboratory OSMONICS KOCH ultrafiltration unit.

KEYWORDS: ULTRAFILTRATION, HYDRODYNAMICS, GRAPHENE OXIDE, POLYMERIC MEMBRANES

1. Introduction

Membrane processes are especially useful for removing contaminants from dilute aqueous solutions. The quality of drinking water and, on the other hand, reducing the contamination of wastewater released into the environment are among the most important problems facing the world today. Scientific research concerning this subject is oriented towards improving the efficiency and selectivity of membranes with simultaneous reduction in energy consumption [1-2]. Recently, membranes containing various nanoparticles and carbon based nanomaterials have become increasingly popular thanks to the growing availability of these materials and their mechanical and chemical endurance. Nanoadditives in the form of carbon nanotubes, graphene oxide or graphene itself have numerous applications [3-9]. Graphene has been tested as an additive to the membranes intended for desalinating seawater, producing drinking water and separating gases [10-12]. Unfortunately, the production of graphene is still very expensive, thus its derivative, graphene oxide, has become more common. Graphene oxide is much cheaper and can be laboratory produced via modified Hummers' method. It is a method of oxidizing pulverized graphite into graphite oxide. KMnO_4 is used as the oxidizing agent [13]. Graphene oxide has amorphous structure and its properties are dependent on the type and distribution of functional groups containing oxygen such as the hydroxyl, carboxyl and epoxy group. It can be dispersed in water and organic solvents as well as in various polymeric and ceramic matrices, improving their mechanical and electrical properties [14-15]. In most cases, the membranes containing graphene oxide are used as selective partitions for the separation of gases and liquids [16-19]. The application of nanoparticles causes certain technical problems, for example, it is hard to control the distribution of particles and pore sizes in the membranes containing graphene and its derivatives. Usually, however, the main problem lies in obtaining proper structure of the material containing carbon nanoparticles and determining possible mechanisms of the transfer of water through the membrane [6-8].

Polyvinylidene fluoride is widely used in membrane research because of its special properties such as high thermal stability, good chemical resistance and the ability to form membranes [20]. More and more often new modifications of membrane compositions are being introduced to improve their hydrophilicity and at the same time to prevent fouling without changing other process parameters [21].

The aim of the study was to establish the proper composition of polymeric membranes produced with the addition of carbon nanoparticles in the form of graphene oxide (GO) so that they would be stable and mechanically durable. The function of GO particles distributed throughout the volume of the polymer was to increase the permeation of water through the membrane. The study was also aimed at evaluating the influence of the polymer molar mass (and hence its structure) on the membrane preparation process as well as the membrane hydrodynamics during ultrafiltration.

2. Preparation of the membranes

The membranes were produced via the phase inversion method with or without a polysulfone (PSU) support. The active layer of the polymer matrix was made of polyvinylidene fluoride (PVDF) dissolved in dimethylacetamide (DMAC). Polyethylene glycol (PGE) was employed as a plasticizer. Afterwards, the membranes were enriched with graphene oxide (GO) nanoparticles distributed throughout the whole volume of the polymer. All the reagents were purchased from Sigma Aldrich (USA).

2.1. Reference membranes – polymer matrix without GO

15 g of PVDF in the form of granules (molar mass 530,000 g/mol) or powder (molar mass 534,000 g/mol) were dissolved in 80 g of DMAC (molar mass 87.12 g/mol) through magnetic stirring for 24 h at ambient temperature. In order to improve its mechanical properties and enhance its plasticity and porosity, the polymer matrix was enriched by adding 5 g of the plasticizer (PGE) having a molar mass of 200 g/mol. In this manner, a polymer matrix with the reference composition was prepared. Then, a 250 μm thick membrane was formed from the matrix with an Elcometer 3530 casting knife. The membrane so produced was conditioned in distilled water for about 24 h. As a result, porous and symmetrical membranes were obtained (Mem1 and Mem2). Their composition is summarized in Table 1.

To improve the mechanical properties of the reference membranes, a support layer was applied, made of polysulfone (PSU) with a molar mass of 60,000 g/mol dissolved in dimethylformamide (DMF). The support layer was formed with a casting knife and then dried under ambient conditions for about 30 min. Afterwards, the active layer, made from PVDF with one of two different molar masses, was formed on the support layer, and thus double-layer membranes (Mem1*, Mem3) were obtained. The procedure for preparing the membranes with a support layer is schematically shown in Fig. 1.

As it turned out, forming multilayer membranes was not as easy as it initially seemed. Several obstacles were encountered while combining the active layer with the support. Unfortunately, the active layer containing granules of polyvinylidene fluoride ($M = 530,000\text{g/mol}$) did not form a homogeneous membrane with the polysulfone support (Mem1*). An air pocket occurred between the layers, which hampered further tests. Consequently, this membrane was dismissed from further study.

2.2. Membranes with the addition of GO

In the next stage of the study, the PVDF membranes (with or without a support layer) were enriched with graphene oxide (GO). The carbon nanoparticles were distributed throughout the whole volume of the polymer in an amount of 2 mg per 100 g of the

polymer matrix. GO was ultrasonically dispersed in 10 g of DMAC for 1 h and then combined with the polymer matrix, which is schematically illustrated in Fig. 1. Membranes without support were formed according to the second line of the picture. Table 1 contains the compositions of all the created membranes.

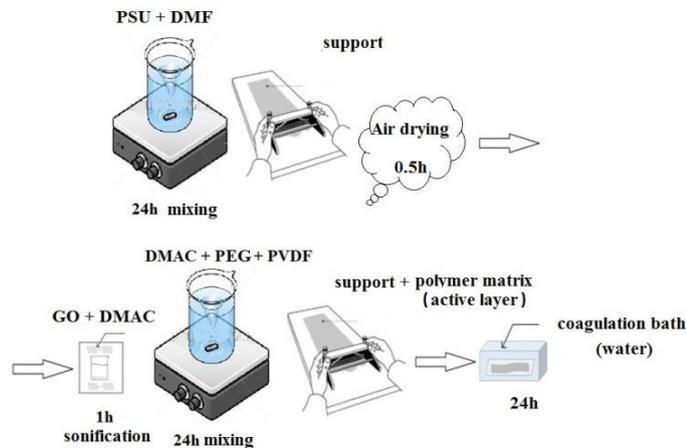


Fig. 1. Preparation of the active layer with graphene oxide on PSU support

Table 1. Compositions of the produced membranes

Membrane	Active layer				Support layer	
	PVDF		PGE	GO	PSU	PGE
	m [g]	M [g/mol]	m [g]	m [mg]	m [g]	m [g]
Mem1	15	530000	5	-	-	-
Mem1*	15	530000	5	-	15	5
Mem2	15	534000	5	-	15	-
Mem3	15	534000	5	-	15	5
Mem4	15	530000	5	2	-	-
Mem5	15	534000	5	2	-	-
Mem6	15	534000	5	2	15	5

From this point, the following symbols will be used to refer to the membranes and their composition: S – support, GO – graphene oxide, P_{granules} , P_{powder} – PVDF with a molar mass M of 530,000 g/mol and 534,000 g/mol, respectively.

3. Results and interpretation

As a result of the experiments, membranes with or without the PSU support and with or without the addition of GO were obtained. These membranes were later evaluated via determination of their thickness, contact angle, tensile strength and morphology (microscopic images of the surface). The contact angle was measured with a Surfens-universal instrument purchased from Optik Elektronik Geratechnik. The mechanical properties (Young's modulus [MPa] and tensile strength [MPa]) were assessed with an Instron 3345 apparatus. The quantities so determined are gathered in Table 2.

Table 2. Mechanical properties and contact angle of the membranes produced with and without the addition of GO

Membrane	Thickness [mm]	Tensile strength [MPa]	Young's modulus [MPa]	Contact angle [°]
Mem1	0.101±0.006	0.41±0.08	40.32±1.32	82÷91
Mem2	0.099±0.005	1.13±0.14	75.16±8.81	75÷82
Mem3	0.079±0.006	2.01±0.13	136.49±17.33	66÷75
Mem4	0.107±0.004	1.83±0.27	123.41±13.87	59÷62
Mem5	0.112±0.003	2.71±0.03	179.09±18.12	53÷56
Mem6	0.132±0.003	5.26±0.23	232.29±21.12	36÷44

As can be noticed, adding GO decreased the contact angle from close to 90° to as low as approximately 40°, which was caused by an increase in hydrophilicity of the membrane [22].

3.1. Hydrodynamic studies

The water permeability of the membranes was assessed in the ultrafiltration process using an OSMONICS KOCH apparatus under transmembrane pressures between 1.0 and 6.0 MPa. In the process, a membrane with an area (A) of 0.002826 m² was tested. The volumetric permeation flux was determined using Eq. (1):

$$J_v = \frac{V}{A \cdot t} \quad (1)$$

where: J_v - volumetric permeation flux [m³/(m²·h)], V - volume of the permeate [m³], A - area of the membrane [m²], t - time [h]

The membrane resistance was calculated from Eq. (2) using the known permeation flux:

$$R_m = \frac{\Delta P}{J_v \cdot \eta} \quad (2)$$

where: R_m - hydraulic resistance of the membrane [1/m], ΔP - transmembrane pressure [Pa], η - viscosity of water at 25°C [Pa·s]

Fig. 2 shows the permeation flux calculated for the membranes produced without a support layer (basic membranes). The application of PVDF with different molar masses and different physical forms (granules or powder) definitely influenced the permeation flux. In the case of PVDF with a greater molecular mass, at $\Delta P = 6$ MPa the flux was even 16 times higher. After thorough analysis, a decision was made to enrich all the reference membranes with graphene oxide in order to improve their mechanical properties and increase their permeability to water. The values of fluxes through so produced membranes are compared in Figs. 3–5.

Fig. 3 shows the increase in the flux of water for the membranes enriched with GO, regardless of the type of PVDF applied. For membrane Mem5, the increase was fourfold. Worse results were recorded for membrane Mem6 containing a support layer and membrane Mem4 produced from PVDF with a smaller molar mass. Fig. 4 compares the permeation flux through the membranes produced without a support layer, enriched and not enriched with graphene oxide. It is clear from the graph that a several fold increase in permeability was obtained thanks to the addition of GO. Moreover, the membranes produced using PVDF with a greater molar mass (powder) and not yet enriched with GO provided a similar flux as the membranes made of granular PVDF, already

enriched with GO. If we additionally consider the difficulties in using granular PVDF, the powdered polymer seems better suited for the production of membranes and as such should be selected as a basis for further experiments.

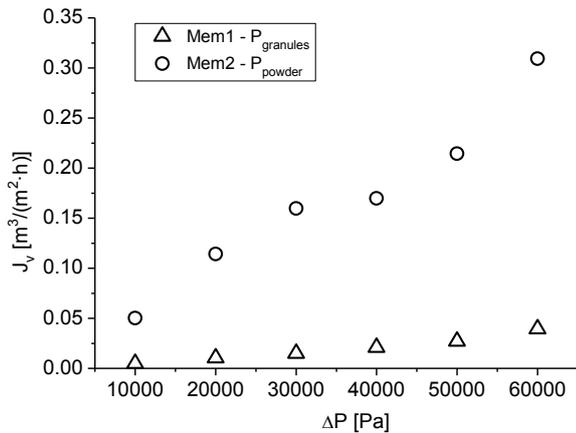


Fig. 2. Permeation flux through the reference membranes produced without GO

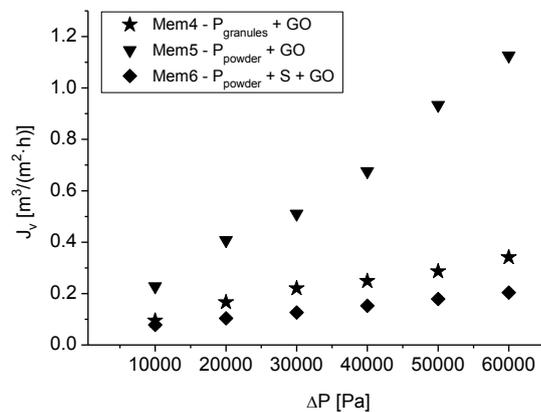


Fig. 3. Permeation flux through the membranes produced with GO

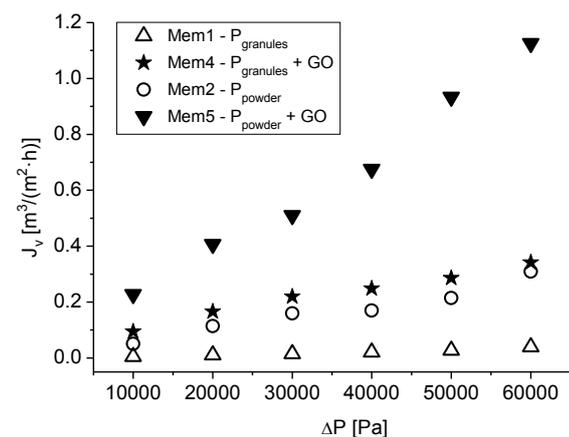


Fig. 4. Comparison of the permeation flux through the membranes without a support layer, with and without the GO addition

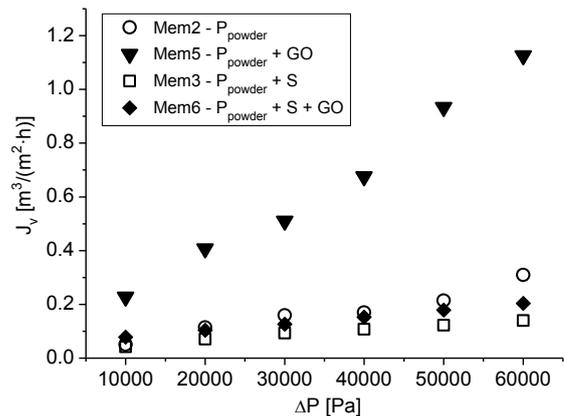


Fig. 5. Comparison of the permeation flux through the membranes produced with and without GO

Fig. 5 shows the flux of water through the membranes produced from the powdered polymer (with a greater molar mass) with/without a support layer and with/without graphene oxide. It can be observed that the membranes containing the polysulfone support layer displayed only a slight increase in permeability after adding GO, compared to the membranes consisting of only the active layer. Most probably, this behavior resulted solely from the resistance of the PSU layer. Regrettably, the improvement in mechanical properties does not always go hand in hand with increased permeability.

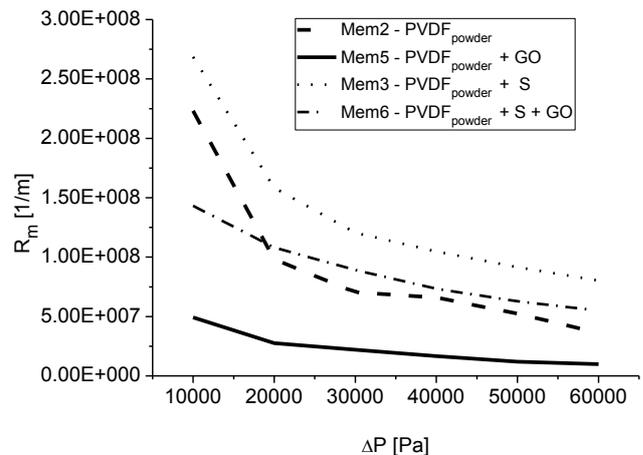


Fig. 6. Total resistance of the membranes produced with and without GO

Fig. 6 compares the resistance of the membranes made from powdered PVDF with/without a support layer and with/without graphene oxide. As can be noticed, the resistance decreased after adding GO nanoparticles. This phenomenon is corroborated by Fig. 5, where it is visible that membrane Mem5 provided the highest permeability to water.

4. Conclusions

The paper describes a procedure for preparing polymeric membranes via the phase inversion method. In the course of the study, elastic and mechanically durable membranes were obtained. Permeation fluxes through the investigated membranes were compared with one another in relation to the molar mass of the base polymer constituting the active layer (PVDF in the form of granules with a molar mass of 530,000 g/mol or powder with a molar mass

of 534,000 g/mol). Higher permeation fluxes were achieved with the membranes lacking a support layer, produced from the powdered PVDF. Moreover, certain problems were encountered when forming a membrane from the granular polymer such as the increase in mixing time and the occurrence of air pockets while joining the active layer with the support layer. These problems hampered further experiments with this membrane. Therefore, it should be emphasized that the quality of membrane preparation is strictly related to the molar mass of the applied polymer as well as its physical form.

It was also established that the addition of graphene oxide significantly increased the permeability of the investigated membranes to water which was stated in previous own works [23,24]. Much higher permeation fluxes were obtained for the membranes without a support layer, enriched with graphene oxide. It can be concluded that the polysulfone support layer generated additional permeation resistance. Besides, it was proven that the presence of carbon nanoparticles in the membrane made its surface more hydrophilic, which manifested itself with the decreasing contact angle.

4. Literature

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