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CHARACTERISTICS OF POLYMERIC ULTRAFILTRATION MEMBRANES PRODUCED WITH THE USE OF GRAPHENE OXIDE

WYTWARZANIE I CHARAKTERYSTYKA POLIMEROWYCH MEMBRAN ULTRAFILTRACYJNYCH Z DODATKIEM TLENKU GRAFENU

Abstract: This article describes a method for producing polymeric membranes by adding carbon nanostructures in the form of graphene oxide (GO). The reference membrane (having typical composition) was formed via phase inversion, using polyvinylidene fluoride (PVDF) dissolved in dimethylacetamide (DMAC). The polymeric matrix was additionally enriched with a plasticizer, i.e. polyethylene glycol (PEG). Afterwards, graphene oxide ultrasonically dispersed in dimethylacetamide was added to basic matrix. The membranes were further compared with one another by measuring their contact angle and hydrodynamics. The results were compared with the literature reports. The transport properties of the membranes were assessed with experimental ultrafiltration equipment (KOCH Membrane System). Also, their permeate flux and mass transfer resistance were determined.

Keywords: graphene oxide, formation of polymeric membranes, membrane transport

Introduction

Nowadays wastewater coming from various industries is a growing problem for the environment [1]. Many methods are used to purify them, but membrane techniques, often enriched with natural and synthetic nanoparticles, are becoming more and more popular [2, 3]. Membrane techniques are especially useful for removing contaminants from dilute aqueous solutions [4]. Quality of drinking water and wastewater released into the environment is one of the world's biggest concerns; therefore, scientific research aims at enhancing membrane efficiency and selectivity without increasing energy consumption.

This paper suggests applying graphene oxide (GO) nanoparticles to the production of polymeric membranes in order to improve their selectivity with regard to aqueous solutions. Investigating the membrane structure and controlling the membrane preparation process can help produce new materials and assess the influence of carbon nanoparticles on the separation performance, for example, in macromolecular or ionic solutions. Reports on this subject have recently appeared in leading journals dealing with membrane science.

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Membranes functionalized with different nanoparticles [5-7] and carbon-based nanomaterials have lately become very popular because of their growing availability, mechanical durability and chemical resistance [8-13]. Graphene has been tested as a component of membranes designated for seawater desalination, drinking water production and gas separation [14-17]. The use of nanoparticles causes certain technical difficulties, for instance, pore size distribution in the membranes containing graphene is hard to be controlled. Usually, however, the main problem lies in achieving an appropriate structure of the material containing carbon nanoparticles and defining possible mechanisms of water transport across the membrane [10, 12].

Initially, membranes were produced by adding graphene; however, the commercial manufacture of graphene has been very expensive thus far. For this reason, graphene has been replaced with its derivatives such as carbon nanotubes and graphene oxide [17, 18]. The latter is much cheaper and easier to produce even under laboratory conditions, which is usually done using the Hummer's method [19]. Unlike graphene, graphene oxide quite readily yields to surface modifications. The membranes containing chemically transformed graphene oxide nanosurfaces have become the most theoretically and experimentally investigated nanomaterials, due to their atomic dimensions. Their properties come from the presence of oxygen-containing functional groups, i.e. hydroxyl, carboxyl and epoxy groups, as well as negative electric charges [20, 21]. Graphene oxide has amorphous structure and its properties depend on the type and distribution of functional groups containing oxygen. It can be potentially used in many areas such as the production of composite materials, medicine, optics and nanobiotechnology [22]. In most cases, graphene oxide membranes are employed as selective barriers in the separation of liquids and gases [23-27]. Nano-flakes of graphene oxide are used as nanofillers increasing hydrophilicity and limiting the fouling phenomenon in polymeric membranes. Besides, the presence of graphene oxide substantially increases membrane permeability [28]. Graphene oxide is also used in filtration and adsorption processes for purification aqueous solutions containing dyes [12, 29-34] and heavy metal ions [35, 36].

In light of the above, this article is concurrent with new research trends and may complement the studies on the production of new membrane-forming materials. The study described in the article consisted in evaluating the performance of laboratory produced ultrafiltration membranes, including membranes containing graphene oxide distributed throughout the whole volume of the polymer. The specific properties of graphene oxide (such as the ability to change wettability and high electrical conductivity) turned out to affect the interactions between water or a separated solution and the membrane, thereby influencing its transport and separation characteristics, for example, by increasing water permeability. The literature sources cited above combine this phenomenon with simultaneous retention of other water particles or molecules by the membrane. It can therefore be assumed that such membranes could potentially be used for water desalination (including sea water), wastewater and sewage treatment as well as water softening, for example, during pretreatment in cogeneration power plants.

In the last decade a very popular membrane material has become poly(vinylidene fluoride) - PVDF. It has received great attention as a membrane material with regard to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobicity. Other polymers used for the membranes preparation such as polysulfone (PS), polyethersulfone (PES) and polyimide (PI) exhibit poorer properties comparing with PVDF. It should be noted that polypropylene (PP) and

polytetrafluoroethylene (PTFE) exhibit higher hydrophobicity. The preparation of PP and PTFE membranes due to the complexity in solvent selection is limited. PVDF easily dissolves in ordinary organic solvents. The porous PVDF membranes can be produced via phase inversion method by simple immersion and precipitation processes. The progress has been made in the fabrications PVDF membranes with higher performance for membrane distillation, membrane contactor as well wastewater treatment and sewage purification [37].

Table 1 [38] presents surface tension for several polymers. The hydrophobicity of the materials is associated also with contact angle, measured in the present work.

Table 1

Critical surface tensions of major polymeric membrane materials [38]

Polymer	Critical surface tension [N/m]
Polyacrylonitrile (PAN)	0.044
Polysulfone (PS)	0.041
Polyphenylene oxide (PPO)	0.041
Polyethylene (PE)	0.031
Polypropylene (PP)	0.029
Polyvinylidene fluoride (PVDF)	**0.025-0.0285**
Polyfluoroethylene (PFE)	0.022
Polytetrafluoroethylene (PTFE)	0.0185
Fluorinated ethylene propylene (FEP)	0.016

Preparation of the membranes

The first part of the study helped establish the composition of the reference membrane produced by phase inversion. The necessary chemical reagents were purchased from Sigma Aldrich. The reference membrane (Mem1) was prepared by dissolving 15 g of polyvinylidene fluoride (PVDF) having a molar mass of 534,000 g/mol in 85 g of dimethylacetamide (DMAC) (87.12 g/mol) using magnetic stirring for 24 h at room temperature. Afterwards, the polymeric matrix was enriched with 5 g of polyethylene glycol (PEG) having a molar mass of either 200 g/mol (Mem2) or 400 g/mol (Mem3), in order to enhance its mechanical properties and plasticity. Polyethylene glycol (PEG) is one of the main hydrophilic polymer additive which is mostly used for the blending with PVDF. The major role of PEG in the preparation and the surface modification of the PVDF membrane is more like pore forming agent (blowing agent) rather than hydrophilic agent. This additive is water solvable and can be removed by washing with a solvent during membrane preparation [39].

In the next part of the study, graphene oxide was added to selected matrices. After 1 h of ultrasonic dispersion in 10 g of DMAC, it was combined with the polymer and the whole mixture was being stirred for 24 h. As a result, the following membranes were produced:
- membranes without the plasticizer: containing 0.5 mg of GO (Mem4) and 1 mg of GO (Mem5),
- membranes with the plasticizer of 200 g/mol molar mass: containing 0.5 mg of GO (Mem6) and 1 mg of GO (Mem7),
- membranes with the plasticizer of 400 g/mol molar mass: containing 0.5 mg of GO (Mem8) and 1 mg of GO (Mem9).

After 24 h of stirring, membranes 250 μm thickness were formed with an Elcometer 3530 adjustable film applicator. Then, they were conditioned in distilled water for about 24 h and tested in the ultrafiltration process.

The addition of graphene oxide significantly changes membrane morphology [39], which is illustrated with the example in Figure 1.
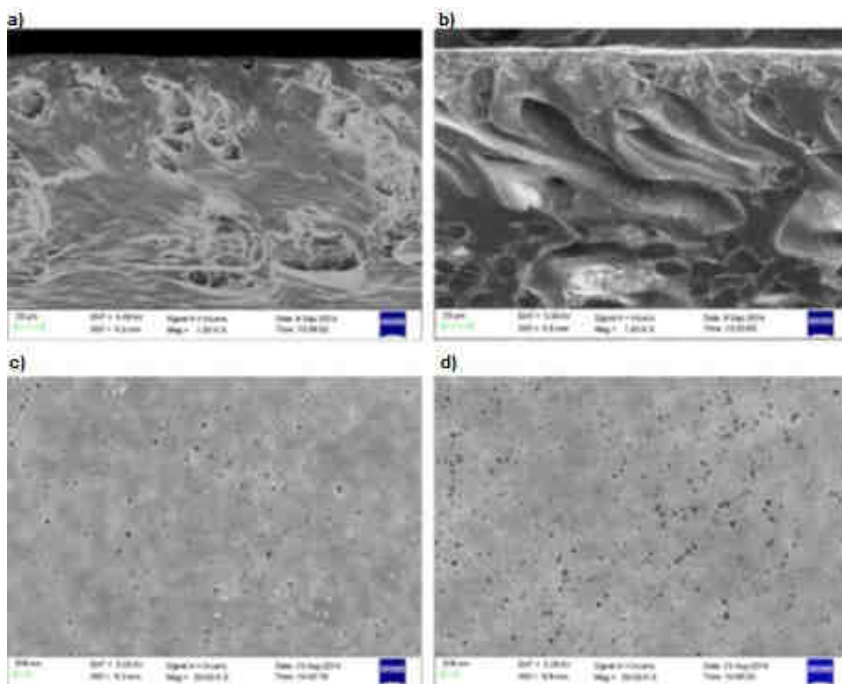

Fig. 1. SEM images of the cross-section and surface of the PVDF membrane made without GO (a, c) and with 5 % GO (b, d)

Results and interpretation

The nine produced membranes were examined by measuring their permeability, with the transmembrane pressure ranging from 1.0 to 6.0 MPa, and contact angle.

The volumetric permeate flux was calculated from equation:

$$J_v = \frac{V}{A \cdot t} \tag{1}$$

where: J_v - volumetric permeate flux [m^3/(m$^2 \cdot$h)], V - permeate volume [m^3], A - membrane surface [m^2], t - time [h].

The membrane resistance R_m was determined from equation:

$$R_m = \frac{\Delta P}{J_v \cdot \eta} \tag{2}$$

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

Figure 2 compares the volumetric permeate flux of all the membranes produced without graphene oxide. After thorough analysis, selected membranes were enriched with graphene oxide at a later stage.
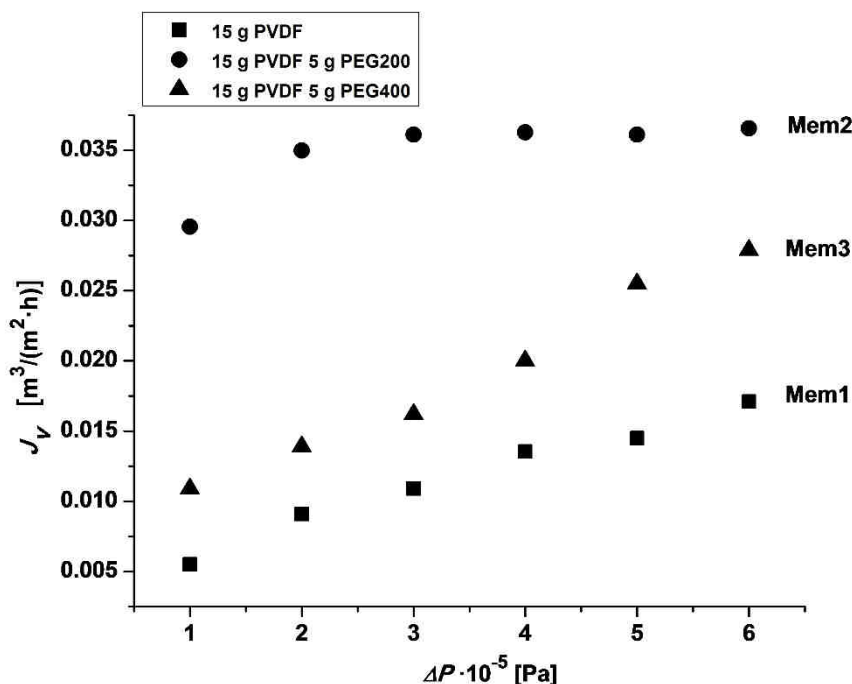

Fig. 2. Volumetric permeate flux of the membranes made without GO

Figure 3 shows the volumetric permeate flux of the membranes produced by adding a) 0.5 mg and b) 1.0 mg of graphene oxide.

It was observed that the membrane made without graphene oxide but with PEG of 200 g/mol molar mass (Mem2) provided a relatively high permeate flux, which tended to stabilize just after reaching a transmembrane pressure of $\Delta P = 3 \cdot 10^5$ Pa. The addition of 0.5 and 1.0 mg of graphene oxide distinctly increased the flux of water, which is illustrated in Figure 4.

Meng et al. [40] presented the influence of temperature (during mixing the polymer matrix) on the microstructure of PVDF membranes. In the study nearly identical polymer matrix as in our work was used, but the researchers added a much bigger amount of graphene oxide. However, it can be noted that smaller content of GO used in our study results in higher permeate flux, e.g. for $\Delta P = 0.1$ MPa, $J_v = \sim 600$ dm^3/(m$^2 \cdot$h) (Fig. 5).

The R_m values calculated for Mem1, Mem4 and Mem5 (produced with and without the use of graphene oxide) are shown in Figure 6. As can be seen, the membrane resistance decreased with growing concentration of the carbon nanostructures.

The contact angle was determined for all prepared membranes using goniometer Surftens-universal (Optik Elektronik Geratechnik). Figure 7 shows the contact angle measured for membranes Mem2 and Mem7 as an example. It can be noted that the presence

of graphene oxide caused the contact angle to decrease from 54° to 20°. Such behavior is typically accompanied by an increase in hydrophilicity [41].
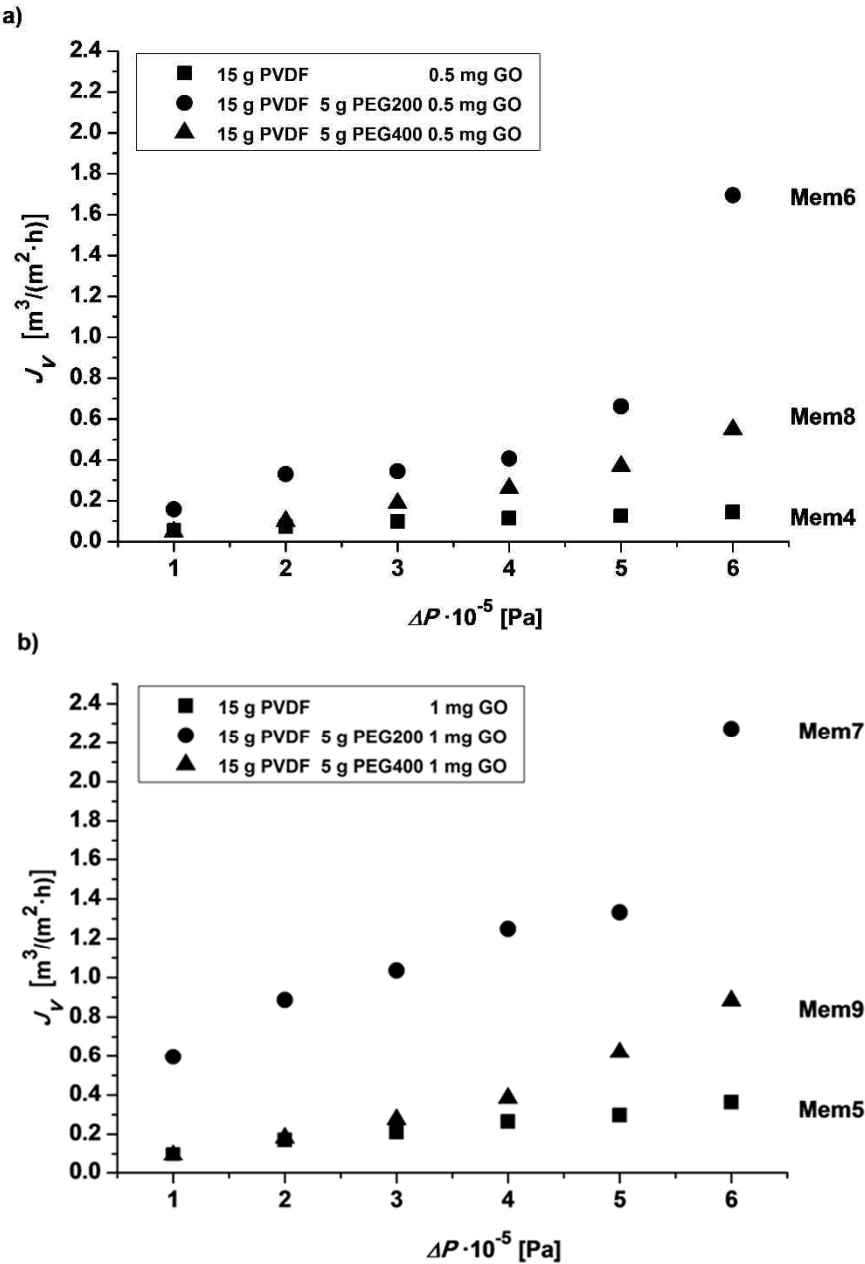

Fig. 3. Volumetric permeate flux of the membranes made with: a) 0.5 mg of GO and b) 1 mg of GO
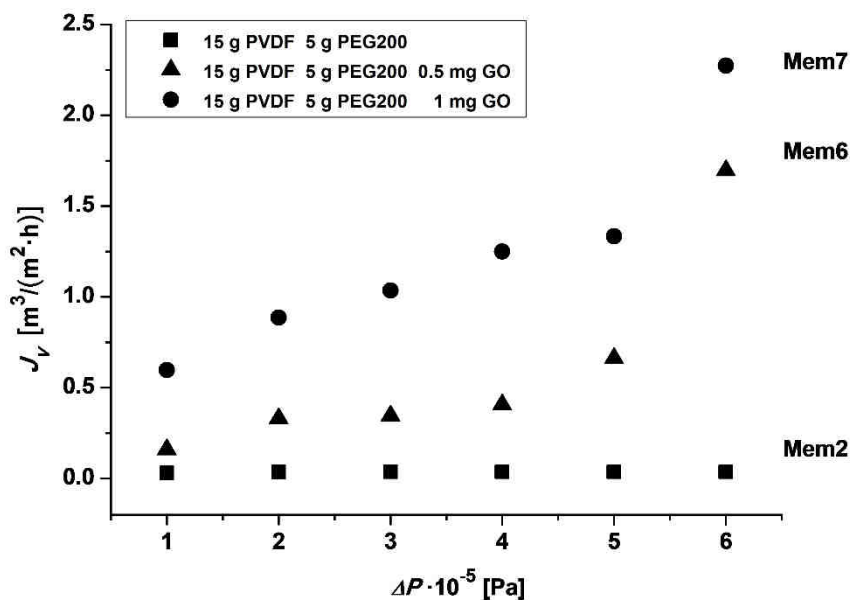
Fig. 4. Comparison of the volumetric permeate flux calculated for the membranes made with and without GO
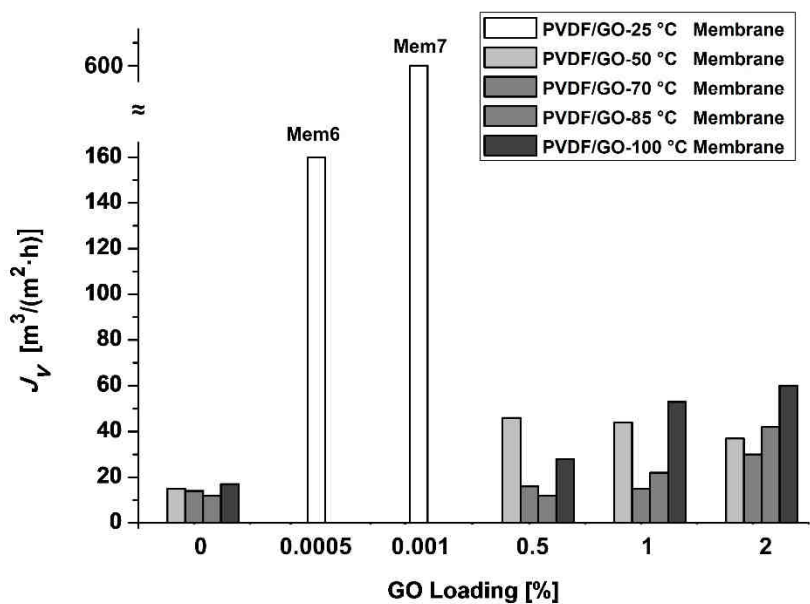

Fig. 5. Comparison of permeate fluxes with different amount of GO as additive [37]; own research
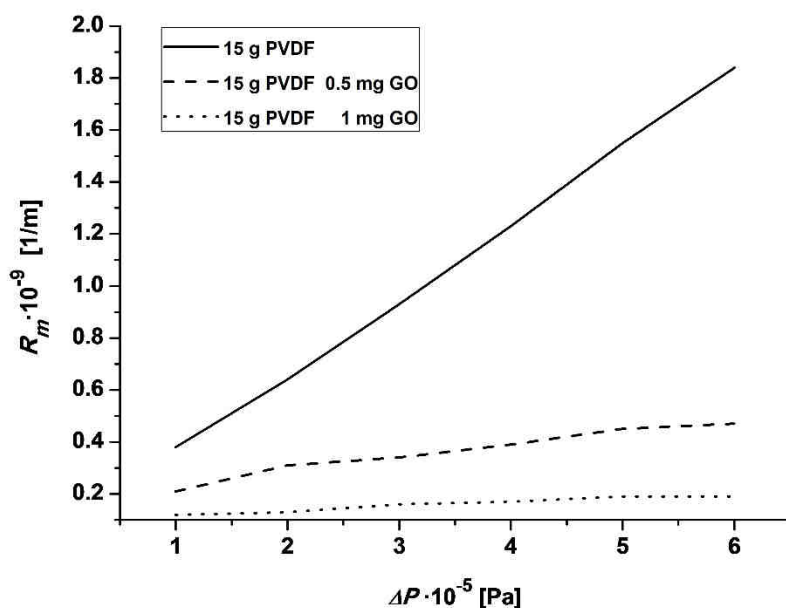
Fig. 6. Resistance of the membranes made without the plasticizer (and with or without GO)
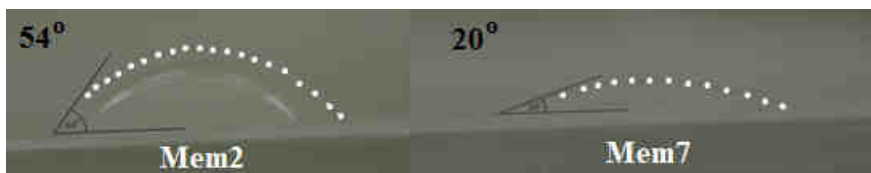

Fig. 7. Contact angle of the membranes made without and with GO

The results are shown in work [41] were different than in our studies. The hydrophilicity of the PVDF/GO membranes was also characterized by measuring the contact angle. There was no effect of the addition GO on the value of the contact angle. For different load GO from 0 to 2 % in relation to membrane mass contact angle of about 75° was observed. This is inconsistent with previous research studies [42-45] which have found that embedding GO into the polymer matrix can lead to a more hydrophilic membrane. The authors explain this too small loading of GO in PVDF membrane could not cause 'dramatically change the overall hydrophilicity of the membrane, considering the high hydrophobicity of PVDF'. Comparison of own studies with cited works is shown in Figure 8. It is worth noting that our membrane containing only 0.0005-0.001 % of graphene oxide.
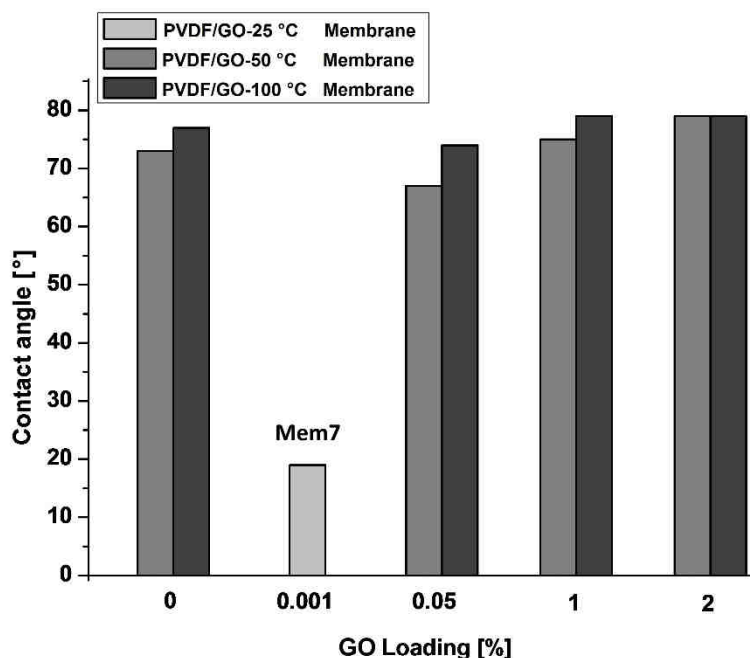
Fig. 8. Effect of GO loading on water contact angles of membranes PVDF/GO-50, PVDF/GO-100 [37] and our (Mem7)

Summary and conclusions

In the study, elastic and mechanically durable membranes were laboratory produced using the phase inversion method. Some of the membranes were enriched with either/both a plasticizer or/and graphene oxide. The separation performance of the membranes was evaluated by determining their volumetric permeate flux and contact angle.

As a result, it was established that the addition of graphene oxide had caused a substantial (up to a 60-fold) increase in the membrane permeability. The permeate flux of the membrane containing polyethylene glycol having a molar mass of 200 g/mol was equal to 0.035 $m^3/(m^2 \cdot h)$ at $\Delta P = 6 \cdot 10^5$ Pa. The same membrane produced by adding graphene oxide provided a flux of 2.30 $m^3/(m^2 \cdot h)$. The presence of graphene oxide made the membrane more hydrophilic, which was quantified by measuring the contact angle.

The presented study was intended as an initial step required to optimize the membrane composition; therefore, further separation experiments are planned. They will employ model substances of known molecular mass, including aqueous solutions of macromolecular and ionic compounds.

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