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# Hydrodynamics of ultrafiltration polymer membranes with carbon nanotubes

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## ABSTRACT

This paper presents modifications of ultrafiltration polymeric membranes made from cellulose acetate with the addition of single-wall carbon nanotubes, polyethylene glycol and polyvinylpyrrolidone. In the study, the membranes were prepared according to the phase inversion method. Their hydrodynamic properties in the ultrafiltration process were examined. Additionally, the pore size, hydraulic membrane resistance and contact angles were determined. It was observed that carbon nanotubes added to the membranes increased their permeability and surface hydrophobicity.

*Keywords:* Carbon nanotubes; Cellulose acetate membranes; Permeability

## 1. Introduction

Many industries are interested in applying membrane technology for its potential use in separation, purification and concentration processes for instance in water treatment and desalination.

Since the first synthetic membranes were manufactured, new membrane-building materials have been investigated. Currently, the research is not only focused on examining new polymers but also on conditioning them through physical and, more frequently, chemical treatment. Moreover, the beginning of the twenty-first century brought an interest in molecular materials, which upon inclusion in the polymer matrix improve its quality.

Recently, membranes with the addition of various nanoparticles [1–3] and nanomaterials produced from carbon precursors [4–6] have been the most widely studied. Carbon nanoparticles in the form of graphene oxide, graphene or carbon nanotubes (CNTs) have many possible applications. CNTs have a unique cylindrical nanostructure. Previous research has shown that CNTs are used as additives in polymer matrices of ultrafiltration membranes [7–10]. The membranes are usually prepared using the phase inversion method. The tubes should be uniformly distributed in the full volume or active layer of the polymer. However, their vertical orientation in the membrane material is a major technical challenge, especially in large-scale processes. It is confirmed that the production of polymeric membranes involving nanotubes and nanoparticles adequately distributed in the active layer of the membrane can increase the efficiency of separation of different substances from aqueous solutions both at macro and molecular level [11–15].

This research has had a unique approach to the examination of the influence of CNTs distributed in the entire membrane and resulting changes in transport abilities of the membrane. The key aim of the study was to prepare polymeric membranes with the addition of single-walled nanotubes and analyse their structure and transport properties with regard to water. Initially, the study has concentrated on obtaining mechanically stable membranes with enhanced water permeability. In the future research, the membranes will be used to separate selected substances from aqueous solutions.

## 2. Membrane preparation

The polymeric matrix was formed using cellulose acetate (CA) purchased from Acros Organics, part of Thermo Fisher

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Scientific, Belgium (with molecular weights of 30,000, 50,000, 100,000 g mol$^{-1}$) dissolved in acetic acid (AA) (99.5% pure, purchased from Honeywell, Germany). A plasticizer polyethylene glycol (PEG) (200, 400, 600 g mol$^{-1}$, Sigma Aldrich, USA) and a pore precursor polyvinylpyrrolidone (PVP) (30,000 g mol$^{-1}$, Fluka, USA) were also added to the solution. These membranes were prepared by phase inversion as reference membranes.

The membranes containing nanostructures were prepared via mixing the above-mentioned components with single-walled CNTs suspended in an organic solvent. The nanotubes were purchased from Strem Chemicals, USA (CAS number: 308068-56-6, single-walled/double-walled, 90%, 2 nm in diameter with lengths of 5–30 micron; ash content <1.5 wt%).

The CNTs were dispersed in 10 g of AA for 1 h, then added to the polymer solution containing the pore precursor and the plasticiser and mechanically stirred for 2 h. The total mass of the solution was 100 g. Then, the solution was degassed by means of a vacuum pump. After about 2 h, the membrane was formed through casting using a casting knife (Elcometer 3530) and then rinsed in distilled water at approximately 25°C. PVP was eluted from the membrane to form the pores. Afterwards, the obtained 250-μm-thick membrane was conditioned in distilled water for about 24 h. For further experiments, each membrane was cut into three pieces.

The structure (porosity and thickness) and hydrodynamic transport properties of the membranes were investigated. The ultrafiltration experimental setup (LabCell CF-1 KOCH) was used. Parameters such as permeate flux, pore size and membrane resistance were calculated for the reference membranes as well as the membranes with the addition of CNTs.

## 3. Experiments and calculations

Table 1 contains the composition of the reference membranes.

Firstly, the membrane permeability in the ultrafiltration process was examined. Also, the contact angles and the pore sizes were measured.

Table 1
Compositions of the reference membranes without CNTs (m = mass; MW = molecular weight)

| Membrane | CA | | PVP | | PEG | |
|---|---|---|---|---|---|---|
| | m (g) | MW (g mol$^{-1}$) | m (g) | MW (g mol$^{-1}$) | m (g) | MW (g mol$^{-1}$) |
| Mem1 | 15.5 | 30,000 | 1 | 30,000 | 5 | 200 |
| Mem2 | 15.5 | 30,000 | 1 | 30,000 | 5 | 400 |
| Mem3 | 15.5 | 30,000 | 1 | 30,000 | 5 | 600 |
| Mem4 | 15.5 | 50,000 | 1 | 30,000 | 5 | 200 |
| Mem5 | 15.5 | 50,000 | 1 | 30,000 | 5 | 400 |
| Mem6 | 15.5 | 50,000 | 1 | 30,000 | 5 | 600 |
| Mem7 | 15.5 | 100,000 | 1 | 30,000 | 5 | 200 |
| Mem8 | 15.5 | 100,000 | 1 | 30,000 | 5 | 400 |
| Mem9 | 15.5 | 100,000 | 1 | 30,000 | 5 | 600 |

The permeate flux was calculated using Eq. (1):

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

where $J_v$ is the permeate flux [m$^3$ (m$^2$·h)$^{-1}$]; $V$ is the permeate volume (m$^3$); $A$ is the membrane area (m$^2$); and $t$ is the time (h).

The membrane resistance was calculated using Eq. (2):

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

where $R_m$ is the hydraulic resistance of the membrane (1 m$^{-1}$); $\Delta P$ is the transmembrane pressure (Pa), and η is the viscosity of water (Pa·s).

The sizes of the largest pores were measured using the bubble point method [16,17]. The procedure for the bubble point test is described in American Society for Testing and Materials Standards, Method F316 [18]. The pore diameters were calculated using Eq. (3):

$$d = \frac{4 \cdot \sigma \cdot \cos\theta}{\Delta P} \cdot 10^{-6} \tag{3}$$

where $d$ is the pore diameter (μm); σ is the surface tension (N m$^{-1}$); and θ is the contact angle (°).

## 4. Results

Fig. 1 shows the permeate volumetric flow rates for all the reference membranes. Membrane No. 4 (Mem4) was selected for further considerations because of its favourable mechanical properties and the lowest permeate flux. The mechanical properties were determined using Instron 3345 apparatus: Young's modulus – 123.4 ± 5.55 MPa, tensile stress at break – 0.65022 ± 0.00647 MPa.

For this purpose, CNTs in the amounts of 0.5, 1.0 and 1.5 mg were added to the polymer solution during the preparation of Mem4.

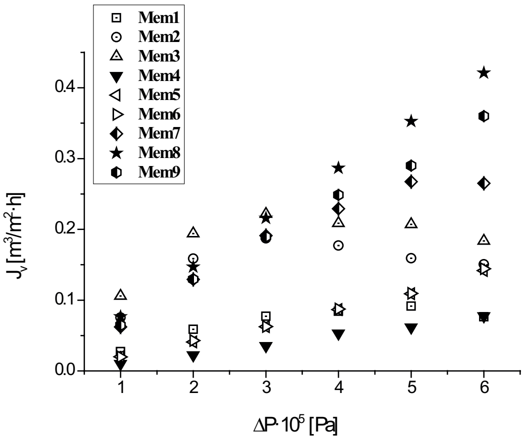

Fig. 1. Permeate fluxes of the produced membranes.

The changes in permeability of Mem4 with and without CNTs are presented in Fig. 2. The addition of 1.5 mg of nanotubes has resulted in a threefold rise in the membrane permeability.

The calculated hydraulic resistance of Mem4 prepared with and without the addition of CNTs is presented in Fig. 3. The inclusion of nanostructures causes the membrane resistance to decrease.

In order to calculate the pore sizes the contact angle needs to be measured. Table 2 shows the contact angles measured for the membranes with and without CNTs with the standard deviation of ±3°. The addition of CNTs, which makes the membrane more hydrophobic [19], increases the contact angle from 45° to 58°. Table 3 shows the pore sizes in the examined membranes.

Polyethylene glycol, being hydrophilic, not only makes the membrane more plastic but also changes its morphology through increasing porosity. The authors [20] have demonstrated that membranes with a 5% PEG addition have evidently higher porosity. All the examined types of membranes were prepared using polyethylene glycol having three different molecular weights – 200, 400 and 600 g mol$^{-1}$. The higher plasticiser molar masses, the higher permeate flux (Fig. 4).

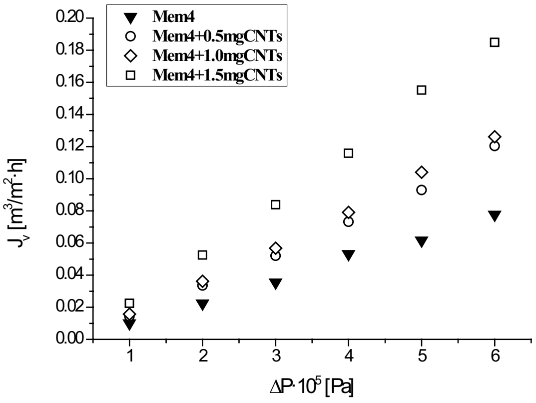

Fig. 2. Permeability of membrane No. 4 with and without CNTs.

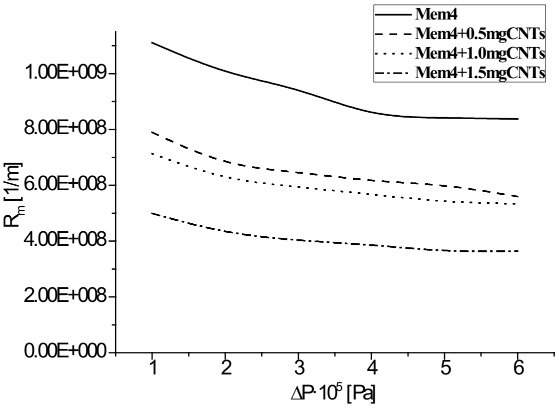

Fig. 3. Hydraulic resistance of membrane No. 4 with and without CNTs.

Table 2
Contact angles measured for the membrane No. 4 without and with CNTs

| | Mem4 | Mem4 +0.5 mg CNTs | Mem4 +1.0 mg CNTs | Mem4 +1.5 mg CNTs |
|---|---|---|---|---|
| q (°) | 45 | 49 | 54 | 58 |

Table 3
The largest pore sizes of the membrane No. 4 without and with CNTs

| | Mem4 | Mem4 +0.5 mg CNTs | Mem4 +1.0 mg CNTs | Mem4 +1.5 mg CNTs |
|---|---|---|---|---|
| *d* (μm) | 9.25 | 3.14 | 3.76 | 2.77 |

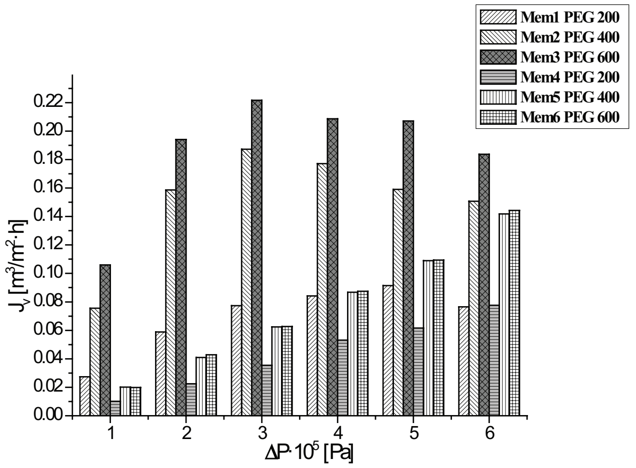

Fig. 4. Changes of the permeate flux in relation to the PEG molar mass.

## 5. Final remarks

In the presented experiments, the polymeric membranes were prepared using the method of phase inversion. As a result, elastic and durable membranes were obtained. During the experiments, permeate fluxes of the examined membranes were compared with regard to their composition.

It was observed that CNTs added to the membranes during the preparation process increased their permeability as well as surface hydrophobicity, which was confirmed by measuring the contact angle. At the same time, diameters of the pores became greater, which can be explained by embedding of the nanotubes in the pores already existing in the polymeric matrix.

Membrane composition optimisation has been the fundamental stage of initial experiments presented in this paper. In the next step, model substances having known molecular masses as well as aqueous solutions containing different macromolecular compounds will be studied in relation to the separation abilities of the prepared membranes.

## Symbols

$J_v$ — Permeate flux, $m^3 (m^2 \cdot h)^{-1}$
$V$ — Permeate volume, $m^3$
$A$ — Membrane area, $m^2$
$t$ — Time, h
$R_m$ — Hydraulic resistance of the membrane, $1\ m^{-1}$
$\Delta P$ — Transmembrane pressure, Pa
$\eta$ — Viscosity of water, Pa·s
$d$ — Pore diameter, μm
$\sigma$ — Surface tension, $N\ m^{-1}$
$\theta$ — Contact angle, °

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