

# NOVEL HYBRID POLYETHERSULFONE MEMBRANES MODIFIED WITH POLYVINYLPIRROLIDONE AND Ag/TITANATE NANOTUBES

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**Abstract:** In this work, the influence of addition of polyvinylpyrrolidone (PVP, 10kDa, 1-4.8wt%) and Ag-modified titanate nanotubes (Ag/TNTs, 0.1wt%) on physicochemical and transport properties of polyethersulfone (PES) ultrafiltration membranes was studied. The membranes were prepared via wet phase inversion method using *N,N*-dimethylformamide (DMF) as a solvent and water as a non-solvent. The Ag/TNTs nanocomposite was obtained via photodeposition method using  $\text{AgNO}_3$  as a precursor. It was found that the addition of PVP into the casting dope affected the cross-section structure of the membranes and their surface topography. The presence of PVP improved the dispersion Ag/TNTs agglomerates in the membranes structure. A positive influence of the introduction of the nanocomposite into the membranes matrix on their permeability was also proved.

**Keywords:** TITANATE NANOTUBES, SILVER, POLYVINYLPIRROLIDONE, POLYETHERSULFONE, MEMBRANE

## 1. Introduction

Due to many advantages such as low energy or chemical consumption, automation and modularity of installations as well as high and stable quality of permeate the membrane processes are widely used for water and wastewater treatment. Despite these benefits, they have some drawbacks, and the main of them is the decrease of the permeate flux in time, resulting from the so-called fouling and biofouling phenomena, especially in case of micro-filtration (MF) and ultrafiltration (UF) processes. A promising attempt to solve this problem is introduction of different types of (nano)fillers and modifiers into the membrane structure. There are some reports regarding the use of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , halloysite nanotubes (HNTs), carbon nanomaterials (e.g. graphene, fullerenes, carbon nanotubes (CNTs) and different metal nanoparticles such as Ag, Au, Cu and Pd [1-4]. The application of Ag has attracted special attention due to its antibacterial properties and a positive effect on membranes hydrophilicity.

Silver can be introduced into the membrane structure by itself [5], or deposited on a carrier, such as CNTs, HNTs, zeolites or  $\text{SiO}_2$  [6-8]. Likewise,  $\text{TiO}_2$  nanotubes or titanate nanotubes (TNTs) can be used as carriers of Ag nanoparticles [9]. There are some reports indicating the positive effect of titanate nanotubes on membrane properties such as hydrophilicity, pure water flux and antifouling performance. Padaki et al. [10] observed that the favorable effect of TNTs on the properties of polymer membranes may be caused by a large amount of hydroxyl groups present on the surface of the nanotube, which contributes to improvement of the hydrophilic properties of the membranes. The effect of TNTs functionalized with sulfonic acid on the performance of polyethersulfone (PES) UF membranes was examined by Alsohaimi et al. [11]. It was reported that the modified membrane was characterized by the improved bacteriostatic and separation properties.

A positive influence of modification of membranes with hybrid Ag/TNTs was reported in our earlier works on PES UF membranes [12,13]. However, we have applied a simple casting dope solution containing the polymer and solvent only. Although the presence of Ag/TNTs improved the permeability of the membranes, they were still characterized by moderate permeate fluxes due to the absence of any pore forming agent. One of well-known porogens is polyvinylpyrrolidone (PVP). In literature there are reports proving a positive impact of PVP on membrane transport properties [14]. Since the effect of PVP on the characteristics and performance of PES UF membranes modified with Ag/TNTs is unexplored, the aim of the present work was investigation on that subject. The research were focused on the influence of Ag/TNTs (0.1wt%) and PVP (10kDa, 1-4.8wt%) on physicochemical and transport properties of PES ultrafiltration membranes.

## 2. Materials and methods

### 2.1. Materials

Polyethersulfone was supplied by BASF (Germany). Anatase  $\text{TiO}_2$  powder, PVP (10kDa) was purchased from Sigma Aldrich Chemicals (USA). DMF, HCl (35-38wt%),  $\text{AgNO}_3$ , NaOH,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  (96wt%) were provided by Avantor Performance Materials Poland S.A.

### 2.1 Preparation of titanate and silver-modified titanate nanotubes

Pure TNTs were prepared using hydrothermal treatment of anatase  $\text{TiO}_2$ . In the first step, 2g of  $\text{TiO}_2$  were ultrasonicated with 60  $\text{cm}^3$  of 10M NaOH for 1 h at room temperature. Then, the suspension was transferred to the autoclave and treated at 140°C for 24h. After washing with HCl and deionized water, the final powder was dried at 80°C for 12 h and ground using agate mortar.

The Ag/TNTs were prepared using photodeposition method [14]. A defined amount of pure TNTs was introduced into 100mM solution of  $\text{AgNO}_3$  in a glass reactor and stirred (2 h, 250 rpm) at ambient temperature and pressure. Next, the suspension was irradiated with a UVC lamp (TNN 15/32, Heraeus Noblelight GmbH, 15 W,  $\lambda_{\text{max}} = 254$  nm) for 2h with continuous stirring. Afterwards, the slurry was centrifuged and washed with deionized water. Then, the product was dried at 80°C for 12 h and ground using agate mortar.

### 2.2. Preparation of membranes

The membranes were prepared using casting dopes with compositions presented in Table 1.

**Table 1:** Composition of casting solutions.

Sample name	PES [wt%]	DMF [wt%]	PVP [wt%]	Ag/TNTs [wt%]
M0	15	85	-	-
M1	15	84.9	-	0.1
M2	15	84	1	-
M3	15	83.9	1	0.1
M4	14.8	82.8	2.4	-
M5	14.8	82.7	2.4	0.1
M6	14.4	80.8	4.8	-
M7	14.4	80.7	4.8	0.1

First, the unmodified membranes (M2, M4, M6) were obtained by dissolution of a defined amount of the polymer and 0.56; 1.40 or

2.80 g of PVP in DMF (50 cm<sup>3</sup>). For comparison purpose, a solution without PVP addition was also prepared to cast the unmodified M0 membrane. Next, the casting dopes were left for degassing (2 h) and cast on a glass plate using the applicator (Elcometer 4340, Elcometer Ltd., UK) equipped with the casting knife (gap set at 0.1mm). Finally, the films were immersed in the non-solvent (pure water (Elix, Millipore), 20°C) for 24 h. The hybrid membranes (M1, M3, M5, M7) were obtained as follows. First, PES and of PVP (where applicable) were dissolved in 40 cm<sup>3</sup> of DMF. Next, the suspensions of NPs in 10 cm<sup>3</sup> DMF (NPs/DMF) were sonicated for 30 min using Vibra-cell VCX-130 ultrasonic liquid processor (Sonics, USA; output power 130 W, frequency 20 kHz, amplitude 80%). Subsequently, the suspension of NPs/DMF was dispersed in the dissolved polymer by stirring (200 rpm) with heating at 55-60°C and sonication at 20-25°C for 15 min. Both steps (stirring and sonication) were carried out by turns for 2 h.

### 2.3. Characterization of Ag/TNTs nanocomposite and membranes

The morphology of TNTs and Ag/TNTs nanocomposite was examined via transmission electron microscope (TEM) FEI TecnaiF20. The topography of the membranes surface was studied using atomic force microscopy (AFM). NanoScope V Multimode 8 scanning probe microscope (Bruker Corp.) equipped with the silicon nitride ScanAsyst – Air probe was applied. The scanned area was 10 μm × 10 μm. The measurements were executed in the ScanAsyst mode. The cross-sections of the membranes were examined using Hitachi SU8020 Ultra-High Resolution Field Emission Scanning Electron Microscope (UHR FE-SEM). The membranes samples were coated with a 10 nm thick chromium layer (Q150T ES coater, Quorum Technologies Ltd., UK). Two types of techniques were used i.e. analysis using secondary (SE) and back scattered electrons (BSE). The accelerating voltage was 5 kV and 15 kV for SE and BSE, respectively.

The transport and separation properties of the membranes were examined using a laboratory scale UF installation (Fig 1). The installation consisted of a suction pump, two stainless steel membrane modules (with a 1.194 mm feed spacer) and manometers with needle valves. The transmembrane pressure (TMP) applied during pure water ultrafiltration experiments was set at 1, 2 and 3 bar, and the temperature was maintained at 20±1°C. The membrane separation area was 0.0025 m<sup>2</sup>. All the experiments were carried out at least three times.

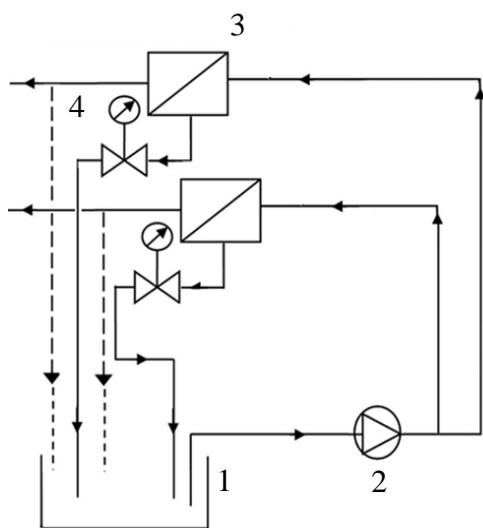


Fig. 1 Scheme of ultrafiltration installation; 1-feed tank; 2-pump; 3 – membrane module; 4-needle valve with manometer.

## 3. Results and discussion

### 3.1. Characterization of obtained nanomaterials

Fig. 2 A and B shows microstructure of pure TNTs and Ag/TNTs obtained by the photodeposition method, respectively.

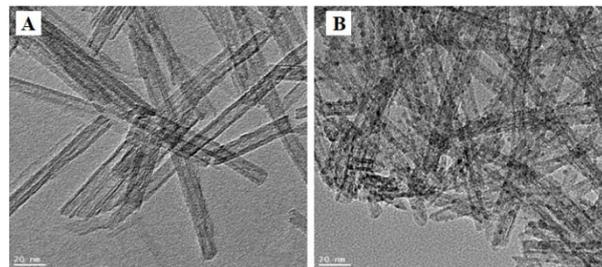


Fig. 2 TEM images of (A) pure TNTs and (B) Ag/TNTs.

The pure TNTs have multi-walled tubular structure with a length in the range from 50 to 200 nm and diameter of 6-8 nm. Fig. 2(B) shows that the Ag nanoparticles are evenly distributed on the TNTs surface. Most of the silver nanoparticles have diameters of 2-5 nm.

### 3.2. Characterization of the prepared membranes

In Fig. 4 the SEM-SE and SEM-BSE images are presented. The membranes without PVP addition are much thinner than the membranes prepared using the pore forming agent. Moreover, the porous structure of both types of membranes (with and without PVP) differs significantly. The cross section of M1 membrane is asymmetric and exhibits a dense top layer and a porous bottom layer, with large finger-like and some round-shaped pores surrounded by a spongy structure. In case of the membrane prepared with application of 1wt% of PVP (M3) the relatively narrow finger-like and the large oval pores in the bottom part turned into the long, slanted macrovoids. In the cross sections of M5 and M7 membranes, under the thin skin layer, a middle layer with narrow finger-like pores and the loose bottom layer with large shapeless macrovoids surrounded by a spongy structure can be seen. The obtained results revealed that the increase of the concentration of PVP up to 2.4 and 4.8wt% resulted in a delamination of the membranes structure. Similar results were described in other works [15-17]. Amirilargani et al. [16] explained the formation of the large pores in the bottom part of the membranes cross-section by high affinity of PVP for the solvent and low in relation to the polymer. These properties are the reason of increasing the thermodynamic instability of the casting solution. That leads to the instantaneous demixing in the non-solvent bath, which results in formation of macrovoids. In other words, PVP is a hydrophilic and water-soluble pore-forming polymer, therefore its addition into the casting dope increases the solvent (DMF) – non-solvent (water) exchange rate at the stage of phase inversion. This leads to a loose structure of a membrane and formation of macrovoids [17].

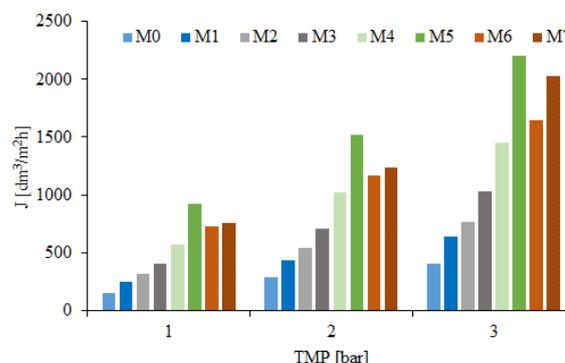


Fig. 3 Influence of transmembrane pressure on pure water fluxes (PWF) of the prepared membranes.

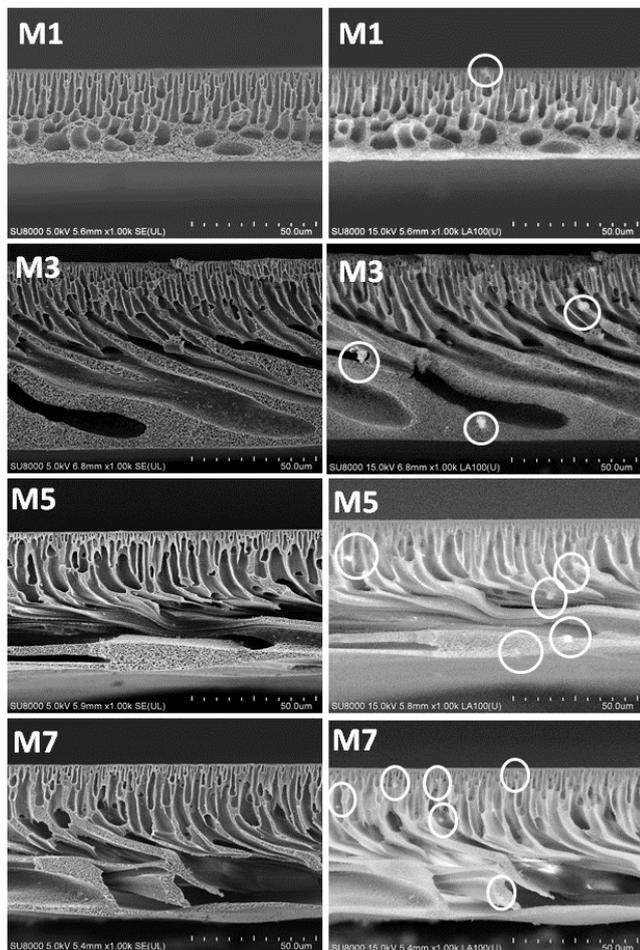


Fig. 4 SEM-SE (left side) and SEM-BSE (right side) microphotographs of M1, M3, M5 and M7 membranes.

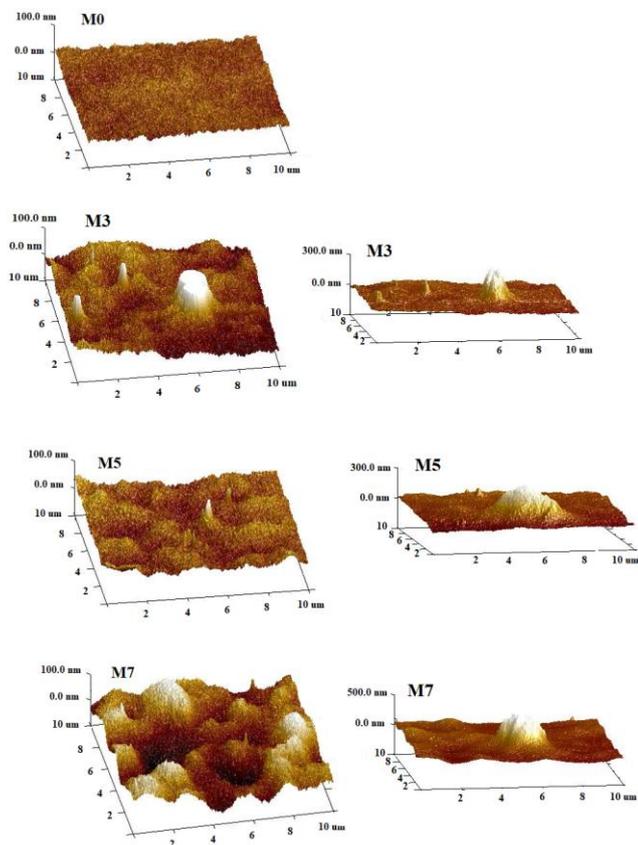


Fig. 5 The topography of the surface of the obtained M0, M3, M5 and M7 membranes.

Fig. 5 presents AFM images of the surface of the membrane without PVP addition (M0) and the mixed matrix membranes prepared using various amount of the porogen. The topography of M0 membrane is relatively smooth and uniform. The incorporation of even a small dose of PVP resulted in the corrugation of membranes surface. The increasing PVP amount caused a further increase of roughness, therefore the M7 membrane has a more non-uniform surface with numerous valleys and hills compared to M5. Regardless of the PVP content, both small and large Ag/TNTs agglomerates were observed.

It was noticed based on Fig. 4 that the addition of PVP may improve the dispersion of Ag/TNTs agglomerates. For M1 the amount of agglomerates visible in the cross-section was low (only one agglomerate in Fig. 4) which means that the dispersion of Ag/TNTs was not very good. Moreover, the average size of agglomerates was larger ( $4.7 \mu\text{m}$  ( $\text{SD}=1.5 \mu\text{m}$ )) than for the membranes with addition of PVP ( $4.6$  ( $\text{SD}=0.6 \mu\text{m}$ );  $2.8$  ( $\text{SD}=1.1 \mu\text{m}$ ) and  $2.6 \mu\text{m}$  ( $\text{SD}=1.4 \mu\text{m}$ ) for M3, M5 and M7)). The addition of PVP not only had impact on the dimensions of NPs agglomerates but improved their dispersion through the whole membrane matrix. The white circles in Fig. 4 show the places where Ag/TNTs were detected. It can be seen that the increasing amount of PVP results in increasing amount of white dots on SEM-BSE images, which correspond to the NPs agglomerates. For M7 membrane with the highest amount of PVP the number of dots was also the highest in comparison to the other membranes obtained with lower dose of PVP.

Fig. 3 summarizes the water permeability of the prepared membranes. Generally, in all cases the addition of PVP resulted in an increase of pure water flux (PWF) values. Compared to the M0 membrane, the PWF for M2, M4 and M6 membranes measured at  $\text{TMP} = 3$  bar increased by about 1.9, 3.6 and 4.1 times, respectively. The obtained results are associated with the loose structure of the membranes observed in Fig. 4, as well as their improved hydrophilicity due to PVP addition [15-17].

The incorporation of Ag/TNTs nanocomposite into the membranes matrix resulted in further improvement of their permeability. Analyzing the PWF values at  $\text{TMP} = 3$  bar for M3, M5 and M7 in comparison with M2, M4 and M6 membranes, respectively, an increase of the flux for about 260, 750 and  $380 \text{ dm}^3/\text{m}^2\text{h}$  was found. The observed improvement can be attributed to further increase of membranes hydrophilicity due to the presence of hydrophilic nanoparticles. Moreover, the Ag/TNTs can act as additional channels for water transport through the membranes.

The results presented in Fig. 3 revealed that the highest improvement of water permeability was obtained when both Ag/TNTs and PVP were applied. The PWF at  $\text{TMP} = 3$  bar reached the values around  $2250 \text{ dm}^3/\text{m}^2\text{h}$  for M5 and  $2050 \text{ dm}^3/\text{m}^2\text{h}$  for M7 membrane.

#### 4. Conclusions

In this study the polyethersulfone membranes prepared by the wet phase inversion method and modified with Ag/TNTs and PVP were obtained successfully. The physiochemical and transport properties of the membranes were investigated. The changes in the membranes cross-section appearance due to the application of PVP and NPs were noticed. An asymmetric structure of M1 membrane characterized by a dense top layer and narrow finger-like pores was significantly affected by the addition of PVP. The mixed matrix membranes fabricated with application of PVP at the highest concentrations (2.4 and 4.8wt%) exhibited large macrovoids and visible delamination in the bottom part of their cross-sections. The addition of PVP led also to an increase of the membranes thickness. Moreover, the incorporation of PVP improved the dispersion of Ag/TNT agglomerates inside membrane. The highest water permeability was observed for the membrane modified with both Ag/TNTs and PVP at a concentration of 2.5wt%.

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