

# Synthesis and characterization of polysulfone - carbon nanotubes - polyethylene imine composite membranes

M. MICULESCU<sup>a</sup>, A. MUHULET<sup>b</sup>, A. NEDELCU<sup>b</sup>, S. I. VOICU<sup>b,\*</sup>

<sup>a</sup>University Politehnica from Bucharest, Faculty of Materials Science, 313 Splaiul Independentei, Bucharest, 060042, Romania

<sup>b</sup>University Politehnica from Bucharest, Faculty of Applied Chemistry and Materials Sciences, 1-7 Gheorghe Polizu, Bucharest, 011061, Romania

---

In this study we investigate synthesis of a new composite membrane polysulfone – polyethylene imine - carbon nanotubes through a new technique which consists in introducing polyethylene imine in polysulfone membrane during coagulation process in water. The produced membranes were characterized by scanning electron microscopy, FT-IR spectroscopy and have been used in the separation of bovine serum albumin or heavy metals retention from aqueous solutions.

(Received June 6, 2014; accepted November 13, 2014)

*Keywords:* Polysulfone, Carbon nanotubes, Polyethylene imine, Composite membrane

---

## 1. Introduction

Among the currently known functional materials, membranes concern a special place due to their properties of selectivity and specificity and because of the many practical applications in various fields such as environmental protection, biomedicine, food industry, electronics [1]. Composite membranes proved many advantages because they are made from a polymer support, which as a rule gives the mechanical and thermal properties, and a filler which may be polymer [2] or various kinds of particles, such as carbon nanotubes [3], fullerenes [4], magnetic particles [5].

Polysulfone is one of the most well-known polymers used in order to obtain polymeric membranes because of the excellent mechanic and thermal properties, the possibility of functionalization by electrophilic aromatic substitution reactions, as well as the ability to withstand the sterilization process, which makes it usable in biomedical applications. However, it presents two biggest drawbacks, such as strong hydrophobicity and low resistance to UV radiation [6]. Are known polysulfone-polyaniline doped composite membranes for fuel cells [7], polysulfone-carbon nanotubes for hemodialysis, the nanotubes covalently bounded on the polymer retaining heavy metal cations by surface adsorption [8], polysulfone-carbon nanotubes for functionalization of carbon nanotubes, membrane acting as a membrane reactor [9] or polysulfone magnetic particles [10]. Since their discovery, carbon nanotubes [11] have been extensively studied and used as a nanospecies filler for polymers, their properties bringing many advantages of the composite material, such as increased mechanical and thermal resistance, and in case of using for membranes synthesis brought added selectivity due to high surface adsorption capacity of different chemical species on the surface.

Polyethylene imine is a polymer with multiple uses in various fields such as papermaking, gene therapy (it is a very effective in vitro genes transporter, but the applications in this field are still limited due to cytotoxicity - is considered a highly charged polycation which interacts with the cell surface an causing surface damage), support in catalysis, being electrically charged at low pH values [12]. Biomolecules transport field made progress towards increasing the efficiency of the process, either by polymer hydrophobation or synthesis of carbon nanotubes-polyethylene imine composites. Non-covalent functionalization of carbon nanotubes in the polymer by its adsorption on nanotubes surface has been reported for improving the transport of genes or DNA fragments [13]. A big advantage is the fact that the polymer can react with carbon dioxide, by formation of carbamate-type linkages, this making it useful for synthesis of CO<sub>2</sub> separation materials or for obtaining sensors for CO<sub>2</sub> detection [14]. Polysulfone polyethylene imine type composite membranes have not been reported so far due to the incompatibility of the two polymers to be in the same solution. Polysulfone dissolves in polar organic solvents (N-methyl-pyrrolidone, N, N-dimethylformamide, dimethylsulfoxide), while the polyethyleneimine is dissolved in water (solvent which is usually used in the precipitation of polysulfone). This makes it impossible to find a compromise that a membrane containing both polymers to be synthesized from the same solution. However, literature refers to polysulfone membrane with above polyethylene imine film deposit [15].

In this study we investigate synthesis of a new composite membrane polysulfone – polyethylene imine - carbon nanotubes through a new technique which consists in introducing polyethylene imine in polysulfone membrane during coagulation process in water. The produced membranes were characterized by scanning electron microscopy, FT-IR spectroscopy and have been

used in the separation of bovine serum albumin or heavy metals retention (lead and mercury) from aqueous solutions, the retention capacity have been studied. An advantage of using this polymer as the filler is given as to its properties and as for the polyethylene imine is insoluble in cold water, this fact providing the possibility of using membranes in filtration processes and allowing the permeation tests.

## 2. Experimental

Polysulfone was provided by BASF, sort Ultrason S3010. For polysulfone N-methyl-pyrrolidone (NMP) was used as a solvent, purchased from Fluka, and for the non-solvent a mixture of deionized water was used. Carbon aminonanotubes were brought from Nanocyl and the polyethylene imine, 60% water solution was purchased from Fluka.

The polymer solution was prepared dissolving the polymer in NMP at a concentration of 12% weight, vigorous stirring for 24 hours. Carbon nanotubes have been dispersed in the polymer solution at a concentration of 1% weight to the polymer in ultrasound field for 60 minutes. For composite membrane synthesis a less used in practice route was chosen, namely its introduction in the membrane in coagulation bath. The polymer solution is deposited on a glass support to a standard thickness of 250  $\mu\text{m}$ . During the clotting process, polyethylene imine penetrates polysulfone membrane structure. In order to complete the synthesis, through the composite membrane are also filtered two different polyethylene imine solutions, one of 20% and other of 40%. Polysulfone membranes were synthesized without fillers in order to have a witness for membranes performances comparing. Also, composite polysulfone - carbon nanotubes membranes were obtained at 1% nanotubes concentration by previously reported method in the literature [8].

Synthesized membranes were characterized by scanning electron microscopy SEM using a FEI XL 30 ESEM TMP microscope (prior to the analysis, the samples were coated with gold in order to prevent their destruction) [16-19] and by IR spectroscopy FT-IR on a Bruker Tensor 27 spectrometer equipped with diamond ATR device. Fluxes and protein retention were measured on a Sartorius equipment. For quantitative determination of protein retention the measuring UV absorbance Viz technique was used for feed solution before and after passing through the membrane, with a Campsec spectrometer [20].

## 3. Results and discussion

The most common method to obtain composite polymer-polymer membrane is such that the two polymers are mixed in solution at a concentration of membrane drawing, followed by the coagulation method. Other two methods consists in filtering the polymer particles by an already formed membrane or adsorption in a membrane of a monomer followed by its polymerization (such as a

membrane soaking aniline, followed by immersing the membrane in an oxidant, which results in a composite polyaniline membrane or soaking a pyrrole membrane following the same procedure and obtaining a composite membrane with polypyrrole). In case of the present synthesis, none of these methods could be applied due to the incompatibility of the two polymers with the solvents in which they were dissolved. Meanwhile another compromise had to be touched linked of the fact that polyethylene imine can locally dissolve polysulfone if they are in equilibrium in the solvents (water, respectively NMP). That is why the polyethylene imine concentration in the coagulation bath was relatively low compared to the initial concentration (25% and 35% vs. 60%). This drawback may also be avoided by keeping the membranes in alcohol, after synthesis, the porous structure of the polysulfone support membrane is not allowing polyethylene imine to get out.

Membranes was characterized by SEM microscopy, both active and porous surface and in section. Thereof, on polysulfone-carbon nanotubes membranes, it can be seen on their surface the presence of polymer micro-spherulites due to the phase inversion process (polymer residues leaving the porous structure and depositing on the membrane surface). These micro-spherulites are absent on the surface of composite membranes with polyethylene imine, this probably due to equilibrium that occurs in membrane synthesis, the presence of the second polymer not allowing polysulfone debris to leave the membrane structure. Also, differences can be seen between the two types of membrane thickness, varying from 40 $\mu\text{m}$  for polysulfone - carbon nanotubes membrane to 140-160  $\mu\text{m}$  in composite membranes with polyethylene imine (the thickness difference is due to swelling time of polysulfone membrane with polymer filler).

FT-IR spectrum shows some significant changes between the membrane with carbon nanotubes and the one which further comprises polymer. First of all the intensity of bands for the composite polyethylene imine membrane is half, which indicates a very good homogeneity of the material. The band at 1650  $\text{cm}^{-1}$  generally specific for the NMP rest, disappears in case of composite membrane indicating a more efficient phase inversion process. However, some tapes from polysulfone are screened and covered by the specific molecular combination of polyethylene imine (in particular in the region of 1200-1300  $\text{cm}^{-1}$  where specific bands of aromatic kernels are covered by specific bands of the aliphatic chain), which indicates a higher polysulfone pores filling with polymer filler (its share is larger in the material volume). It is known that for a membrane obtained from a 12% polymer solution, the pores volume is in the range of 85-90 %, in this case, the FT -IR spectroscopic data indicates that the percentage of the two polymers in total mass of material is comparable.

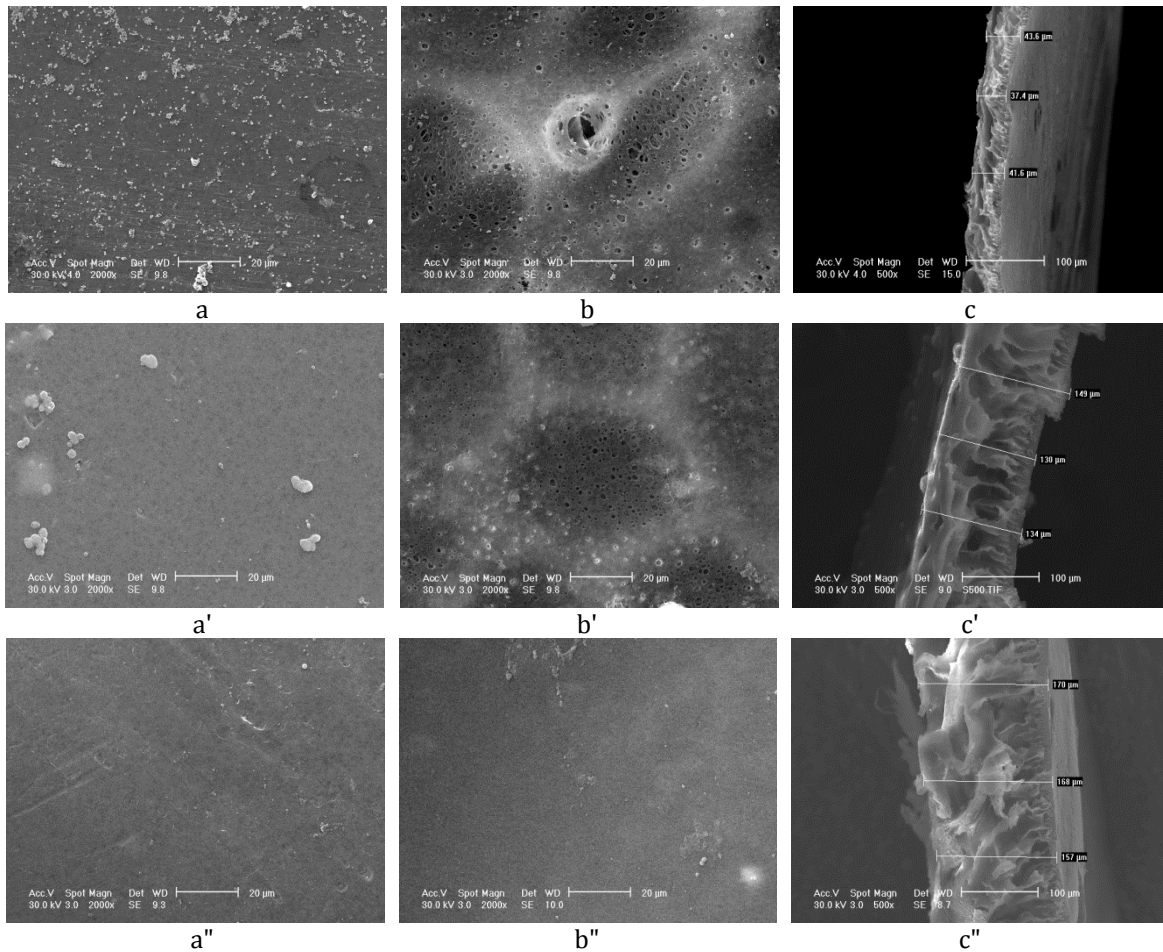
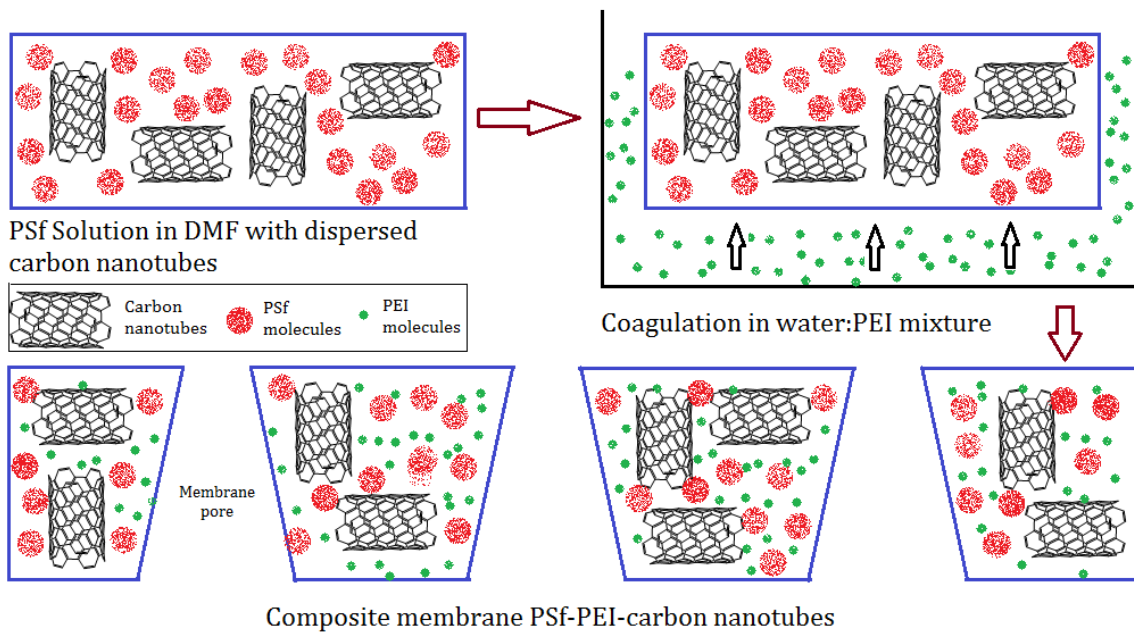


Fig. 1. Schematic representation of producing method for synthesized composite membranes (top) and Scanning electron microscopy (bottom): active surface (a), porous surface (b), section (c), a, b, c - polysulfone membrane with carbon nanotubes, a', b', c' - composite membrane of 25% polyethylene imine, a'', b'', c'' - composite membrane of 35% polyethylene imine .

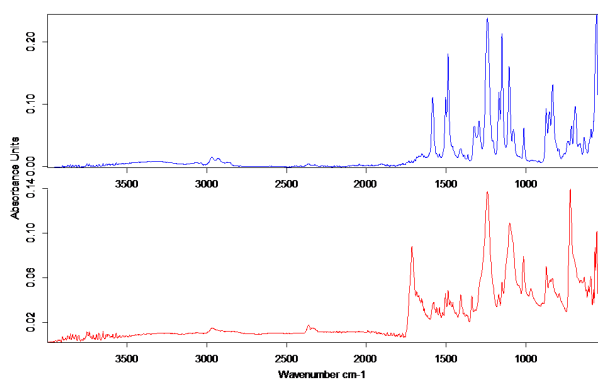


Fig. 2. FT-IR spectrum for composite membrane polysulfone - carbon nanotubes (top) and for composite membrane polysulfone - polyethylene imine - carbon nanotubes (bottom).

Water flows were measured to hydrodynamic characterize the synthesized composite material (Fig. 3) at 25 °C in order to avoid dissolution of polyethylene imine using a 500 mL water volume on a 45 mm diameter membrane. The decrease in flow in case of carbon nanotubes membrane is due to their hydrophobicity. Membranes are not very stable, as evidenced by lower initial flow of polysulfone membranes, respectively polysulfone with carbon nanotubes, the composite membrane with polyethylene imine showing greater stability due to compact structure.

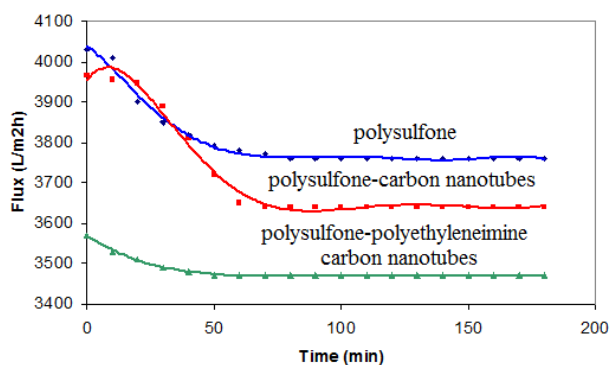


Fig. 3. Water flows for synthesized membranes.

To check the filtering capacity of synthesized membranes we studied separation and retention of bovine serum albumin. The results are shown in Figure 4. It can be seen that the polymer-polymer composite membrane retention capacity is better comparing to polysulfone membranes, respectively polysulfone - carbon nanotubes, due to polyethylene imine ability to form non-covalent interactions between free electrons from imine groups and the ones of the amino or carboxyl groups of the protein structure, thus achieving an non-covalent immobilization of the protein in the membrane structure. Relatively low values of retention can be explained by clogging of the membrane due to low porosity, as a consequence of both

concentration of the polymer solution from which it starts, and also presence of polyethylene imine in case of composite membrane. Better retention using carbon nanotubes membranes can be explained by protein adsorption on their surface, but because the percentage of nanotubes in the membrane structure is not very high, the result do not show a spectacular increasing retention capacity.

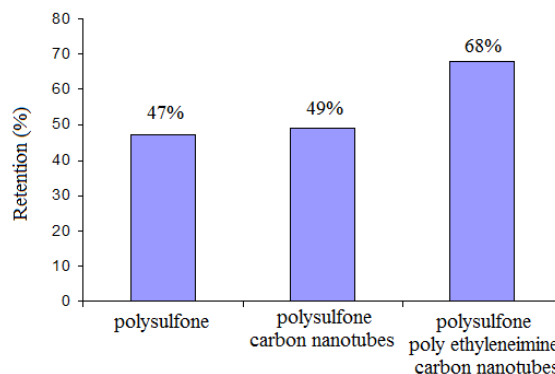


Fig. 4. Bovine serum albumin retention on synthesized membranes.

Retention capacity of heavy metals has been studied for  $Pb^{2+}$  and  $Hg^{2+}$ . For this reason two solutions have been used  $(CH_3COO)_2Pb$ , respectively  $(CH_3COO)_2Hg$  dissolved in water at a concentration of  $10^{-5}M$ . The results are illustrated in Table 1.

Table 1. Retention of heavy metals on synthesized membranes.

Membrane	$Pb^{2+}$ (mg/cm <sup>2</sup> )	$Hg^{2+}$ (mg/cm <sup>2</sup> )
Polysulfone	0.32	0.28
Polysulfone-carbon nanotubes	12.71	11.54
Polysulfone-polyethylene imine-carbon nanotubes	28.23	23.84

If in the case of polysulfone membrane, the weak result is due solely to cations retention in the porous structure of the membrane, for nanotubes membrane, the retention mechanism is cations adsorption on the surface of nanotubes. Polyethylene imine composite membrane shows high value of restrained cations due to free electrons from polymer structure imine groups.

#### 4. Conclusions

Synthesis and characterization of a new composite membrane polysulfone-carbon nanotubes-polyethylene

imine was presented with a new technique of introducing partial amount of polymer materials (polyethylene imine) from coagulation bath during the process of membrane synthesis by phase inversion. Membranes were characterized by scanning electron microscopy SEM, respectively FT-IR, emphasizing the presence of polyethylene imine in membrane structure. Bovine serum albumin retention on composite membrane showed superior performance of this membrane, due to the free electrons of the imine groups that establish non-covalent interactions with amino and carboxyl groups in the protein structure, which is the reason why this membrane showed better performance on retention of lead and mercury from aqueous solutions.

### Acknowledgements

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/ID134398.

### References

- [1] C. Corobea, D. Donescu, S. Raditoiu, S. I. Voicu, G. Nechifor, *Revista de Chimie* **57**(9), 981 (2006).
- [2] C. Baicea, A. C. Nechifor, D. I. Vaireanu, O. Gales, R. Trusca, S. I. Voicu, *Optoelectron. Adv. Mater. – Rapid Comm.* **5**(11), 1181 (2011).
- [3] S. I. Voicu, F. Aldea, A. C. Nechifor, *Revista de Chimie* **61**(9), 817 (2010).
- [4] D. Sterescu, D. Stamatialis, M. Wessling, *Journal of Membrane Science* **310**, 512 (2008).
- [5] A. C. Nechifor, M. G. Stoian, S. I. Voicu, G. Nechifor, *Optoelectron. Adv. Mater. – Rapid Comm.* **4**(8), 1118 (2010).
- [6] S. I. Voicu, N. D. Stanciu, A. C. Nechifor, D. I. Vaireanu, G. Nechifor, *Romanian Journal of Information Science and Technology* **12**(3), 410 (2009).
- [7] F. D. Balacianu, A. C. Nechifor, R. Bartos, S. I. Voicu, G. Nechifor, *Optoelectron. Adv. Mater. – Rapid Commun.* **3**(3), 219 (2009).
- [8] G. Nechifor, S. I. Voicu, A. C. Nechifor, S. Garea, *Desalination* **241**, 342 (2009).
- [9] A. C. Nechifor, V. Panait, L. Naftanaila, D. Batalu, S. I. Voicu, *Digest Journal of Nanomaterials and Biostructures* **8**(2), 875 (2013).
- [10] V. I. Luntraru, O. Gales, L. Iarca, E. Vasile, S. I. Voicu, A. C. Nechifor, *Optoelectron. Adv. Mater. – Rapid Commun.* **5**(11), 1229 (2011).
- [11] B. C. Serban, S. I. Voicu, S. D. Costea, C. Cobianu, US Patent Office, US 7,695,993 B2.
- [12] I. C. Bellettini, L. G. Nandi, R. Eising, J. B. Domingos, V. G. Machado, E. Minatti, *Journal of Colloid and Interface Science* **370**, 94 (2012).
- [13] B. Behnam, W. T. Shier, A. H. Nia, K. Abnous, M. Ramezani, *International Journal of Pharmaceutics* **454**, 204 (2013).
- [14] B. C. Serban, V. G. Dumitru, C. Cobianu, S. D. Costea, N. Varachiu, S. I. Voicu, US Patent Office, US 7,867,552 B2.
- [15] J. D. Schiffman, Y. Wang, E. P. Giannelis, M. Elimelech, *Langmuir* **27**, 13159 (2011).
- [16] F. Miculescu, I. Jepu, C. Porosnicu, C. P. Lungu, M. Miculescu, B. Burhala, *Digest Journal of Nanomaterials and Biostructures* **6**(1), 307 (2011).
- [17] G. E. Stan, C. O. Morosanu, D. A. Marcov, I. Pasuk, F. Miculescu, G. Reumont, *Applied Surface Science* **255** (22), 9132 (2009).
- [18] F. Miculescu, I. Jepu, C. P. Lungu, M. Miculescu, M. Bane, *Digest Journal of Nanomaterials and Biostructures* **6**(2), 769 (2011).
- [19] F. Miculescu, M. Miculescu, L. T. Ciocan, A. Ernuteanu, I. Antoniac, I. Pencea, E. Matei, *Digest Journal of Nanomaterials and Biostructures* **6**(3), 1117 (2011).
- [20] S. I. Voicu, A. Dobrica, S. Sava, A. Ivan, L. Naftanaila, J. *Optoelectron. Adv. Mater.* **14**(11-12), 923 (2012).

\*Corresponding author: svoicu@gmail.com