Digest Journal of Nanomaterials and Biostructures Vol. 8, No. 2, April - June 2013, p. 875 - 884

# SYMMETRICALLY POLYSULFONE MEMBRANES OBTAINED BY SOLVENT EVAPORATION USING CARBON NANOTUBES AS ADDITIVES. SYNTHESIS, CHARACTERIZATION AND APPLICATIONS

A.C. NECHIFOR, V. PANAIT, L. NAFTANAILA, D. BATALU,
S.I. VOICU*
*Politehnica University of Bucharest, Department of Analytical Chemistry and Environmental Protection, 1 Polizu St., 011061 Bucharest, Romania,*

This paper presents the synthesis and characterization of a symmetric polysulfone membrane obtained by solvent evaporation using carbon nanotubes as additives in polymer solution. The membranes were synthesized from N, N' - dimethyl formamide with dispersed amino carbon nanotubes. The obtained symmetric membranes by solvent evaporation were characterized by Scanning Electron Microscopy, Fourier transformed infrared Spectroscopy, Thermal Analysis and were used as membrane reactors for carbon nanotubes functionalization. The composite membrane with functionalized carbon nanotubes were characterized by NMR spectrometry.

(Received April 12, 2013; Accepted June 14, 2013)

*Keywords:* Polysulfone symmetric membrane, Carbon nanotubes, Membrane reactor

## 1. Introduction

In the last decades, the polymeric materials have been intensively studied due to their application possibilities [1-3] Since the begging of this century, when the first microporous membranes were obtained by Bechold [4], was intuitively recognized the potential of synthetic membranes for separation of species dissolved in a solvent, but industrial applications of membranes remained limited until the development of the first asymmetric membranes by Loeb and Sourirajan [5] in 1962. These membranes present a practical value due to an extremely thin active layer with a thickness of approximately 0.1 to 0.5 µm from the surface membrane. This layer is supported by microporous structure of the membrane with an average thickness between 0.1 and 0.2 mm, which provide mechanical stability to the membrane. Due to this very thin active layer, the hydrodynamic resistance of a asymmetric membrane is very low compared with symmetric membranes with the same selectivity [5, 6].

Synthetic polymeric membranes can be obtained by several methods, the most versatile being the synthesis by phase inversion. Most commercial membranes are produced by different phase inversion techniques. The concept of phase inversion was introduced by Kesting [6, 7] in the 70s and can be summarized as follows: a homogenous polymer solution is transformed into a two-phase system in which the solid phase is the polymer that will form the membrane, while the liquid phase (which is in a very small amount in polymer structure) will occupy and lead to pore formation.

In order to prepare membranes it is necessarily to use medium or high concentrated polymer solutions. In such systems, the crystallization time becomes important because the key steps for the membrane formation are nucleation and the growth of the crystal structure. Moreover,

---

* Corresponding author: svoicu@gmail.com

where crystallization is induced by a change in the system composition, a competition between the transfer rate and the nucleation rate will appear. A low mass transfer rate will compared to the nucleation rate will induce a low crystallization phenomena and a membrane cannot be obtained.

A too quickly mass transfer will lead to the formation of many nucleation centers but with a limited ability to grow the polymer structure [5].

The symmetric membranes present a lower importance for separation processes, but are mostly used as membrane reactors. Catalytic membranes without separative function have successfully been applied as microstructured reactors [8, 9]. If the reactant mixture is forced to flow through the pores of a membrane which have been impregnated with catalyst, the intensive contact allows for high catalytic activity with negligible mass transport resistances [9, 10]. Previous work [11] reported the functionalization of carbon nanotubes with covalent immobilization of enzymes by the use of a polysulfone asymmetric membrane as a membrane reactor. Based on the reactivity of carbon nanotubes, the functionalization reactions can be divided in two groups. The first one is based on chemical oxidation of the nanotubes leading to carboxylic, carbonyl and/or hydroxyl functions. The second group is based on direct addition to the graphitic-lie surface of the nanotubes [11, 12].

This paper presents the synthesis of a symmetric polysulfone-carbon nanotubes composite membrane, by the use of a method (solvent evaporation) witch leads to asymmetric membranes. The membranes were synthesized from N, N' - dimethyl formamide with dispersed amino carbon nanotubes. The obtained symmetric membranes by solvent evaporation were characterized by Scanning Electron Microscopy, Fourier transformed infrared Spectroscopy, Thermal Analysis and were used as membrane reactors for carbon nanotubes functionalization. The used amino carbon nanotubes were covalent functionalized with crown ethers derivatives.

## 2. Experimental

### 2.1 Synthesis of polysulfone-amino carbon nanotubes composite membranes

Polysulfone (Ultrason S3010 provided by BASF) was dissolved in N, N' - dimethyl formamide (DMF) at a concentration of 15% mw. Amino carbon nanotubes (Nanocyl) were added to the formed polymer solution at 1% related to polymer and dispersed by sonication for 1h. The polymeric film with dispersed carbon nanotubes was deposited onto a glass at a standard thickness of 250 μm and the membeanes were synthesized by solvent evaporation at $60^oC$. The obtained membranes were washed consequently with iso-propanol and deionized water for the polymer and carbon nanotubes traces and impurties from membrane surface removal.

### 2.2 Functionalization of amino carbon nanotubes.

The nanotubes were functionalized with crown ethers using cyanuric chloride as linker. Amino crown ether (Sigma Aldrich) and aza-crown ether (Sigma Aldrich) were functionalized with cyanuric chloride in dioxan in the presence of triethylene amine (for neutralization of hydrochloric acid resulted in reaction) [13, 14]. The reaction equations are presented in Fig. 1.

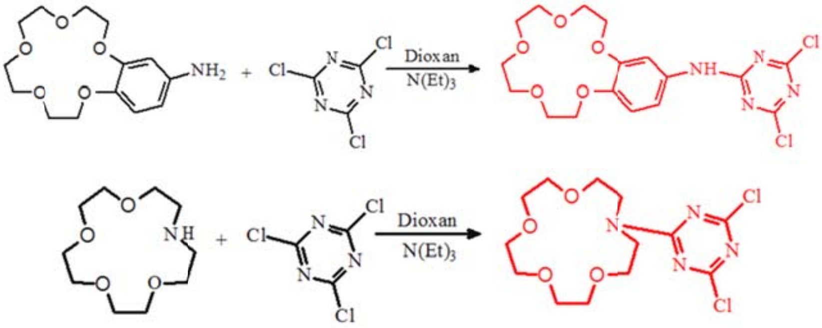


*Fig. 1 Reaction equations for the synthesis of crown ethers derivatives*

For the functionalization of amino carbon nanotubes was performed using the membrane as a reactor. Free parts of nanotubes in membrane pores were functionalized with crown ether derivatives in a mixture of water and dioxan at 70°C. The mixture of water with organic solvent is necessarily because the pure dioxan can affect the polymer by dissolving it. The reaction equations are presented in Fig. 2.

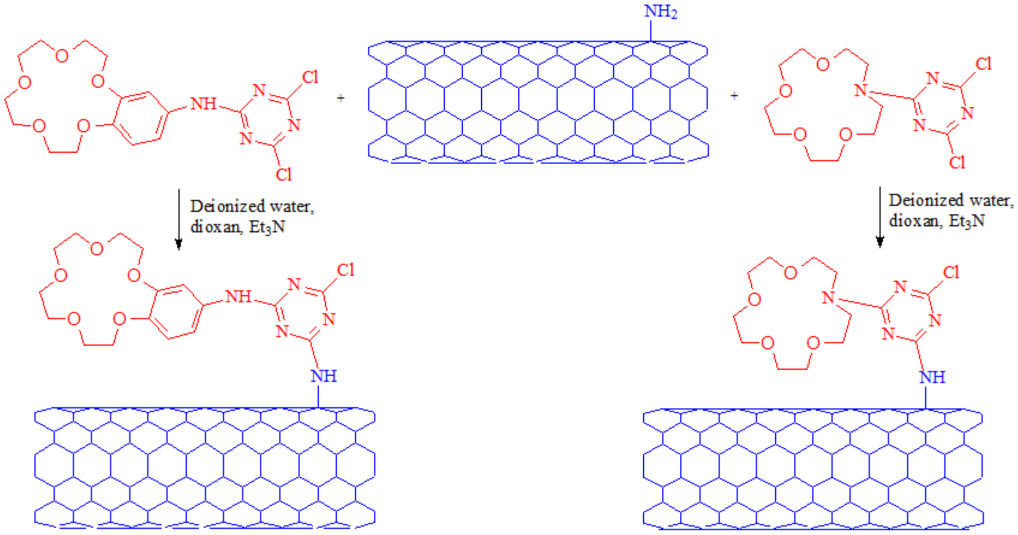


*Fig. 2 Reaction equations for the functionalization of carbon nanotubes*

### *2.3 Characterization techniques*

The membranes were characterized by Scanning Electron Microscopy (FEI Instrument, the samples were covered with a thin layer of gold [15-17]), thermal analysis (TGA-DSC) using an Universal V4.5A TA instrument and FT-IR spectroscopy analysis (Bruker Tensor 27 with ATR annex) and NMR spectrometry Bruker 400 MHz.

## **3. Results and discussions**

Usually, by phase inversion technique, asymmetric membranes are obtained (a big difference between pore sizes on each side of the membrane). If the phase inversion is realized using a bath with a non solvent for the polymer, the speed formation for the membrane is high (not more than 2 min), but if the membrane is synthesized by solvent evaporation, the speed formation for the membrane is very low (several hours or even days, depending by the boiling point of the polymer solvent and the environmental temperature).

The formation mechanism and obtained membranes were investigated by several analysis methods which will be explained below. The main absorption bands are 1150 cm$^{-1}$ ($SO_2$ group from polysulfone), 2870 cm$^{-1}$ (attributed to $CH_3$ groups from polysulfone), 3210 cm$^{-1}$ (attributed to aromatic rings from polysulfone), and 1620 cm$^{-1}$ (attributed to $NH_2$ group from amino carbon nanotubes) [11]. In the FT-IR spectrum (Fig. 3) we can observe that on polysulfone-carbon nanotubes composite membrane a band at 1647 cm$^{-1}$ disappears. This the typical band for the plane specific vibration of C=O bond from DMF solvent (detailed in Fig. 4). This can be explained by the presence of carbon nanotubes and to the fact that they cannot be wetted by solvents. In the structure of a polysulfone membrane, a significant amount of polymer solvent remains in the membrane pores (enough quantity to give specific absorption in the IR spoectrum). In the presence of carbon nanotubes, this does not happen due to the delocalized electrons on the surface of nanotubes which makes impossible the interaction of nanotubes polar solvent molecules. This explain the disappearance of the solvent from membrane structure. More than that, this must be correlated with the fact the evaporation temperature for DMF is 180°C, so the membrane formation is a very slow process and this is also a reason for the shape and dimensions of membrane pores. In the FT-IR spectrum it also can be observed a slight shift of absorption bands to the left with 1-2 cm$^{-1}$ (due to the electrical properties and influence of carbon nanotubes through polymer).

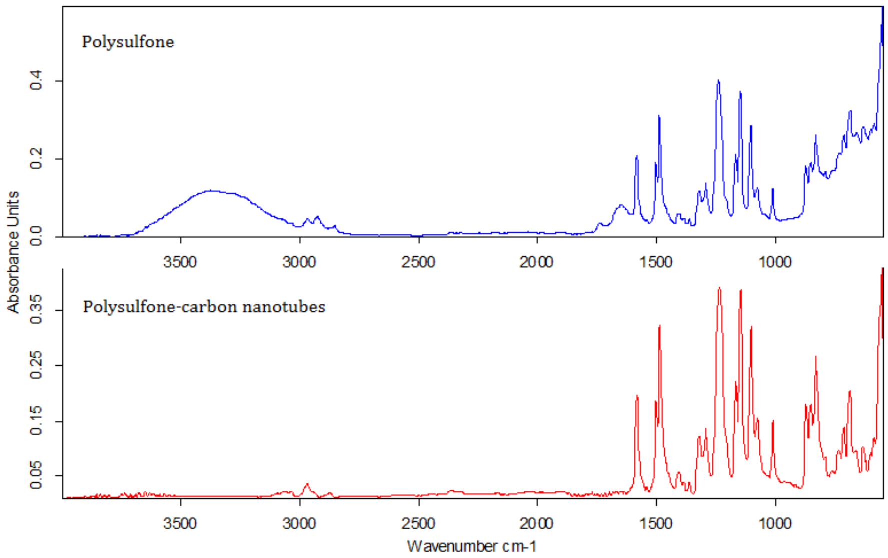


*Fig. 3 The FT-IR spectrum of polysulfone and polysulfone-carbon nanotubes composite membranes*

These chemical shifts suggests a non-covalent interaction between carbon nanotubes and polymer. Another interesting aspect is the fact in the membrane with carbon nantubes, the water is not present at all, specific bands for hydrogen bond associations (2800-3600 cm$^{-1}$) being absent. This observation should also be correlated with the inability of carbon nanotubes to be wetted by any solvent. The formation mechanism for these membranes is similar to the phase inversion in the presence of a solvent, but in this case, the non-solvent is represent by the water vapors from atmosphere.

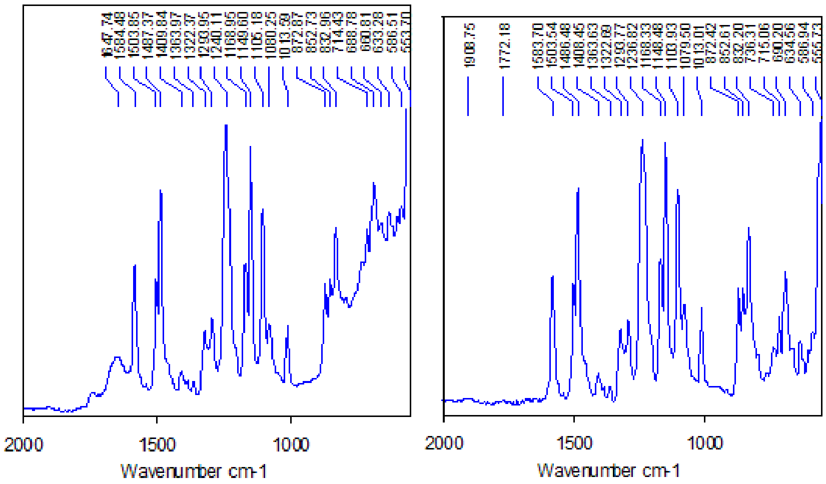
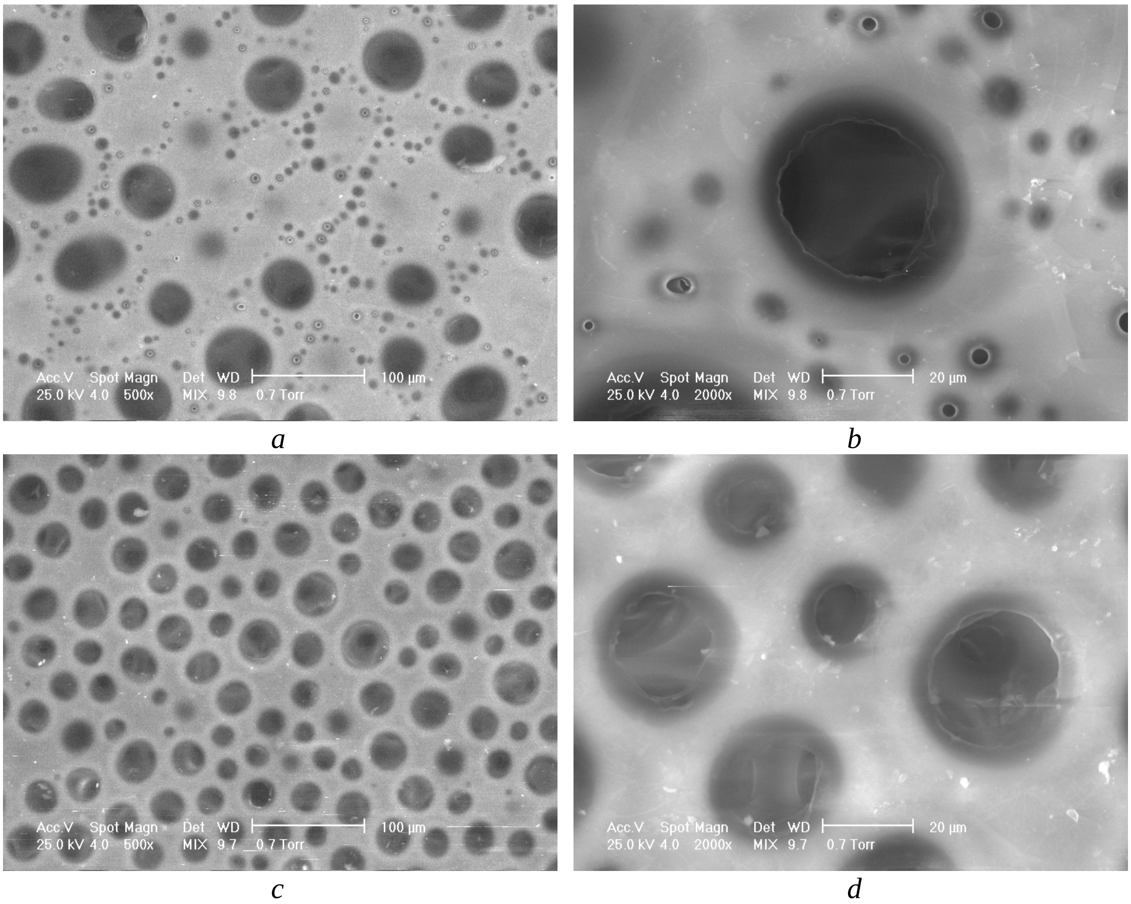


*Fig. 4 Details of polymer bands absorptions on FT-IR spectrum on polysulfone (left) and polysulfone-carbon nanotubes composite membrane (right)*

From Scanning Electron Microscopy micrographs (Fig. 5) we can observe two membrane surfaces. We cannot say that one is the active surface and the other one is the porous surface because both exhibits pores with shape and dimensions comparable. But, the membrane surface which was not in contact with the substrate (glass) present two types of pores: one large with dimensions comparable to those on the other side and some smaller, surrounding the large pores. The presence of these small pores can be explained by the slow coagulation process during solvent evaporation. The large pores are determined by the mass transfer which occurs during the evaporation of the main amount of solvent and the smaller ones can be explained by a post-evaporation process of solvent traces from polymer block. Clearly, these small pores are determined by a very small amount of solvent, evaporated later than the main quantity. The average dimension of pores is between 20 and 50 µm and the small ones has a diameter around 2-4 µm. These pore dimensions recommend these membranes for classic filtration or clarification processes (separation of particles larger than 50 µm).

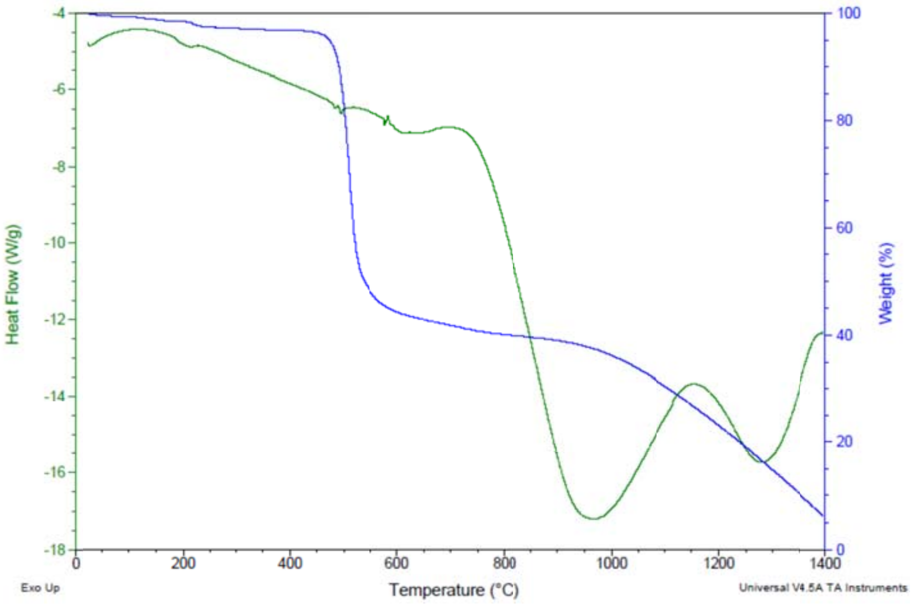


*a* *b*

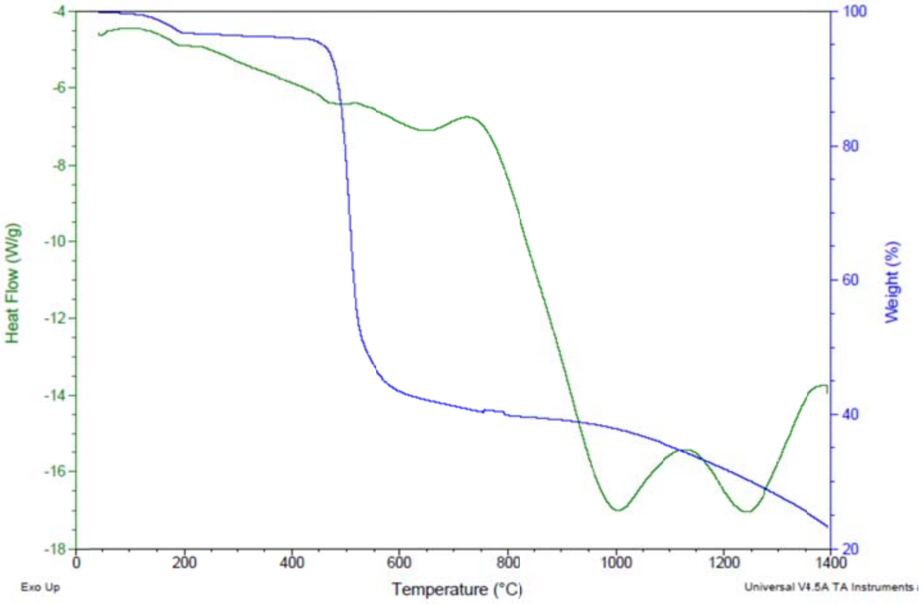
*c* *d*

*Fig. 5 Scanning Electron Microscopy of one side of the membrane (a - x500 and b - x2000) and of the other side of the membrane (c - x500 and d - x2000)*

The thermal behaviour of the synthesized membranes was analyzed by Thermal Gravimetric Analysis (Fig. 6). Due to the small amount of carbon nanotubes, the thermal properties are not very different, but a small difference in the thermal degradation can be observed. The weight loss for polysulfone-carbon nanotubes composite membrane is slightly and at the begging of the degradation the allure of the curve suggests the absence of water from membrane structure which is in accord with FT-IR data.



*Polysulfone membrane*



*Polysulfone - carbon nanotubes composite membrane*

*Fig. 6 The Thermal Gravimetric Analysis curves for obtained membranes*

In order to evaluate the membrane performances, the solvent permeation testes were realized. It was tested the membrane permeability for deionized water, methanol, ethanol, iso-propanol at room temperature and atmospheric pressure. The data for alcohols permeation are presented in Fig. 7 and for water permeation at different temperatures are presented in Table 1. The membranes presents high fluxes due to the pore dimensions. The variation of fluxes with time is negligible which suggests a very stable behaviour of polymer structure to solvent cross-flow. This can be explained by a cross-linking effect of carbon nanotubes to membrane, having as consequence the increase of mechanical properties of the composite material. This conclusion is supported by the water fluxes at different temperatures. Normally, with the increase of temperature, the water flux presents a high increase due to pore dilatation [18]. Here, the variations are not so high due to the membrane stability. This behaviour is important due to the requirements for thermal stability if the carbon nanotubes from membrane structure are involved in chemical reactions.

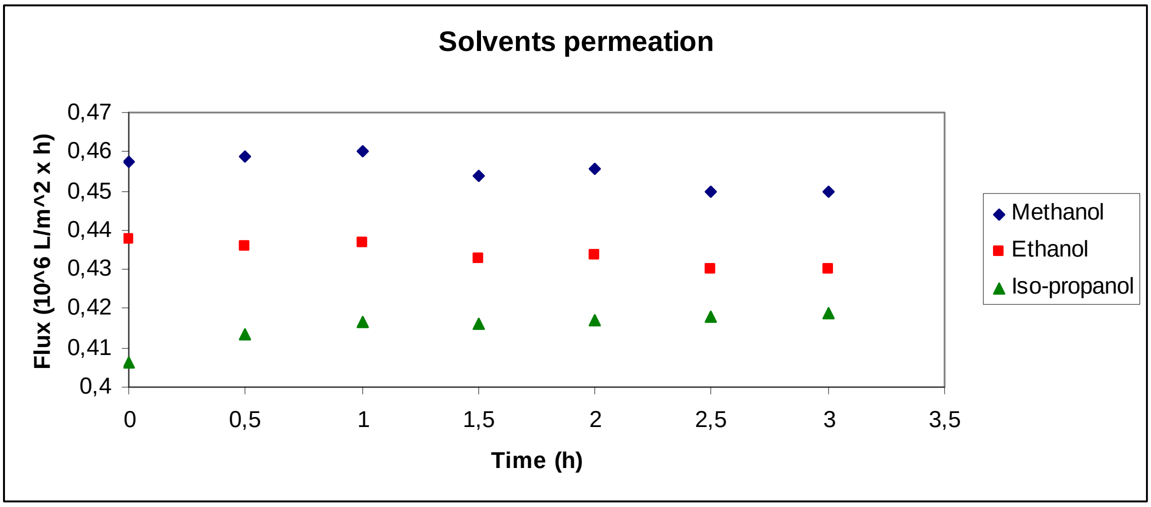


*Fig. 7 Solvents permeation (methanol, ethanol, iso-propanol) through polysulfone-carbon nanotubes composite membrane*

*Table 1. Water fluxes at different temperatures*

| Temperature ($^{o}$C) | 20 | 30 | 40 | 50 | 60 | 70 |
|---|---|---|---|---|---|---|
| Water Flux ($10^6$ L/m$^2$ x h) | 0,2435 | 0,2439 | 0,2441 | 0,2631 | 0,2698 | 0,2732 |

Previous work demonstrated the possibility to functionalized carbon nanotubes based on the fact that parts from carbon nanotubes are free in membrane pores. The used carbon nanotubes in this research presents free amino groups at surface (5%) in enough quantity to make possible the functionalization process (Fig. 8).

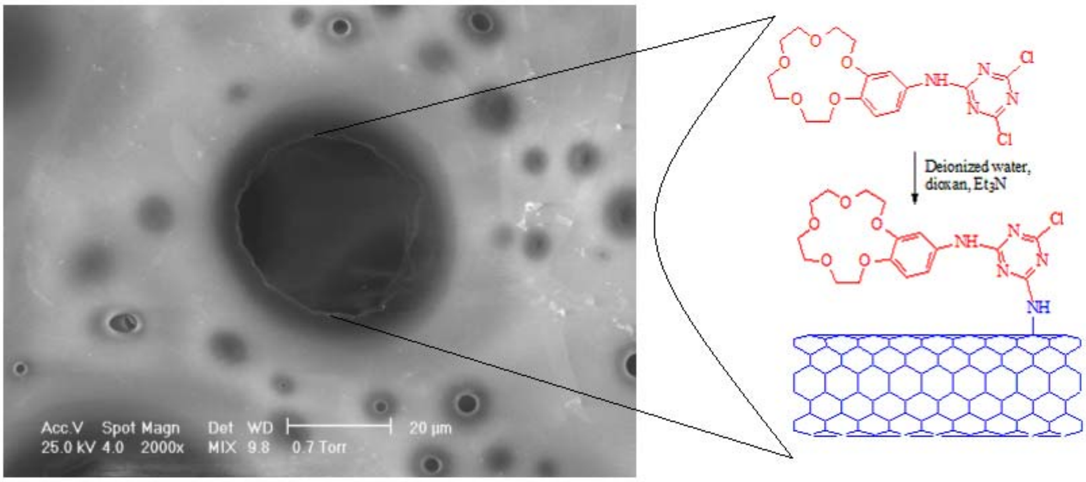
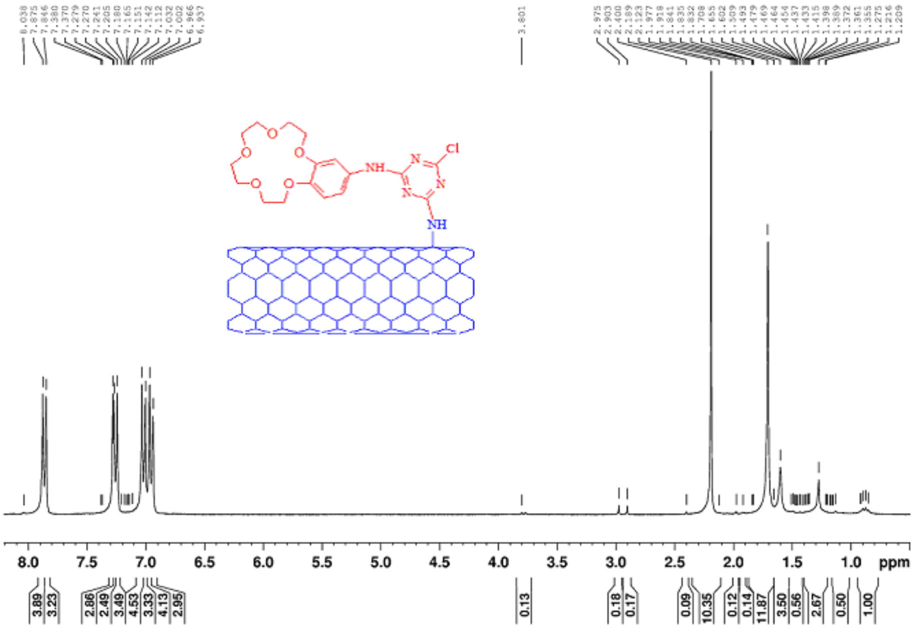
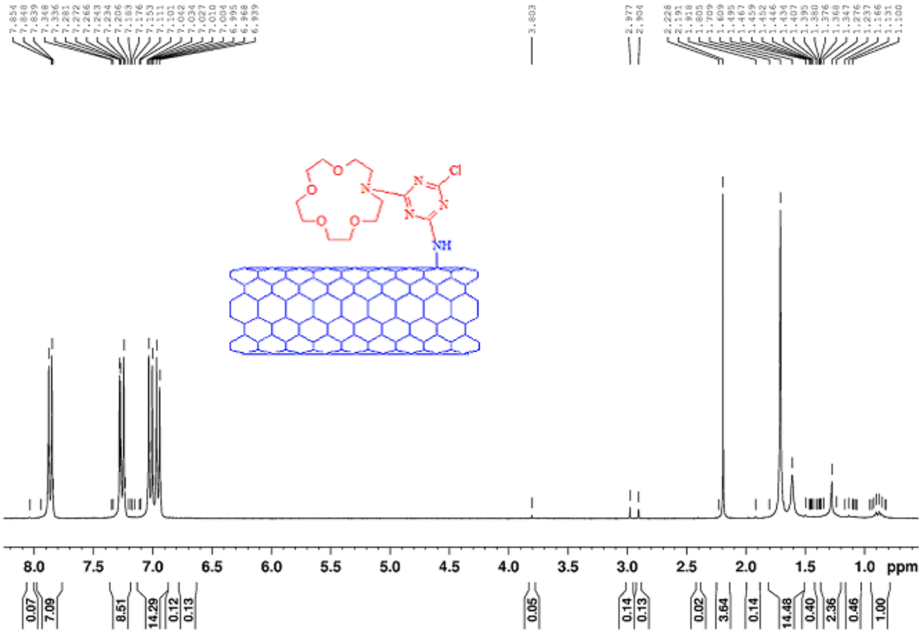


*Fig. 8 Schematic representation of functionalization reaction in membrane pores*

The access of reagents to reaction centres is realized by diffusion mechanism through membrane pores. The main advantage of this method is the homogenous functionalization (even if the free reaction centres are not in high number in membrane pores, there are many available than in a solution). Cyanuric chloride is a widely used linker for immobilization of different chemical species due to the characteristics of aromatic ring. After the first reaction at a chloride atom, the aromatic ring is deactivated and on this way the reactions in which two molecules from the same species can react will be avoided. After this deactivation the possibility to perform a second reaction at a second chloride atom is the increase of reaction temperature [11].



*NMR spectra of polysulfone-carbon nanotubes functionalized with amino-benzo crown ether*



*NMR spectra of polysulfone-carbon nanotubes functionalized with aza crown ether*

*Fig. 9 NMR spectrum of composite membranes with functionalized carbon nanotubes*

The NMR analysis was performed by dissolving the membrane in deuterated chloroform. The chemical shift at 1.845 ppm is attributed to $NH_2$ protons from amino carbon nanotubes, 6.941 ppm, 6.969 ppm, 7.006 ppm, and 7.033 ppm are attributed to H from aromatic ring and 1.376 ppm is attributed to proton from –CH3. The chemical shifts at 2.975 ppm (in the case of amino-benzo-crown ether) and 2.977 ppm are attributed to the proton from -NH- which demonstrate the functionalization of carbon nanotubes. The small intensity of the signal can be explained by the small number of amino groups which can be involved in functionalization reaction.

For different applications, the membrane can be used as it is (for example for the separation of different cations or membrane sensors), or the carbon nanotubes can be recovery from the membrane structure, by dissolving the membrane in a large quantity of polymer solvent [11]. Functionalized carbon nanotubes can be used for the manufacturing of sensors or biosensors.

## 4. Conclusions

The synthesis and characterization of a polysulfone-carbon nanotubes composite membrane was presented in this paper. The membrane was synthesized by solvent evaporation (procedure which usually leads to asymmetric membranes), but symmetric material was obtained. This was explained by the presence of carbon nanotubes and the observation was supported by analysis methods. The membrane was used as a membrane reactor for carbon nanotubes functionalization with crown ethers derivatives.

## Acknowledgements

Authors recognize financial support from the European Social Fund through POSDRU/89/1.5/S/54785 project: Postdoctoral Program for Advanced Research in the field of nanomaterials.

## References

[1] M. Ulbricht, Polymer **47**(7), 2217 (2006).
[2] R. Ianchis, D. Donescu, M.C. Corobea, C.L. Nistor, C. Petcu, R. Somoghi, R.D. Fierascu, Optoelectron. Adv. Mater. - Rapid Commun. **5**(12), 1352 (2011).
[3] G. Nechifor, S.I. Voicu, A.C. Nechifor, S. Garea, Desalination **241**, 342 (2009).
[4] H. Bechold, Biochem. Z. **6**, 397 (1907).
[5] S. Loeb, S. Sourirajan, Advan. Chem. Ser. **38**, 117 (1962).
[6] R.E. Kesting, Synthetic Polymer Membranes, McGrow Hill, New York, 1972.
[7] J.G. Wijmans, Preparation of asymmetric membranes by the phase inversion process, Ph.D. Thesis, Twente Enschede, The Netherlands, 1984.
[8] A.G. Dixon, Int. J. Chem. React. Eng. 1 (R6), 1 (2003).
[9] T. Westermann, T. Melin, Chemical Engineering and Processing: Process Intensification **48**, 17 (2009).
[10] V.T. Zaspalis,W. van Praag, K. Keizer, J.G. van Ommen, J.R.H. Ross, A.J. Burggraaf, Appl. Catal. **74**(2), 205 (1991).
[11] S.I. Voicu, A.C. Nechifor, O. Gales, G. Nechifor, Proceedings of SPIE - The International Society for Optical Engineering, 8068, art. no. 80680Y, (2011).
[12] B. Bhushan, (ed.), Springer Handbook of Nanotechnology, Springer-Verlag Berlin Heidelberg, 3 (2004).
[13] F.D. Balacianu, A.C. Nechifor, R. Bartos, S.I. Voicu, G. Nechifor, Optoelectron. Adv. Mater. – Rapid Commun. **3**(3), 219 (2009).
[14] A.C. Nechifor, M.G. Stoian, S.I. Voicu, G. Nechifor, Optoelectron. Adv. Mater. – Rapid Commun. **4**(8), 1118 (2010).
[15] F. Miculescu, I. Jepu, C. P. Lungu, M. Miculescu, M. Bane, Digest Journal of Nanomaterials and Biostructures **6**(2), 769 (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] 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).
[18] S.I. Voicu, A. Dobrica, S. Sava, A.Ivan, L. Naftanaila, J. Optoelecron. Adv. Mater. **14**(11-12), 923 (2012).