

Polysulfone-carbon Nanotubes Composite Membranes

Synthesis and characterization

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This paper presents the synthesis of new nanostructured composite membranes based on polysulfone and different types of carbon nanotubes (single wall SWNT or multi wall DWNT). The membranes were obtained from different solvents (N, N'-dimethylformamide, aniline), with both types of nanotubes dispersed in polymer mass and covalently bonded to the polymer (in this case we have used multiple-walled carbon nanotubes with amino groups on the surface and formylated polysulfone). The obtained membranes and membrane materials were characterized by FT-IR spectroscopy, NMR spectroscopy, thermal analysis, SEM microscopy.

Keywords: polysulfone, carbon nanotubes, nanostructured membranes

Carbon nanotubes were discovered in 1991 by Sumio Iijima, who studied the deposition of cathode material during synthesis of fullerenes by carbon evaporation. He found that the central core of the cathode deposit contains a variety of graphite structures including nanoparticles and nanotubes, a type which has not been observed previously [1]. Meanwhile, independent from Iijima, researchers at the Institute of Physical Chemistry in Moscow discovered carbon nanotubes, but they have obtained a generally report between length and diameter much smaller. These nanotubes have been named by Russian scientists barrelens. In 1992, Thomas Ebbesen and Pullikel Ajayan, in the Iijima's lab have shown how the nanotubes can be obtained in large quantities by varying the conditions of evaporation in the electric arc [2]. These successes have led to an explosion in research directed practice in the synthesis and characterization of carbon nanotubes in the world. Since then, the interest of researchers to characterize and develop applications of these nanotubes was becoming more of a desire to exploit the remarkable qualities of electronic and mechanical properties. Currently, nanotubes are used in applied research and even production in a number of areas: nanoelectronics, sensors, displays, hydrogen storage devices, batteries, polymer matrix composites, protective suits, reinforced materials, nano-sized reactors and electrodes, to mention only a few [3]. Composites of polymer-carbon nanotubes, first reported in [4] are now intensively studied, particularly composites based on epoxy resins and polymethyl methacrylate. Polymer composites based on carbon nanotubes with different structures were synthesized using the following matrix: MWNT-polyvinyl alcohol [5], MWNT-polyhydroxyaminoether [6], MWNT-polyurethane acrylate [7, 8], SWNT-polyurethane acrylate [9], SWNT-polycarbonate [10], MWNT-polyaniline [11], MWNT-polystyrene [12], SWNT-polyethylene [13], MWNT-polyacrylonitrile [14], MWNT-oxotitan phthalocyanine [15], MWNT-poly(3-octiltiofen) [16], SWNT-poly(3-octiltiofen) and MWNT-poly(3-hexiltiofen) [17]. Composites of polymer-carbon nanotubes, firstly reported by Ajayan [18] are now intensively studied, particularly composites based on epoxy resins and polymethyl methacrylate.

Regarding mechanical characteristics influence three aspects of the new composite performance must be

considered: strength and toughness of nanotube yarns, orientation, and the establishment of forces that occur on polymer-nanotube interface crucial for the formation of a stable composite. Carbon nanotubes with a single wall (SWNT) are more easily dispersed in a polymer matrix (in order to obtain isolated nanotubes) than multi-walled nanotubes (MWNT) due to weak electrostatic interactions and friction occurring nanotubes with a single wall [19]. Interactions and mechanisms leading to formation of nanocomposite polymer based carbon nanotubes are the forces of relaxation such as mechanical, chemical bonds and van der Waals interactions between nanotube and polymer. A high value of electrostatic interaction between the nanotube and polymer matrix shear transfer that will cause further tension to the neighboring nanotube polymer fiber. This is why it is recommended the use of single wall nanotubes with lengths ranging from 10-100 μm to create the tensions and mechanical forces such chemical interactions are not possible [20]. It was calculated that the critical minimum length of carbon nanotubes with a single wall required to form such mechanical interaction with polymer matrix must be 1 μm [21]. Also the potential of existing defects in the structure of nanotubes, are limiting their ability to interact with the polymer [22]. Mechanical loads transferred to the fiber polymer when used multi-walled nanotubes to obtain epoxy resin composites is much higher than for nanotubes with single wall, which makes the material much more stable. The performed tests have determined that a concentration of 5% SWNT in an epoxy matrix induces a large deformation of material. The influence of interfacial interactions that occur between polymer and carbon nanotube and the material properties was studied [23].

The reason for choosing the polysulfone as a membrane material for this study is due to its excellent characteristics such as: high chemical, thermal and mechanical resistance and can be used in a wide range of substitution aromatic electrophile reactions for functionalization (formylation, chlorometylation) and derivatization (to immobilize different chemical species like crown ethers, enzymes) [24-27].

In this paper new type of polymer membranes with carbon nanotubes based on polysulfone are synthesized and physically and chemically characterized.

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Materials and methods

Synthesis of composite membranes by dispersing the carbon nanotubes in a polymer solution

Preparation of polysulphone solution

In an Erlenmeyer flask with glass stopper is inserted the required amount of dimethylformamide (DMF) (Merck) and under magnetic stirring, portions of the amount of purified polymer (polysulphone provided by BASF, sort Ultrasonic S3010) are added, to achieve the desired concentration (15% polysulphone in DMF). Using the pure and dry polymer, the obtaining of the desired polymer solution occurs within 24 h. Before use, the solution is de-aerated by staying in vacuum desiccator for 30 min. After the formation of polymer solution the carbon nanotubes are added (SWNT products Nanocyl, purity 95% or DWNT products Nanocyl, purity 95%). For a better dispersion of carbon nanotubes in the polymeric solution, the solution was sonicated for 15 minutes. The same procedure was applied for obtaining a polysulphone in aniline (15%) with dispersed carbon nanotubes (DWNT products Nanocyl, purity 95%).

Formation of membranes

A quantity of polymer solution, 5ml, is deposited onto a spectral glass support and it was extended to a standard thickness of 250 μ m. Polymer film deposited on glass is submerged in the coagulation bath containing an aqueous solution of iso-propanol (50%) (in the case of polymer solution in DMF) or in a bath containing cyclohexanol (in the case of polymer solution in aniline). After coagulation, the membrane is washed with distilled water and methanol to remove traces of the solvent and the coagulant.

Synthesis of polysulfone composite membranes by reaction between amino carbon nanotubes and formylated polysulfone.

Polysulfone was formylated by a Vilsmeier-Haak synthesis using DMF and POCl₃ (Fluka) [28]. After the performance of reaction, the carbon nanotubes are added (DWNT surface modified NH₂ groups Nanocyl products, purity 99%). For the purposes of functionalisation reaction, the solution is homogenized in an ultrasonic thermostatic bath for 48 h at 75°C. All types of nanotubes were introduced at a rate of 5% related to polymer (fig. 1).

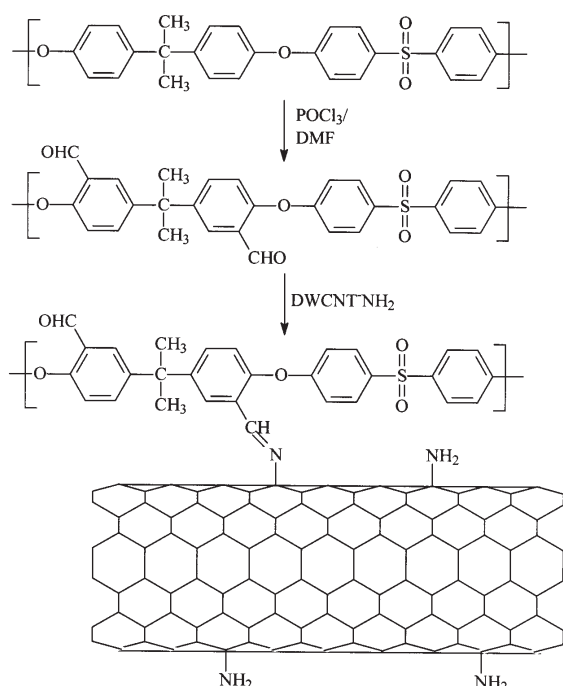


Fig. 1. Schematic representation of chemical reaction between formylated polysulfone and amino carbon nanotubes

Methods and instrumental analysis

a) The scanning electron microscopy was performed using a FESEM Hitachi S4500.

b) The infrared spectroscopy analysis was performed using a Bruker Vertex 70 instrument with diamond ATR annex.

c) The thermal analysis was performed using a TA Instruments 2950.

d) The atomic force microscopy was performed using an APE Research Instrument.

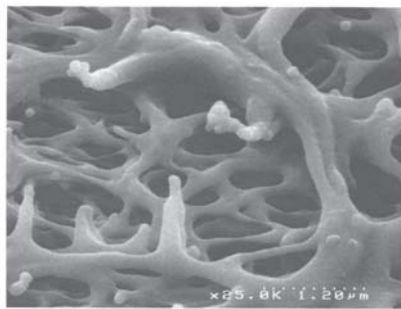
Results and discussions

In 2006 it was reported the obtaining of a composite membrane, polysulfone-carbon nanotubes, which was the first reported polymer composites based on polysulfone and carbon nanotubes [29]. Composite membrane was obtained by phase inversion with water solution. The polymer with carbon nanotubes was obtained by mixing a solution of polysulfone in N-methyl-pyrrolidone (NMP) with a solution of multi-walled carbon nanotubes in the same solvent. Synthetic route chosen by this group involves a special treatment applied to carbon nanotubes, which affects the electrical properties. Thus, for dispersion of carbon nanotubes in N-methyl pyrrolidone, nanotubes are treated with concentrated strong acids: sulfuric and nitric acids. By treatment with strong acids, sulfonic acid groups and carboxyl acid groups are generated onto the carbon nanotubes surface, which makes the solubility of nanotubes to increase due to interactions that arise between functional groups and solvent molecules. Treatment with strong acids causes, however, an impairment of holidays in the atomic network structure of nanotubes.

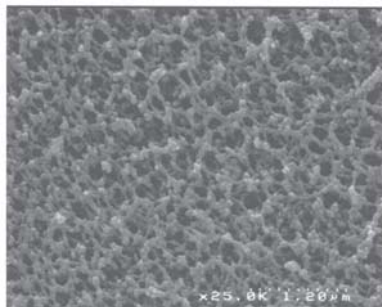
Research synthesis method chosen in this paper does not change the properties of nanotubes as it requires no chemical treatment of skeletal carbon nanotubes, which are subjected to physical or chemical reactions involving only the surface functional groups (-NH₂). Polymer composite materials based on carbon nanotubes, obtained so far, which refers to covalent interaction between nanotubes and polymers, are done usually by functionalisation nanotubes with different monomers, followed by their polymerization [30]. Membranes, obtained by the described procedure, were characterized by FT-IR spectroscopy, thermal analysis (TGA, DTA), scanning electronic microscopy (SEM), atomic force microscopy (AFM).

Electronic surface microscopy surface of the prepared membranes shows (fig. 2) significant differences between the morphology of membranes, depending on the type of solvent and the type of binding. In membranes obtained from the same solvent, DMF (fig. 2-a), by dispersion, it is observed on the surface, a highly cross-linked specific morphology, the look of woven network and superficial pore size of the order of a micrometer. Membranes which are made up of double-walled nanotubes (fig. 2-b) and were obtained from the same solvent, DMF, have much smaller pores, and presented with a more compact surface structure. Immediate explanation is that this morphology is due to surface forces of nature which arise between the nanotube and polymer, much higher due to the structure of double wall carbon nanotubes, but also due to higher compatibility in polymer solution.

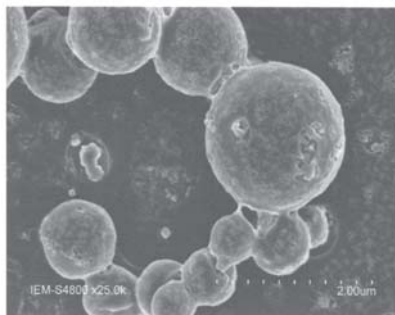
Figures 2-c and d presents interconnected micro-spheres raised, contributing to the different morphological appearance, of the membranes obtained from aniline (as solvent, fig. 2-c). The same micro spheres appear onto the surface of polysulfone membranes obtained form DMF by



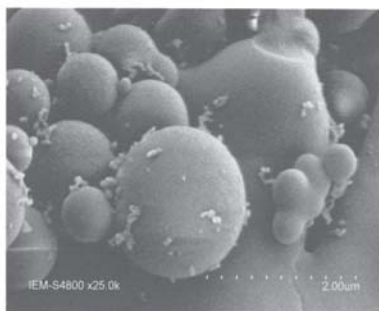
a



b



c



d

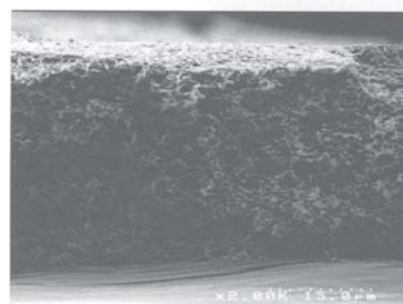
Fig. 2. SEM images of membranes surfaces: a-PSf-SWNT composite membrane, b-PSf-DWNT from DMF composite membranes, c-PSf-DWNT from aniline, and d-PSf-DWNT by covalent bonding between polymer and nanotube (all microscopies are presented at x25000 magnification)

dispersion of double walled carbon nanotubes. Unlike the micro spheres from the surface of membrane polysulfone/double walled carbon nanotubes/DMF, in the case of membranes obtained from aniline and in the case of membranes with covalently bonded carbon nanotubes, the micro spheres are integrated in the entire membrane structure.

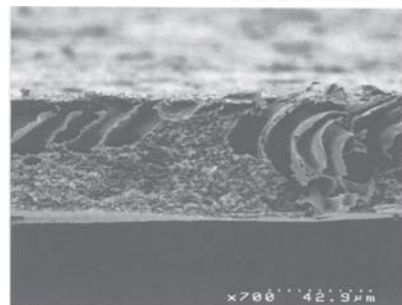
An interesting morphology presents polysulphone membrane surface obtained from aniline. At this membrane, the polymer was organized in spheres, like a strand, due to hydrophobic interactions and dipole-dipole

interaction. In the areas where the polymer membrane is organized in spheres between which there seems to be a link they appear as a string. Such self assemblies, rows and circles, were noted on magnetic nanoparticles [30] that are dispersed in organic solvents - magnetic nanofluids. This fact cannot be explained only by magnetic interactions, the weak chemical bonds being more probable.

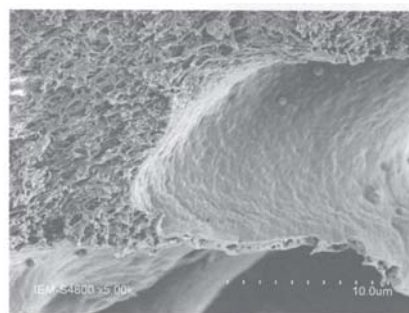
SEM microscopy sections of membranes synthesized present some issues in morphological characteristics. For the membrane obtained by mixing the polysulphone and carbon nanotubes, the structure is very similar to simple



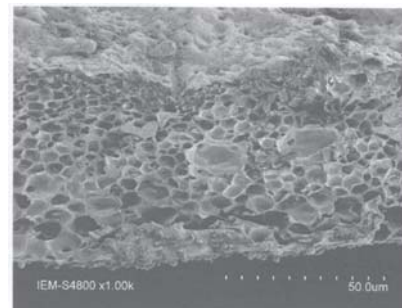
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b

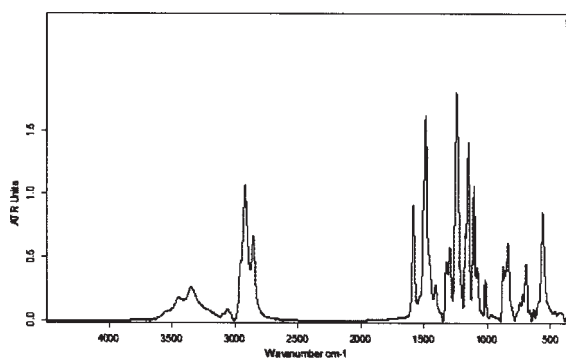


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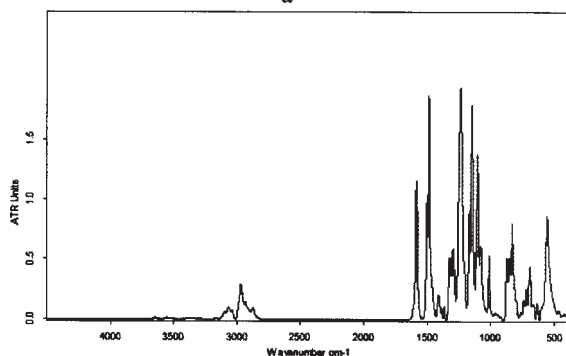


d

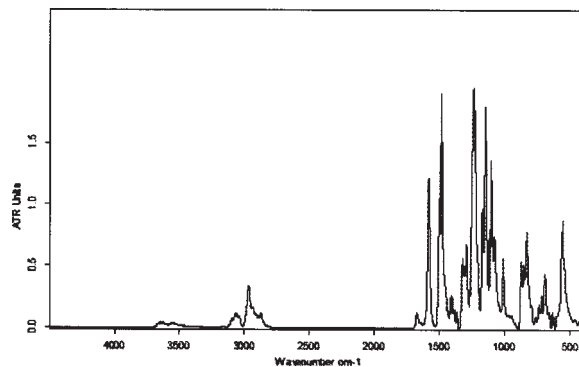
Fig. 3. SEM images of membranes cross-sections: a-PSf-SWNT composite membrane, b-PSf-DWNT from DMF composite membranes, c-PSf-DWNT from aniline, and d-PSf-DWNT by covalent bonding between polymer and nanotube (all microscopies are presented at x25000 magnification)



a



b



c

Fig. 4. FT-IR spectrum of PSf-DWNT membrane from aniline (a), PSf-SWNT membrane from DMF (b) and PSf-DWNT membrane with covalent interaction between polymer and carbon nanotubes (c).

polysulphone membranes, differing only compactness of membrane. This morphology shows that the membranes obtained by mixing carbon nanotubes with the solution of polysulphone in DMF were determined by the interaction structure between polysulphone and carbon nanotubes. Membranes with double-walled carbon nanotubes are more compact because interfacial tensions that arise between polymers and carbon nanotubes determine this structure.

Membrane structure obtained from aniline presents a honeycomb (spongy) morphology, while the membrane obtained by covalent binding between polymer and nanotube, has a structure similar to the comb, but more compact.

Although carbon nanotubes have not an infrared spectrum with bands whose intensity provide important information on the system in emerging spectral study performed (fig. 4) it was motivated to comment on the characteristic spectral bands of the polymer, but also on the movements of these bands caused by interaction between polysulphone and modified carbon nanotubes. Infrared spectroscopy analysis was performed on a Bruker Vertex 70 device using the device with the ATR crystal diamond. In the FT-IR spectra is observed a shift towards lower values of polysulphone specific bands, this shift being due to electronic interactions between nanotubes and polymers (fig. 4-a and 4-b). In the membrane obtained by covalent binding of polymer nanotubes can be observed a specific band intensity vibration attenuation relationship - C=O and the appearance in the spectrum bands in the range 1500-1600 cm^{-1} specific training links-C = N-(fig. 4-

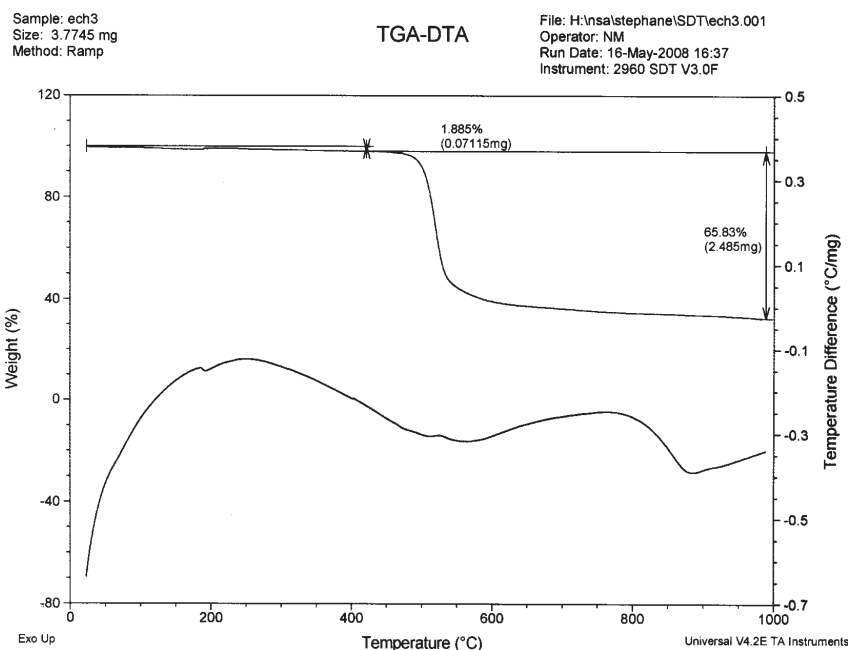


Fig. 5. The TGA-DTA diagram of PSf-SWNT composite membrane

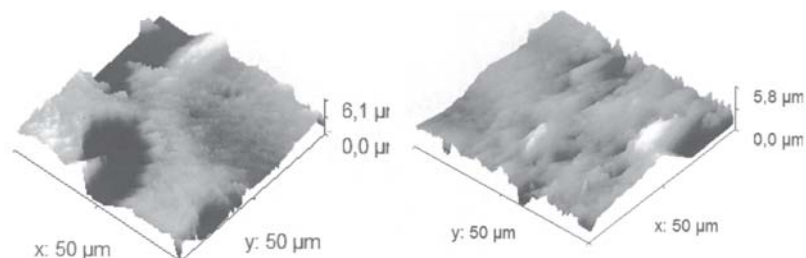


Fig. 6. AFM images of PSf-SWNT composite membrane (a) and PSf-DWNT from DMF composite membrane (b).

C). To complete the study of membrane characterization the obtained materials were investigated by thermal analysis with TA Instruments 2950 (fig. 5). By TGA analysis can be determined the percentage of carbon nanotubes that remains in the membrane structure. If the membrane is obtained by mixing the polymer with carbon nanotubes, nanotube content is 1.885%. However, if the membrane is obtained by covalent binding of amino carbon nanotubes with formylated polysulphone, the nanotube content is 2.360%. Observation shows that a significant proportion of the used nanotubes is lost in the coagulation bath during the phase inversion [31-33].

The AFM microscopy (fig. 6) performed on two membranes (polysulfone with single wall carbon nanotubes – a, and polysulfone with double walled carbon nanotubes obtained from DMF – b) reveals the fact that there are not big topology differences between those two membranes and also shows a big contact surface, property that makes these membranes suitable for gas separations.

Conclusions

In this paper the synthesis of new polysulfone-carbon nanotubes composite membrane was presented. The membranes were prepared by carbon nanotubes dispersion into a polymer solution and also by covalent bonding between amino carbon nanotubes and formylated polysulfone. The membranes were characterized by FT-IR spectroscopy, thermal analysis, SEM and AFM microscopy. The membranes prepared by covalent bonding between carbon nanotubes and polymer present superior properties than other membranes.

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