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XXIX

Preparation of mixed matrix membranes for water treatment

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INDEX

Abstract

The treatment of wastewater and its reuse is a very important topic in industrial processes. This because not only avoids drawing on natural resources, but also enables a significant reduction in the amount of wastewater discharged into the natural environment. Wastewater can also be used for various purposes where drinking water quality is not mandatory, including agricultural irrigation, the cleaning of industrial equipment, the watering of green spaces, and street maintenance, etc. In fact, the water reuse has become essential in all areas in the world that suffer from water shortages [1].

Different methods are used for wastewater treatment. These processes can be to divide in: primary, secondary and tertiary treatment. Primary treatment (screening, filtration, centrifugation, sedimentation, coagulation, gravity and flotation method) includes preliminary purification processes of a physical and chemical nature while secondary treatment deals with the biological treatment of wastewater. In tertiary treatment process wastewater is converted into good quality water that can be used for different types of purpose, i.e. drinking, industrial, medicinal etc. supplies [2].

The complexity of industrial processes, the variety of pollutants and the limitation of a single operation, has led to the need for more complex processes and especially to a combination of processes.

Membranes technologies falls on the tertiary water treatment technologies and are actually the most effective separation processes and they are still in rapid development creating new prospects of their applications in clean technologies [3].

The utilization of membrane operations as hybrid systems, i.e. in combination with other conventional techniques or integrated with different membrane operations is considered the way forward for more rationale applications [4]. The possibilities of redesigning various industrial cycles by combining various membrane operations have been studies and in some case realized with a low environmental impact and a low energy consumption [5].

Different processes can be used in various steps of a hybrid system, depending from the size of the pollutants to be removed. Microfiltration (MF) and ultrafiltration (UF) membrane processes, can be used as pre-treatment, while nanofiltration (NF) and reverse osmosis (RO) can used in the final step of the integrated system to remove particles with smaller dimensions (Chapter 1)

The membranes have different morphological characteristics that affect their performance. The study of all the conditions which modulate these characteristics is a crucial point in the choice of membranes to be used in the various separation processes. Therefore, it is important to investigate about new materials and new types of membranes, like as mixed matrix membrane (MMM).

MMM is a heterogeneous membrane consisting of inorganic fillers embedded in a polymeric matrix and can be made into flat sheets and hollow-fiber. Nevertheless, the selection of membrane configuration is greatly dependent on the application and therefore the production of MMMs in useful configuration is undoubtedly a crucial point in membrane development [6]. Also, the selection of inorganic fillers depends of desired membrane performance and their use. More attention was focus on the interesting characteristic of carbonanotubes (CNTs) (chapter 2).

CNTs themselves have remarkable electrical, thermal, and mechanical properties. These nanotubes have the structure of a rolled-up graphene sheet with smaller diameter. Multiwalled carbonanotube (MWCNTs) were used to prepare MMMs for wastewater treatment. Different compounds, as additives in the polymeric membranes were used in high percentage; in the case of MWCNTs was observed as a low amount can change the membrane morphologies, mechanical and transport properties. A crucial point was the choice of membrane materials. Two type, hydrophilic poly(imide) (PI) and hydrophobic poly(vinylidenfluoride) (PVDF) were choose for membrane materials to produce MMMs. Another important point in this study was the use of functionalized MWCNTs that provide a good dispersion in the casting solution first, and in the polymeric matrix after phase separation. The main limitation in the use of CNTs is their poor dispersion in the main solvents used for the preparation of membranes. The functionalization has been proven an efficient method to overcome this limitation improving the compatibility with the polymer matrix. The presence of polar groups on the carbon nanotubes can reduces their tendency to aggregate by van der Waals interactions, while forming hydrogen bonds and electron donor/acceptor interactions with the polymer. Low percentages of CNTs were used for the preparation of membranes. These percentages were sufficient to improve better performance to modified membranes.

PI was select as polymeric materials because combine easy processability in the form of membranes, with a high chemical and thermal stability, over a wide range of operative conditions. Three different PI polymers were used to prepared porous asymmetric membrane by non-solvent induced phase separation (NIPS): a homopolymer (Matrimid) and two co-polymers (Lenzing P84 and Torlon). The effect of membrane preparation conditions on the membrane morphology and transport properties, were investigate. Moreover, mixed matrix based on co-polyimide P84 and functionalized multiwalled carbon nanotubes (oxidized and aminated MWCNTs) were prepared. The different polymeric membranes were compared in the rejection of organic dyes, as model of organic pollutant present in wastewater (chapter 3).

To investigate about the influence of functional groups on the MWCNTs for their interaction with polymeric matrix, three different type of functionalized MWCNTs (oxidized, amined and aminated) were dispersed also in polymeric hydrophobic PVDF membranes. PVDF was selected as polymeric materials of its outstanding properties: excellent chemical resistance and hydrolytic stability; high mechanical strength and stability over a broad pH range; polymorphism (main crystalline phases are: α, β, γ, δ and ε) [7]. The aim was to tailor the interactions with the polymeric matrix in order to realize high performing composite film with improved performance. Bovine serum albumin (BSA) protein was select as compound to evaluate the membrane performance. In particular, the antifouling properties and the permeation flux of mixed matrix membranes, were evaluate as well as thermal and structural and mechanical properties (chapter 4).

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Chapter 1. Wastewater treatment

1.1 Introduction

Water is very important in purr daily life, hence, the necessity to improve and preserve its quality is growing continuously. Point and non-point sources are contaminating our valuable water resources. The main water pollution sources are from industrial, domestic and agricultural activities. The surface and ground water in many places around the world are contaminated and not fit for drinking purposes. By 2020 the global population is supposed to reach up to 7.9 billion and because of this the world may experience the great scarcity of fresh water [1,2,3]

1.2 Water pollutants

Many pollutants are present in wastewater but toxicity is only observed beyond a certain limit called the permissible limit. The type of pollutants present in the wastewater depends upon the nature of the industrial, agricultural and municipal wastewater releasing activities. The different types of water pollutants may be categorized as inorganic, organic and biological. The most common inorganic water pollutants are heavy metals, which are highly toxic and carcinogenic in nature. Additionally, nitrates, sulphates, phosphates, fluorides, chlorides and oxalates also have some serious hazardous effects. In toxic pollutants fall: different pesticides which includes insecticides, hericides, fungicides; polynucleas hydrocarbons (PAHs), phenols, polychlorinated biphenyls, halogenated aromatic hydrocarbons, formaldehyde, polybrominated biphenyl, detergents, oils, greases [4]. In addition to these, normal hydrocarbons, alcohols, aldehydes, ketones, proteins, lignin, pharmaceuticals etc. are also found in wastewater. Between hazardous microbes, include bacteria, fungi, algae, plankton, amoeba, viruses and other worms. These water pollutants remain either in solvated, colloidal or in suspended form [5].

1.3 Emerging organic contaminants (EOCs)

Emerging organic contaminants (EOCs) are a large and relative new group of unregulated compounds that many be derived from domestic, trade and industrial sources. Many of these chemicals have been identified as endocrine-disrupting chemicals (EDCs) which can interfere with the normal functioning of the endocrine system of many aquatic and terrestrial organisms. Other potential EOCs of increasing concern are pharmaceuticals and personal care products (PPCPs). Typical EDCs include steroid estrogens (e.g. alkylphenols, estrone and estriol) and xenoestrogens [6].

Some medications, and the prevalence of antibiotic-resistant upon exposure to hospital and domestic sewage effluents can cause bacterial resistance creating species so called “superbugs” [7,8]. Aquatic organism are particularly susceptible to EOCs because their entire life cycles are spent in continuous contact with water [9].

1.4 Conventional processes for water purification and reuse

Wastewater treatment and reuse is an important issue and scientists are looking for green inexpensive and suitable technologies. Water treatment technologies are used for three purpose: water source reduction, wastewater treatment, and recycling. At present, individual operations and processes are combined to provide a hybrid system called primary, secondary and tertiary treatment. Primary treatment includes preliminary purification processes of physical and/or chemical nature while secondary treatment deals with the biological treatment of wastewater. In tertiary treatment processes wastewater is converted into good quality water that can be used for different types of purpose, i.e. drinking, industrial, medicinal etc. supplies [3].

1.4.1 Primary water treatment technologies

In this category, water is treated at the primary level using screening, filtration, centrifugation, sedimentation, coagulation, gravity and flotation method. Generally, screening is used as the very first step is a wastewater treatment operation. In filtration process, water is passed through a medium having fine pores. The filtration process can be used to remove solids of size below 100 mg l^{-1} and to remove oil of 25 mg l^{-1} which can be reduced by up to 99%. The filtration process is used as pre-treatment to produce water used for other purification processes like as adsorption, ion exchange or membrane separation [3].

Centrifugal separation is used to remove suspended non-colloidal solids (size up to 1µm). The wastewater is applied to centrifugal devices and rotated at different speeds and the solids (sludges) are separated and discharged. The extent of separation of suspended solids is directly proportional to their densities. In addition to this, the speed of the centrifugal machines also responsible for the removal of suspended solids [10].

Screening is followed by sedimentation but this step was not found to be effective because it does not remove colloidal particles in the effluents. In the sedimentation and gravity separation, the suspended solids settle under the influence of gravity [11]. Generally, sedimentation is carried out prior to conventional treatment process [12]. A disadvantage of the sedimentation process is the large space it occupies. The settled particles are collected as sludge. Disposal of sludge is one of the biggest challenges of treatment plants [13]

1.4.2. Secondary water treatment technologies

Secondary water treatment includes biologicals routes for the removal of soluble and insoluble pollutants by microbes [11,14]. The microbes, usually bacterial and fungal strains, convert the organic matter into water, carbon dioxide and ammonia gas [15].Sometime, the organic matter is converted into other products such as alcohol, glucose, nitrate etc. The wastewater should be then free from toxic organics and inorganics. The maximum concentrations of total dissolved solid (TDS), heavy metals, cyanides, phenols and oil should not exceed by 16.000, 2.0, 60.0, 140 and 50 mg l^{-1} respectively. The biological treatment includes the aerobic and anaerobic digestion of wastewater [15].

1.4.2.1 Aerobic processes

When air or oxygen is freely available in dissolved form in wastewater then the biodegradable organic matter undergos aerobic decomposition, caused by aerobic and anaerobic bacteria [16,17]. Besides, the rate of the biological oxidation of organic pollutants may be increased by addition of chemical substance required for removal of bacteria or to reduce their growth. The technique is effective for the removal of biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved and suspended organics, volatile organics, nitrates, phosphate etc. The aerobic process is carried out by trickling filters or activated sludge processes or oxidation ponds. A simplified representation of aerobic decomposition is given by the following equation

$$\text{Organic matter} + O_2 + \text{Bacteria} \longrightarrow$$
$$CO_2 + H_2O + \text{Bacteria} + \text{Byproducts} \qquad (1)$$

The disadvantage of the method is the production of a large quantity of bio-solids, which require further costly treatment and management [3].

1.4.2.2 Anaerobic process

Anaerobic and anaerobic bacteria convert the complex organic matter into simpler organic compounds based on nitrogen, carbon and sulphur. The gases, usually, evolved in this process are nitrogen, ammonia, hydrogen sulphide and methane. This method is used to reduce the biological load of wastewater[18,19]. The anaerobic process can be represented by the following equation

$$\text{Organic matter} + \text{Bacteria} \longrightarrow$$

$$CO_2 + CH_4 + \text{Bacteria} + \text{Byproducts} \qquad (2)$$

1.4.3 Tertiary water treatment technologies

Tertiary water treatment technologies are very important in wastewater treatment strategy as these are used to obtain safe water for human consumption. Same techniques used for this purpose are distillation, crystallization, precipitation, evaporation, solvent extraction, oxidation, advanced oxidation process, precipitation, electrolysis, ion exchange, adsorption, electrolysis [3]. Membrane technology will be treated in the next section.

1.4.3.1 Distillation

In the distillation the water is purified by heating it up to 100°C at which liquid water is vaporized leaving behind the pollutants [20]. The vapors thus generated are cooled into liquid water. The wastewater should be free from volatile impurities and water produced by this technique is about 99% free from impurities. Various types of boilers with multistage and double distillation are used in this process. The size of the boilers depends on the water quantity requirements. The applications of distillation in water treatment include water supplies in laboratories and medical preparations. In addition, the distillation is an effective tool for the preparation of potable water from the sea and brackish water [3].

1.4.3.2 Crystallization

Crystallization is a process in which pollutants are removed by raising their concentrations up to a point where they start to crystallize. It is useful for the treatment of wastewater with high concentrations of TDS including soluble organics and inorganics. Generally, crystallization is used for the wastewater released by cooling towers, coal and gas fired boilers, and paper and dying industries [21].

1.4.3.3 Evaporation

Evaporation, is a separation process that takes advantage of the changing physical states of water, or other solvents, from liquid to vapor. It is unique from other separation processes, in that the water is removed from the contaminants rather than the pollutants being filtered from the water. Before recent technological developments, the capital and energy requirements for evaporation processes had been too intensive for wastewater treatment or recycling applications. The process may be carried out naturally in solar evaporation ponds, or using commercial available evaporation equipment. Mechanical evaporation is an energy-intensive process to concentrate liquid. For this reason, various energy alternatives should be considered. Also, foaming and fouling along with the presence of suspended solids and carbonates are the major problems associated with this technique as they create a maintenance problems [22].

1.4.3.4 Solvent extraction

Organic solvents, immiscible with water have the capacity to dissolve pollutants, and are added to wastewater for the removal of pollutants; this technique is called solvent extraction [23]. The most commonly used solvents are benzene, hexane, acetone and other hydrocarbons. Certain metal ions and chemicals products may be removed by this method. It is used for recycling water and water treatment. The major problem of this technique is that a small quantity of the solvent remains mixed with the water and further purification operations are necessary such as distillation technique [24].

1.4.3.5 Oxidation

In chemical oxidation organic compounds are oxidized into water and carbon dioxide or some other products such as alcohols, aldehydes, ketones and carboxylic acids which are easily biodegradable [25]. Chemical oxidation is carried out by potassium permanganate, chloride, ozone, H_2O_2, Fenton's reagent (H_2O_2 and Fe++ catalyst) and chloride dioxides [26,27]. By this method, pollutants such as ammonia, phenol, dyes, hydrocarbons and other organic pollutants may be removed.

1.4.3.6 Advanced oxidation process(AOP)

At difference of chemical oxidation, which only chemical compound are used, in the advances oxidation processes more than one oxidation process are used. this involve with the accelerated production of the highly reactive hydroxyl free radical [28,29]. These processes include techniques like Fenton's reagent oxidation process, ultra violet (UV) photolysis. Several AOP are able to degradate the organic pollutants at ambient temperature and pressure. Photocatalysis is another example of advanced oxidation processes for organic pollutant degradation [30]. In photocatalysis, a radiations, with a specific wavelength excites an electron from the valence band of the photocatalysis to the conduction band starting a series of reactions which result in the formation of hydroxyl radicals. The hydroxyl radicals have high oxidation potential and therefore can attack most organic pollutants causing oxidation. [31]

1.4.3.7 Precipitation

In precipitation process, the dissolved contaminants are converted into solid precipitates by reducing their solubility and the precipitates are skimmed off easily from water's surface [32]. It is effective for the removal of metal ions and organic but the presence of oil and grease may cause a problem in precipitation. The solubility of the dissolved pollutants is decreased either by adding some chemicals or by lowering the temperature of the water. Adding some organic solvents to the water may also reduce solubility of the contaminant but this technique is costly at a commercial level. The application of this method includes wastewater treatment from the nichel and chromium plating industries and water recycling. The major problem associated with precipitation is the management of the large volume of sludge produced [33]. The overall cost of chemical precipitation is dependent on variables such as (i) characteristics of the wastewater, (ii) chemicals and dosages to be used, (iii) volume of water to be treated, and (iv) level of water purity desired. Moreover, the form and quantity of material to be procured can also affect chemical costs as prices may vary across regions or countries. [34]

1.4.3.8 Ion exchange

Toxic ions present in wastewater are exchanged with the non-toxic ions from a solid material called an ion exchanger [35]. Ion exchangers can be cation or anion exchangers which have the capacity to exchange cations and anions respectively. It is a reversible process and requires low energy contents. Ion exchange is used for the removal of low concentration of inorganics and organics compounds. Applications include the production of potable water, water for pharmaceutical industry, softening, fossil fuels, different industries. Sometimes, the pre-treatment of the water is required; if oil, grease and high concentrations of organics and inorganics are present [36].

1.4.3.9 Adsorption

Adsorption as a surface phenomenon and defined as the increase in the concentration of a particular component at a surface or interface between two phases. Pre-filtration is required due to the presence of suspended particles and oils that reduce the efficiency of the adsorption. Different type of adsorbents are used in adsorption process. Most commonly used adsorbents are activated carbon, fly ashes, metal oxides, zeolites, moss, and biomass. Recently, nanomaterials, such as carbon nanotubes and composite of carbon nanotubes [37] have been utilized for the removal of heavy metals and organic pollutants. Adsorption is used for wastewater treatment and reclamation for water potable, industrial and other purposes. At an industrial level, pollutants are removed from wastewater by using the columns filled with the required adsorbent. The basic problem associated with adsorption are the regeneration of columns and column life [38].

1.4.3.10 Electrolysis

Electrolysis is a technique in which soluble materials are either deposited or decomposed on the surface of electrodes by electrochemical redox reaction [39]. In this method, most metal ions are deposited on the electrode surface while organics are decomposed into carbon dioxide and water or some other product, which are low or non-toxic [95-96]. Electrolysis, as the technique of wastewater treatment, is not developed completely [40].

1.5 Membrane technology

Membranes technologies falls on the tertiary water treatment technologies and are actually the most effective separation processes and they are still in rapid development. New prospects of their applications in clean technologies are increasing. The Commission of the European Communities put the definition of clean technologies as a main objective of proactive strategies: “any technical measures taken at various industries to reduce or even eliminate at source the production of any nuisance, pollution, or waste, and to help save raw materials, natural resources and energy “ [41].

Membrane technologies are in many fields recognized as amongst the best available technologies (BATs). The concept of BATs was applied by integrated pollution prevention and control directive (IPPC), 96/61/EC to the integrated control of pollution to the three media air, water and soil [42]. Leading energy research centers in Europe focused their research on the separation technologies required for clean and sustainable energy systems. The relatively low energy consumption of membrane technology renders it a key component in a clean, green and sustainable energy system.

In fact, membrane technology, compared to conventional technologies, respond more efficiently to the requirements of process intensification strategy because they permit drastic improvements in industrial production, substantially decreasing the equipment-size/production-capacity ratio, energy consumption, and/or waste production so resulting in cheaper, sustainable technical solution [43]. The most interesting developments for industrial applications of membrane technologies today are related to the possibility of integrating various membrane operations in the same industrial process, with overall important benefits in product quality plant compactness, environmental impact and energetic aspect. More progress can be anticipated in term of overall cost reduction and quality improvement, by the growing integration of other membrane operations in the system [44].

Membrane technology is today recognized as key factor for a sustainable growth in many industrial segments. One of significant and recognized benefits of membrane operations is their low direct energy consumption because of the absence of phase transformations [44,45]. The second, important feature is the possibility to reduce reducing indirect energy consumption through the recycling and reuse of raw materials and secondary materials minimizing the formation of wastes [44].

The overall membrane market trend in the world is increasing. For few other technologies the market growth is so rapid: the annual word sales only for the membranes increased by 7.8% and the world growth of the membrane plants is 60-70 time higher than that of membranes [47].

The utilization of membrane operations as hybrid system, in combination with other conventional techniques or integrated with different membrane operations is considered the way forward for more rationale applications [48]. The possibilities of redesigning various industrial sectors by combining various membrane operations have been studies and in some case realized with low environmental impacts and low energy consumption [49].

1.5.1 Membrane technologies in water treatment

Pressure-driven membrane processes are playing an increasingly important role in water treatment. Membranes can overcome many of the limitations of the conventional technology by providing an essentially complete barrier to waterborne contaminants. The entire range of chemical and microbial contaminants can be removed from raw water supplies, maximizing water quality. In many case, one membrane process is followed by another with the purpose of producing water of increasing purity and quality for various purposes [41].

Compared with conventional waste water treatment process, membrane processes have many advantages which also have economical effect:

- Saving of the process stages
- The compact design

- The high purification efficiency by complete retention of particles and bacteria, and , depending on the membrane process, also viruses
- Better removal of organic trace substance by a higher sludge age and the establishing of special micro-organisms
- The possibility to arrange downstream an additional membrane stage to retain organic trace substance [50]

1.6 Membranes processes

There are several membrane processes whit difference in term of molecules separation size and driving force which should be expected (Table1).

Table 1.Technically relevant membrane separation process, their operating principles, and their application [46]

Separation process	*Applied driving force*	*Mode of Separation*	*Applications*	*Ref*
Microfiltration	Hydrostatic pressure (0.5-4 bar)	Filtration (size exclusion)	Water purification, sterilization	[50-51]
Ultrafiltration	Hydrostatic pressure (1-10 bar)	Filtration (size exclusion)	Separation e fractionation of molecular mixture	[52-53]
Nanofiltration	Hydrostatic pressure (5-40 bar)	Filtration (size exclusion); Solution-diffusion mechanism; Donnan-exclusion effect	Separation of sugars, other organic molecules and multivalent salts	[54-55]
Reverse osmosis	Hydrostatic pressure (10-100 bar)	Solution-diffusion mechanism	Sea e brackish water desalination	[56-57]
Forward osmosis	Natural osmosis	Solution-diffusion mechanism	Sea e brackish water desalination	[58-59]
Membrane contactor				[60-61]

At industrial level, the employment of a membrane process for wastewater purification may be feasible, particularly if a useful integration into the production process is possible [50].

In industrial wastewater purification, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) reverse osmosis (RO), membrane distillation (MD) and membrane contactor (MBR) are the main membrane process used.

The membrane processes are classified according to the size or molar mass of the separated substances. Their different molecular separation sizes allow for the choice of the suited process for the task. For more complex task, the combination with other processes is a possibility (Figure 1). This is the example of hybrid system to wastewater treatment [50].

In municipal and industrial waste water treatment, membrane processes are applied to satisfy the following objectives:

- Retention

(e.g. of solid matter including biomass of hazardous materials, of dissolved matter by RO)

- Purification

(e.g. for industrial water treatment, for disinfection by retention of bacteria)

- Fractionation

(e.g. for separation in two or more components)[63]

There are more applications of membrane technology. With the increasing shortage of freshwater supplies, indirect potable reuse is becoming more attractive as a water supply option. In this water supply strategy, membrane can play a crucial role [64]. The strategy expected a hybrid system where several wastewater processes are combine together to obtain clean water (Figure 1). The advantages of this strategy are the cost and time reduction for cleaning operations.

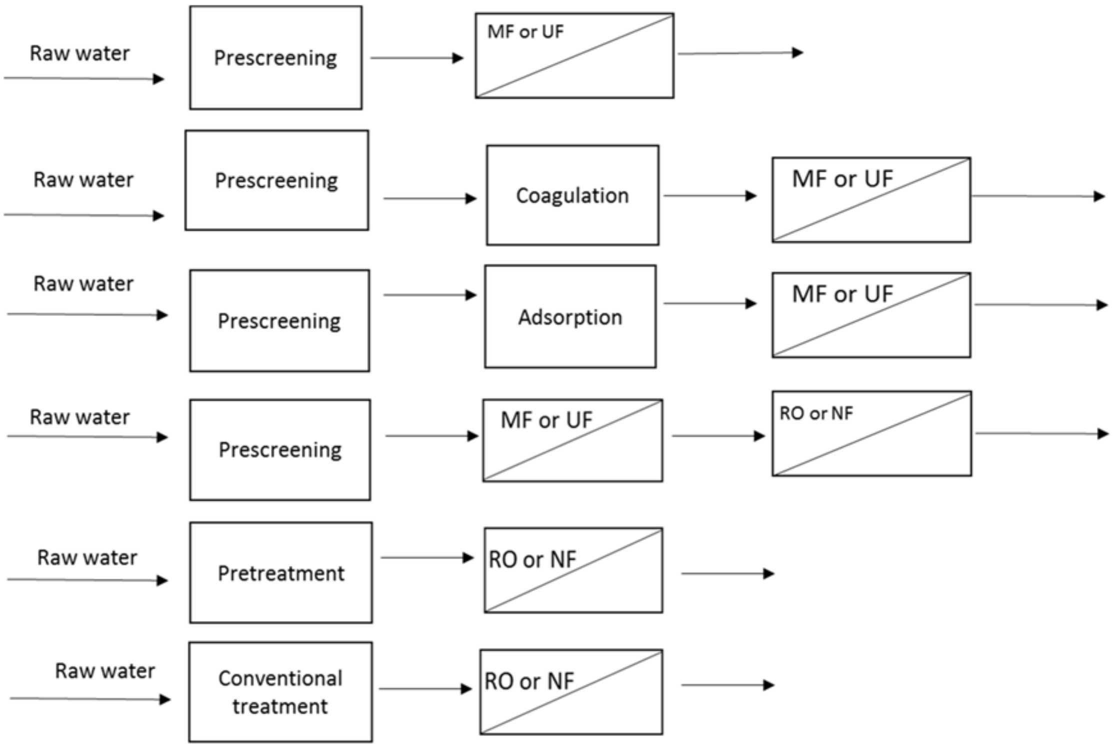

Fig. 1. Typical membrane system for water treatment.

1.6.1 Microfiltration and Ultrafiltration in water treatment

Microfiltration (MF) and ultrafiltration (UF) belong to the pressure-driven membrane process. Nevertheless, UF membrane that has smaller pore sizes than MF seems to represent the best balance between contaminant removal and permeate products among these membrane types. The molecular separation size of solid ≥ 0.1 µm for MF and ≥ 0.005 µm for UF [65].

In wastewater purification, MF and UF are used for the separation and retention of particulate and emulsified waste water constituents. Typical applications include:

Municipal waste water treatment

- Separation of activated sludge and water
- Disinfection
- Pretreatment prior to a reverse osmosis plant
- Phosphate removal after precipitation

Industrial waste water treatment

- Waste water recycling and reuse as process water for different purposes
- Treatment of landfill leachate combined with a biological stage
- Recovery of waste-based paint from spray booth effluents by concentration [50]

The key to the successful operation for higher quality of the feed stream entering RO system, is dependent on feed pretreatment process using MF-UF pretreatment. The principals advantages respect to conventional wastewater processes are:

1. reliable separation performance – even in the challenging feed water conditions (with very high turbidity), the membrane is still able to produce a very consistent permeate quality for RO system [66].
2. small footprint – membrane pretreatment technology is very space efficient than conventional system, taking up less than 50% of the area of a conventional pretreatment system
3. reduction in chemical use and chemical waste disposal – the elimination of coagulant agent used (e.g., ferric chloride) in MF-UF pretreatment coupled with reduced frequency of RO membrane cleaning result in significant reduction in chemical consumption and waste sludge generation (containing high concentration of metal) in wastewater treatment making pretreatment more environmentally friendly [67]
4. low energy consumption – MF-UF system is found to use significantly less energy consuming in the overall pretreatment process compared to the sedimentation-based pretreatment (0.07 versus 0.22 kWh/m3) after taking into the consideration the energy required by feed pump, backwash pump and air scouring/blower [68]
5. reduced environmental impact – compared to conventional pretreatment, MF-UF pre-treatment is reported to be able to reduce more than 30% environmental impact[69].

Operating cost of membrane system is derived from: the energy cost of maintaining the system's hydrostatic pressure and flow rate; the expected membrane life; the cleaning regime required; sitespecific factors, such as the labor requirement. The energy consumption of a membrane system is directly related to flow rate and pressure requirement and pumping cost is related to flow and power. Most microfiltration and ultrafiltration system application operate at low pressure. The energy consumed is, therefore, mostly associated with maintaining a minimum velocity about 2m/s across the membrane surface [70].

1.6.2 Nanofiltration and Reverse osmosis in water treatment

Nanofiltration (NF) is a suitable method for the removal of a wide range of pollutants from groundwater or surface water, in view of drinking water production [71]. NF is used for the removal of natural organic matters (NOM), micropollutants [72]such as pesticides, color [73], bacteria, salinity ,nitrates and arsenic [41].

NF is a pressure-driven membrane process. Concerning operational pressure and separation size, NF is categorized between reverse osmosis and ultrafiltration [50]. Simpson et al. (1987) has described NF as a charged UF system whereas Rohe et al. (1990) has referred it as low pressure RO system. However, NF has advantages of lower operating pressure compared to RO, and higher organic rejection compared to UF.

Typical of NF membranes is most salts with monovalent anions can pass through the membrane, whereas multivalent anions are retained [74].

For the colloids and large molecules, physical sieving would be the dominant rejection mechanism whereas for the ions and lower molecular weight substances, solution diffusion mechanism and charge effect of membrane play the major role in separation process. The NF rejection mechanisms can be summarized into following five steps [75]

– Wetted surface – water associates with the membrane through hydrogen bonding and the molecules which form the hydrogen bonding with the membrane can be transported.

– Preferential sorption/Capillary rejection – membrane is heterogeneous and microporous, and electrostatic repulsion occurs due to different electrostatic constants of solution and membrane.

– Solution diffusion – membrane is homogeneous and non-porous, and solute and solvent dissolve in the active layer of the membrane and the transport of the solvent occurs due to the diffusion through the layer.

– Charged capillary – electric double layer in the pores determines rejection. Ions of same charge as that of membrane are attracted and counter-ions are rejected due to the streaming potential

– Finely porous – membrane is a dense material punctured by pores. Transport is determined by partitioning between bulk and pore fluid.

The principal application of NF membrane in industrial wastewater treatment are:

- relief of ion exchanger or downstream reverse osmosis units
- removal of colour in waste water textile and the pulp and paper industry
- demineralization of wastewater containing surfactant [76]

1.6.3 Reverse osmosis

Reverse osmosis (RO) is a pressure-driven process. The driving force resulting from a difference of the electro-chemical potential on both sides of the membrane. The non-porous RO membranes can retain dissolved material with molecular weight of less than 200 g/mol completely, so that reverse osmosis achieves a higher separation efficiency than nanofiltration [65]. Since, dissolved salts are retained to a very high extent. RO is very important in industrial wastewater treatment for:

- concentration of drainage water from mines containing $CaSO_4$
- treatment of wastewater from textile dyeing (cotton and polyester dyeing)
- concentrate of cellulose washing water
- recovery of phosphoric acid

- /treatment of landfill leachate
- brackish and seawater desalination [50]

The life of RO membranes has been considered to be two to five years depending upon the nature of the wastewater being treated [77]. The flux and the quality of permeate may decrease over a long period due to membrane fouling. To increase the efficiency and life of the membrane, as well as, to improve the overall performance of the system, pre-treatment is usually necessary.

1.6.4 Membrane Bio-Reactor

The membrane bioreactor (MBR) is a system that combines biological treatment with membrane filtration into a single process. the MBR system has evolved, and research on MBR technology has increased significantly, particularly in the last 5 years. There are many applications for the MBR system. In general, the applications can be grouped into three categories of processes involving water filtration membranes, gas diffusion membranes, and extractive membranes (including ion exchange). In the last 15 years, research on MBR application for water and wastewater treatment has been predominant [78]. MBR treatment of municipal wastewater yields high-quality water with reported removal percentages of 95%, 98%, and 99% (or greater) for chemical oxygen demand (COD), biochemical oxygen demand (BOD), and suspended solids (SS), respectively [79]. MBRs have emerged in the field of wastewater treatment processes as one of the best alternatives to the conventional activated sludge (CAS) processes due to some enhanced characteristics including small spatial requirements, higher effluent quality and low sludge productions [80]. In fact, MBR process, which couples biological-activated sludge process and membrane filtration to separate treated effluent from mixed liquor, has become state-of-art in wastewater treatment and becoming increasingly applied [81]. A pilot scale submerged MBR unit was constructed (ARTAS Ltd.,Turkey) and located at Kenkäveronniemi Wastewater Treatment Plant (WWTP) in Mikkeli, Southern Savonia region, Finland as shown in Figure 2.

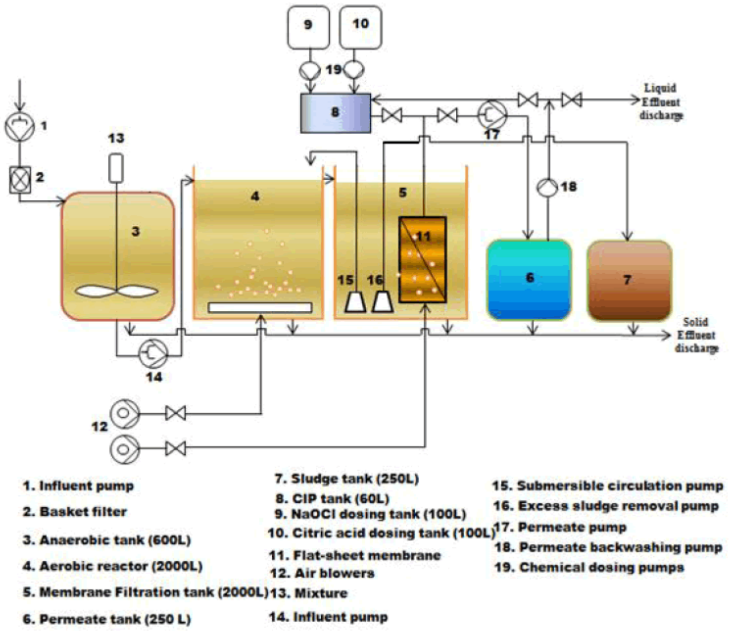

Figure 1: Schematic diagram of the submerged MBR pilot plant installed at Kenkäveroniemi WWTP, Mikkeli, Finland.

Fig.2. Schematic diagram of the submerged MBR pilot plant installed at Kenkäveroniemi WWTP, Mikkeli, Finland [82]

1.6.5 Membrane fouling

Tubular and sheet membranes system tend to have longer working lives (typically five years but sometime more than 15 years). Membranes longevity and performance are adversely affected by stressing the membrane with abnormal temperatures, aggressive chemicals, solvents or other reactive chemicals such as silicone- based compound. The effect of such stressing may be irreversible or very difficult to rectify, necessitating replacement of the membrane module [70].

Industrial wastewater contains organic and inorganic matter. During purification of these wastewater by means of a membrane, the constituents of the feed concentrate and a separation of particles at the membrane surface occurs due to the selective effect of the membrane. During operation time, this produces a cake layer on membrane surface. An increase of filtration resistance, with reduce of the membrane performance, is typically observed [83].

It is possible to make a distinction between fouling and concentration polarization. Membrane fouling and concentration are two aspect of a same problem which it consists in the formation of a layer of retained species on the membrane surface. Both phenomena can reduce the permeation flux the membrane and change the selectivity of the process. Concentration polarization describes the concentration profile of solutes in the liquid phase adjacent to the membrane. It is a reversible mechanism, that disappears as soon as the operating pressure has been released. Fouling includes the matter which has left the liquid phase to form the deposit onto the membrane surface or inside the porous structure. Its consequences are a modification of the transport properties of the membranes (permeability and cut-off).

The development of covering layers due to fouling or scaling can be avoided or reduced if the following aspects are considered during construction and operation on the membrane plant.

The **pretreatment** strategies for a membrane plant have to be chosen according with the requirements of the wastewater composition. Mechanical, physical, biological and chemical procedure (sieve, prefiltration, cooling, neutralization, precipitation) can be used [50].

Optimization of the process configuration is an interesting aspect in fouling reduce. Condition which: backwashing volume, backwashing time in dead-end or overflow velocity in cross-flow cab be reduce covering layer formation.

Another important point is the structural **design of membrane**. Membrane material and membrane structure have the largest influence on the formation of covering layers. Materials properties and the charge of a membrane can influence the membrane contamination. The most important structural characteristic regarding the covering layer formation are the roughness of the membrane surface, the pore diameter, porosity and the pore size distribution. Numerous efforts have been made to increase the efficiency of membranes by modification of their characteristic [84].

For membrane **cleaning**, chemical cleaning agents are used in combination with backwashing or flushing. The cleaning agents is chosen depending on the substances in covering layer. The efficiency of cleaning depends of parameters such as pH value, temperature, contact or reaction time, concentration of the substance, and mechanical forces [85].

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Chapter 2. Basic aspects of polymeric and mixed matrix membranes preparation

2.1Introduction

As it was discussed in the previous chapter, high purification efficiency, the possibility of saving cost, very compact design, better removal of organic pollutants and the possibility to combine various membrane processes, make membrane technology an important strategy in wastewater treatment.

Membrane material and membrane structure have the largest influence on membrane performance and limitation. The choice of materials and preparation technique depend from the membrane application. Also, numerous efforts were made to reduce the major membrane limitation such as fouling.

2. 2 Membrane materials, structures and classification

Considering the large diversity of membranes available suited for technical application it will be useful to introduce the following main classifications criteria:

- Origin
- Material
- Morphology and structure
- Manufacturing process

2.2.1 Origin and materials

Membrane can be of biological and synthetic origin and differ according to structure, functionality and material transfer. Therefore, in wastewater treatment only synthetic membrane are used. Depending on wasetwater composition and characteristic as well as operation requirements, differents materials can be used for membrane, inorganic or organic [1].

Inorganic membranes

Inorganic membrane materials are ceramics, aluminum, high-grade still, glass and fiber-reinforced carbon. Ceramic membrane, between these, at present have the greatest importance in wastewater purification. Materials development include porous ceramics (e.g. Al_2O_3, TiO_2, ZrO_2, ZnO and SiO_2) [2], composite containing two or more materials (e.g. TiO_2-SiO_2, TiO_2-ZrO_2, and Al_2O_3-SiC) and various nanocomposites (e.g. Ag-TiO_2, Zn-CeO_2 , GO and zeolite) [3-4]. In the case of ceramic membranes, photocatalytic materials such as TiO_2 and composites containing TiO_2 have been actively studied due to their multi-functionality and wide applications including remediation of ground water and wastewater [5-6-7]. Along with a separation function, TiO_2 offers photocatalytic ability for decomposition of organic species microorganisms/pollutants, photolysis, and superhydrophilicity, which reduces unwanted adsorption of organic/biological species to the membrane surface [8-9]. Also, TiO_2 is a non-toxic, readily available, and inexpensive material. The mechanism of TiO_2 photocatalysis is based on photoinduced charge separation on the surface of the oxide. Two of the most extensively studied application areas of photocatalytic materials are disinfection [10-11-12] and removal of targeted organic pollutants [13-14].

Some ceramic membranes have physically attached sublayers to obtain desirable separation properties and therefore are susceptible to abrasion and exhibit a minimal backflush ability. The commercialization of ceramic membranes is limited by the module development. Problems are both technical (wetted seals that are not ceramic) and economical (high module costs relative to polymeric membranes when compared on a surface area basis) [15].

Graphene-based materials are one of the most recent material developments in the field of inorganic membranes [16-17]. Among this class of materials, graphene oxide (GO) is the most common. GO nanosheets are hydrophilic due to the presence of oxygen containing functional groups (e.g., hydroxyl, carboxyl, carbonyl, and epoxy groups). Two-dimensional GO sheets offer mechanical stability, tunable physicochemical properties, and well-defined nanometer-scale pores, making them promising for water filtration applications (especially for NF and desalination) [18][19]. When layered in a membrane a permeation channel network is formed for water to migrate between the sheets. This tortuous path travels preferentially over nonoxidized (hydrophobic) surfaces that exhibit virtually no friction for the water molecules as opposed to the hydrophilic oxidized regions. Ultrafast ion permeation through a micrometer-thick GO membrane has recently been reported [20].

Another carbon-based nanomaterial recently adopted in membrane technology are carbon nanotubes (CNTs). Along with removal of biological impurities (e.g., bacterial pathogens and viruses), CNT-based membranes offer cost-effectiveness, robustness, size exclusion, and reduction of biofouling [21][22]. Baek et al. recently demonstrated fast water transport using a vertically aligned CNT membrane (4.8 nm of pore diameter) also featuring antimicrobial properties [23].

Organic membranes

Synthetic polymer membranes are widely used because it is to select a polymer suitable for the specific separation problem from the existing huge number of synthetic polymer. Polymers can be further categorized on rubbery, glassy and semi-crystalline state. If a polymer glass is heated, it will begin to soften in the neighborhood of the glass-rubber transition temperature (Tg) and became quite rubbery. Rubbery polymer is the polymer with viscoelasticity (having both viscosity and elasticity) and very weak inter-molecular forces, generally having low Young's modulus and high failure strain compared with other materials. soft and elastic due to the flexibility of the polymer backbone segments that can rotate freely around their axis [1]. Glassy polymer a rigid and tough polymer resulted from the steric hindrance along the polymer backbone that prohibits the rotation of polymer segments [24]. Both rubbery and glassy polymers have been applied to membrane preparation for the separation of impurities. Polymer materials in general offer a wide variety of structures and properties. Example of organic polymer are: Cellulose acetate (CA) and cellulose nitrates [25-26], polysulfone (PSU), [27] polyethersulfone (PES) [28], polyacrylonitrile (PAN) [29-30], polyvinylidene fluoride (PVDF) [31-32] polypropylene (PP), polytetrafluoroethylene (PTFE) [33], and polyimide (PI)[34] represent the most widely used current organic membrane materials

Despite the benefits for ceramic membranes mentioned above, polymer materials have a general advantage over ceramic membranes like:

- Ease of processing
- Availability of wide structure variation
- Possibility to realize any configuration
- High strength-to-weight ratio
- Ability to have properties tailored to a specific use structural changes
- Flexibility
- Low cost

Desirable properties for the polymer membranes are:

- Controllable pore size
- Narrow pore size distribution and high surface porosity
- Mechanical strength to withstand pressure and resistance to abrasion
- Chemical resistance to allow for a wide range of feed components and cleaning agents
- Hydrophilic; good wettability and low fouling properties or resistance to adsorption of feed components
- Thermostable; retention of the basis properties over a wide temperature range
- Workability; should be easily shaped into sheets or tubes and incorporated into modules[35]

2.1.2 Morphology, Structure and Manufacturing

The structure of membrane may be porous, nonporous, symmetric or asymmetric.

Membranes for pressure-driven separation (UF, NF, RO) have typically an anisotropic cross-section structure (integral or composite) with a thin (~ 50 nm to few micrometres) mesoporous, microporous or nonporous selective layer on the top of a macroporous layer support (100-300 μm thick) providing sufficient mechanical stability, ensuring a high membrane permeability.

Macroporous membranes with an isotropic cross-section (homogenous structure all over the thickness) (100-300 μm thick) are typical for MF, but become also increasingly relevant as base materials for composite membranes, e.g. for membrane absorbers.[36]

An overview of the state-of-the-art polymeric materials used for the manufacturing of commercial membranes, is given in Table (2).

Table 2. Polymer as materials for industrial established separation membrane [36]

Polymer	Morphology			Membrane process
	Barrier type	Cross section	Barrier thickness	
Cellulose acetates	Nonporous	Anisotropic	0.1	GS,RO
	Mesoporous	Anisotropic	0.1	UF
	Macroporous	Isotropic	50-300	MF
Cellulose nitrate	Macroporous	Isotropic	100-500	MF
Cellulose rigenerate	Mesoporous	Anisotropic	100-500	UF,D
Perfluorosulfonic acid polymer	Nonporous	Anisotropic		
Polyacrilonitrile	Mesoporous	Anisotropic	0.1	UF
Polyetherimides	Mesoporous	Anisotropic	0.1	UF
Polyethersulfones	Mesoporous	Anisotropic	0.1	UF
Polyethyleneterephthalate	Mesoporous	Isotropictrack-etched	6–35	MF
Polytetrafluoroethylene	Macroporous	Isotropic	50–500	MF
Polyamide,aliphatic	Macroporous	Isotropic	100–500	MF
Polyamide,aromatic	Macroporous	Anisotropic	0.1	UF
Polyamide,aromatic,in situ synthesized	Nonporous	Anisotropic/composite	0.05	RO, NF
Polycarbonates,aromatic	Nonporous	Anisotropic	0.1	MF

	Macroporous	Isotropic track-etched	6-35	RO, NF
Polyether,aliphaticcrosslinked,in situ synthesized	Nonporous	Anisotropic/composite	0.05	MF
Polyethylene	Macroporous	Isotropic	50-500	MF
Polyimide	Nonporous	Anisotropic	0.1	GS, NF
Polypropylene	Macroporous	Isotropic	50-500	MF
Polysiloxane	Nonporous	Anisotropic/composite	0.1 < 1-10	GS, PV, NF
Polysulfones	Nonporous	Anisotropic	0.1	GS
	Mesoporous	Anisotropic	0.1	UF
Polyvinylalcohol,crosslinked	Nonporous	Anisotropic/composite	<1-10	PV
Polyvinylidenefluoride	Macroporous	Anisotropic	0.1	UF
	Mesoporous	Isotropic	50-300	MF

By far the most of the technically used membranes are made from organic polymer and via phase separation method. Phase separation is a technique whereby the polymer is transformed in a controlled way from a solution state to a solid state. The concept of phase separation include different technique such as, precipitation by controlled evaporation, thermal precipitation from the vapour phase, and immersion precipitation [1].

The difference between the four techniques originate from differences in desolvation mechanism. Phase diagrams can predict, whether or not a solution of a certain polymer in a certain solvent is suitable for membrane formation, for example one with the composition

The general concept of phase inversion method covers a variety of different techniques, including:

a) Precipitation by solvent evaporation
b) Precipitation by controlled evaporation
c) Thermal precipitation
d) Precipitation from the vapour phase

e) Immersion precipitation or nonsolvent induced phase inversion (NIPS)

Most commercially available membranes are prepared by immersion precipitation: a polymer solution (polymer plus solvent) is cast on a suitable support and immersed in a coagulation bath containing a nonsolvent. Precipitation occurs because of the exchange of solvent and nonsolvent. The membrane structure obtained results from a combination of mass transfer and phase separation.

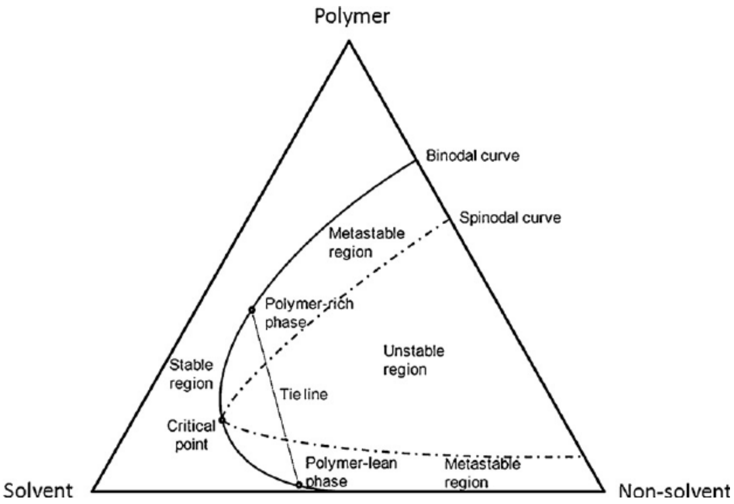

Fig. 2 Schematic representation of a ternary system with a liquid-liquid demixing gap[1]

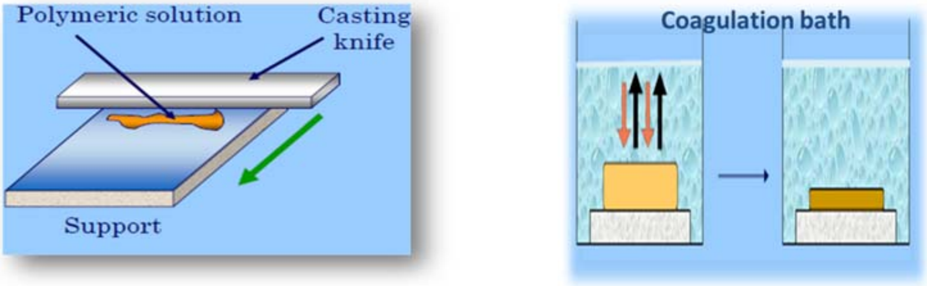

Fig.3 Schematic representation of Non-Solvent induced phase separation (NIPS)

- *Liquid-liquid demixing (binary system)*

All the possible combinations of three components can be plotted in a triangle. The corners represent the pure components, the axes the three binary combinations and a point in the triangle a ternary composition (Fig.2)

The phase diagram is divided into homogenous region, and an area representing a liquid-liquid demixing gap. The liquid-liquid demixing gap is entered when a sufficient amount of nonsolvent is present in the solution. In principle, the same three parts of the demixing gap are present as in the binary diagram. A metastable area exists between the spinodal and the binodal at low polymer concentrations, an unstable area is enclosed by the spinodal, and a second metastable area at higher polymer concentrations. The phase separation proceeds analogously with binary solutions. A line plotted in the phase diagram which connects the initial composition of thr film to the final average compositional change in the solution as a function of time [37].

In the Flory–Huggis description (Eq 1), the size and location of the demixing gap depends on the molar volumes of the components, the polymer-solvent interaction parameter, the polymer-nonsolvent interaction parameter and the solvet-nonsolvent interaction parameter [38].

$$\Delta G_m = RT[n_1 ln\oint_1 + n_2 ln\oint_2 + n_1\oint_2\chi_{12}] \qquad (1)$$

Where ΔG_m is Gibbs energy, n_1 are number of moles and volume fraction $\oint_1$ of solvent; n_2 and $\oint_2$ number of moles and volume fraction of polymer; finally χ_{12} tis the energy of inderdispensing polymer and solvent molecules.

➢ *Liquid-liquid demixing (ternary systm)*

In addition to temperature changes, changes in composition brought about by the addition of a third component, a nonsolvent, can also cause demixing. Under these circumstances, we have a ternary system consisting of a solvent, a nonsolvent and a polymer. The liquid-liquid demixing area must now be represented as a three-dimensional surface.

➢

➢

➢

- *Crystallization*

Many polymers are partially crystalline. They consist of an amorphous phase without any ordering and an ordered crystalline phase. Crystallization may occur if the temperature of the solution is below the melting point of the polymer.

- *Gelation*

Gelation is a phenomenon of considerable importance during membrane formation, especially for the formation of the top layer. Gelation can be defined as the formation of a three-dimensional network by chemical or physical cross-linking.

- *Vitrification*

There are polymers that show neither crystallization nor gelation behaviour. Nevertheless, these polymers finally solidify during a phase inversion process. This solidification process may be defined as vitrification, which is the stage where the polymer chains are frozen in a glassy state, i.e. it is a phase where the glass transition temperature has been passed and the mobility of the polymer chains has been reduced drastically. In the absence of gelation or crystallization, vitrification is the mechanism of solidification in any membrane-forming system with an amorphous glassy polymer [39].

The influnce of the parameters can be summarized as follows.

- A polymer-nonsolvent interaction parameter determines, the surface area of liquid-liquid demixing gap. High polymer-nonsolvent interaction parameters imply that the point of intersection of the demixing gap with the polymer-nonsolvent axis is located at very high polymer concentrations. [40].
- Low mutual affinity between polymers and solvents increase the distance of the demixing gap, especially at low values of X_{12}.

- Low compatibility of solvent-nonsolvents mixture result in large differences in solvent/nonsolvent ratio in the equilibrium phase.
- Solvents and nonsolvents with high mutual affinity strongly increase the magnitude of demixing gap.

In a first approximation changes in molecular weights, molecular weight distributions and molar volumes are negligible compared to the influence of interaction parameters [40-41].

Pioneering work for the interface polycondensation or polyaddition toward ultra-thin polymer barriers on support UF membranes a technique which is now technically implemented in large scale in several different variations, had been performed by Cadotte et al.[43]. The first protocol had been based on the reaction between a polyamine in water filling the pores of the support membrane, with an aromatic diacid chloride in hexane. Alternatively, aromatic diisocyanates were also used. Similar chemistries had later been proposed for the surface modification of UF membranes [43-45].

In the temperature-induced phase-separation process, the precipitation of a casting solution is

achieved by cooling a polymer solution which forms a homogeneous solution only at elevated temperature, for example, polypropylene dissolved in N,N-bis-(2-hydroxyethyl)tallow amine. The temperature-induced phase-separation process generally results in a symmetric porous structure. Under certain experimental conditions, it can also result in asymmetric structures. The temperature induced phase separation is not only applicable to polymers, but it is also used for the preparation of porous membranes from glass mixtures and metal alloys in combination with a leaching procedure [46].

2.3 Membrane fouling

Membrane fouling is still a severe problem limiting the potential of this technique. Fouling may result in an increase in operational cost, due to and increased energy demand, additional labor for maintenance, cleaning chemical cost and shorter membrane life. It requires effective and efficient methods for its control and minimization.

It may possible to prevent fouling before its occurrence by methods such as pre-treatment of the feed streams, chemical modification to improve the anti-fouling properties of a membrane, and optimization of the operational conditions. However, periodic membrane cleaning is still currently inevitable. It is indeed an integral part of most membrane process in modern industries, and must be regularly carried out to remove the fouled materials and restore the productivity of the operation [47].

The reduction of membrane flux is due to two important effects [48].

Firstly, concentration polarization, which as a natural consequence of the semi-permeability and selectivity of a membrane, results in an accumulation of rejected solutes or particles in a mass transfer boundary layer adjacent to the membrane surface [49]. During the filtration of a solution solvent molecules pass the membrane but the larger solutes are rejected and retained at the membrane surface. These rejected molecules are relatively slow to diffuse back to the bulk solution, which causes a concentration gradient just above the membrane surface [50]. Such a high amount of materials accumulating at the membrane impedes the solvent flow through the membrane, and the creates an osmotic back pressure that reduce the effective trans-membrane pressure (TMP) of the system. Concentration polarization is inevitable but is also a reversible phenomenon that does not itself affect the intrinsic properties of a membrane [51].

Secondly, there is membrane fouling taking place when the matter in the feed solution leaves the liquid phase to form a deposit on either the membrane surface or inside its porous structure [48]. In contrast to the reversible nature of concentration polarization, fouling may cause irreversible loss of the permeability of a membrane. In fact, reversibility is a defining characteristic of fouling. Many researches distinguish reversible and irreversible fouling, based on their relative resistance to cleaning [50-51].

Fouling usually arises through several mechanisms including adsorption, pore blocking and cake or gel formation.

Adsorption can take place upon the membrane surface as well as within the pores themselves. The adsorption process started as soon as the membrane is in contact with the feed solution. In this respect adsorption is considered to be an equilibrium process. However, if pressure is applied at the feed side an additional deposition of solutes may occur induced by the convective flow. The interactions generally have three type, due to weak van der Waals forces, electrostatic attraction, or chemical bonding respectively, depending on the functional group involved [54].

Pore blocking occurs due to the full or partial closure of membrane pores by colloids and particles [53-54] and results in an increased local flux through the pores that remains open and a higher rate of mass transfer that may or may not increase the internal fouling, if the flow rate through the whole membrane is kept invariant.

Cake formation is the process by which particles build up layer by layer on the external surface of a membrane, leading to an additional resistance to the permeate flow.

The relative importance of different fouling mechanisms depends on operating conditions, feed stream and membrane properties [51]. There are many ways to clean a fouled membrane. Generally, they can be divided into two categories: physical and chemical method based on whether any chemical agents are applied in the procedure.

Physical cleaning generally involves applying one or more of three cleaning forces: hydraulic, mechanical and electrical. The more efficient hydraulic cleaning is the backwashing. This method is performed with reversed flow pushed from permeate side to the feed side of a membrane. The reversed flow dislodges the deposits from membrane pores and loosens fouling cakes on the external side [57].

Due to fouling propensity of NF/RO membranes, feed water with a certain quality. is required to ensure long-term stability of membrane system. Pretreatment can reduce fouling potential, increase membrane life, and maintain performance level by altering the physical, chemical, and/or biological properties of the feed water [58]. Although conventional filtration pretreatment have been widely used in NF/RO plants, fluctuation of feed water quality during events such as algal bloom or chemical contamination can lead to deteriorations of effluent water quality in conventional filtration pretreatment [59]. Colloids and suspended particles often pass through conventional filtration pretreatment and contribute to irreversible fouling of NF/RO membranes. The use of membrane with large pore size, such as MF and UF, prior to NF/RO stage has become an more practicable, alternative to conventional pretreatment [60]. Currently, UF membranes present perhaps the best balance between contaminant removal and productivity due to UF membranes have a smaller pore size than MF membranes and higher flux than NF membranes. UF can provide high permeate flux and constant water quality ensures during the continuos process [60].However, each membrane has its own characteristics, and each treatment plant must choose pretreatment based on specific contaminant removal requirements. MF membranes are the appropriate choice for removal of larger particulate matter at higher permeate fluxes [61], while NF membranes are used to remove particulate materials, colloids, and bivalent salts.

The combination of UF with coagulation at low dose helped in controlling the RO membrane fouling in the downstream [60-61]. Membrane pretreatment is particularly advantageous for NF/RO systems for treating surface water because, surface water tends to have more organic colloidal and suspended solids, as well as a higher fluctuation due to algal blooms and chemical pollution. In addition, the membrane contactor (MBR) process has been applied to reclaim municipal wastewater due to the strong removal ability of organic and particulate matters, and the subsequent NF/RO systems can operate at high and stable permeate flux in long-term operation [62-63]. Jeong et al. [66] used submerged membrane hybrid system as pretreatment for RO system and found that pretreatment by submerged membranes combined with coagulation-adsorption hybrid system can lead to the best results in term of organic removal and critical flux. MF and UF provides several advantages and can act as an effective barrier to particulate and colloidal fouling for NF/RO system in comparison to conventional multimedia filtration [60]. Membrane pretreatment can prolong the aging time and reduce the frequency of chemical cleaning of NF/RO membranes by improving feed water quality.

Chemical cleaning is a process which primarily uses chemical solutions to remove foulings from membrane surface. Some of these cleaning agents are acids, alkalis, surfactants, disinfectants and combined cleaning materials Alkaline solutions clean organic-fouled membranes by hydrolysis and solubilization, and by generating electrostatic interactions between the negatively charged foulants and membranes when the solution pH is elevated [47]. Surfactants are compounds that have both hydrophilic and hydrophobic groups, and are semi-soluble in both organic and aqueous solvents. Surfactants can solubilize macromolecules by forming micelles around them and help to clean the surface of the fouled membrane [67].

However, a major issue in membrane pretreatment is that MF and UF membranes are fouled in the process. Both surface cake layer or pore blocking occur in MF and UF membranes. The risk of membrane fouling may result in flux decline and cost raise, especially for feed water with a high organic level. Pretreatment technologies for MF/UF membranes has been extensively reviewed by Huang et al. [68].

The membranes with smooth, hydrophilic surface and similar charge to the foulant seem to possess better anti-fouling property. Therefore, a great deal of research efforts has been devoted to improve anti-fouling property by changing properties of selective layer of membranes, generally including surface coating, surface grafting, incorporation of hydrophilic monomers/inorganic particles, and zwitterionic modification [1].

2.3.1 Development of advanced membranes

Different strategies were proposed to improve polymeric membrane performance to membranes. Significant effort has been directed toward enhancing permeation flux, pollution resistance, operation pressure stability, and membrane service life. One such method is surface modification [69] for example, by making these polymeric membranes hydrophilic. It is generally accepted that increasing the hydrophilicity of the membrane may reduce fouling issues because many foulants including proteins and organics are hydrophobic in nature. There are various methods to fabricate hydrophilic polymeric membranes. These include homogeneous blending [67-68] plasma treatment [69-70], surface grafting [71-72] cross-linking [73-74] gamma ray and UV irradiation [75-76], surface coatings with hydrophilic polymers [77-78] and surface segregation methods with amphiphilic block copolymers [82].

Recent reports addressing functional polymeric membranes include use of conductive polymers [83]. PVF/pol(N-isopropylacrylamide-co-acrylic acid) microgels/ DMF in water are the demonstration of temperature- and pH-sensitive membranes with improved antifouling property by phase separation [84]. Another example is the blending of copolymer pol(acrylic acid-copolyethylene glycol methyl ether methacrylate) (p(AA-co-EGMA)) with PSU to prepare flat-sheet polymeric membranes by the phase-inversion method [85]. Also, one-pot in situ crosslinked copolymerization of poly(methyl methacrylate-coacrylic acid) (p(MMA-AA)) and pol(methyl methylacrylate-co-4- vinyl pyridine) (P(MMA-4VPy)) on PES membrane exhibiting pH-response, anti-fouling property, and Cu2+ adsorption capacity [86]. Track-etched polyethylene terephthalate (PET) membranes by grafting 2-hydroxyethyl-methacrylate (HEMA) via atom transfer radical polymerization showing reversible pH-response permeation to environmental pH values by controlling the PHEMA chain lengths [87].

Temperature-modulated water filtration is another example of the use of functional polymers. Poly(N-vinylcaprolactam)-based microgels were employed to coat commercially available hollow-fiber membranes used for MF and UF applications [88]. The main advantages of this method are that microgel functionalization (via adsorption) can be applied to almost all types of membranes and that the membrane modification is simple. The membrane showed reversible thermoresponsive permeability and rejection as well as fouling [89].

The use of self-assembly of block copolymers potentially offers high selectivity due to their narrow pore-size distribution, high permeability resulting from high porosity, and controllable dimensions, surface properties, and chemistries[87-88]. Block copolymers with hexagonally packed cylinders oriented perpendicular to the membrane surface offer an ideal pore morphology [89-90]. Phillip et al. prepared an UF membrane using self-assembled poly(styrene-blocklactide) block copolymer By controlling the solvent (toluene) evaporation rate (fast solvent evaporation kinetically traps the cylindrical formation in a nonequilibrium morphology), polylactide cylinders are formed perpendicular to the substrate (commercially available microporous membrane was used as a support layer) [94].

One of the latest development in membrane material design is the use of hybrid (inorganic–organic) materials, with the possibility in overcoming limitations associated with polymeric membrane systems. The deficiencies of organic polymeric materials and the comparative disadvantages of the inorganic membranes have prompted the development of the more competent membrane materials to over-come these limitations. The fabrication of mixed matrix membrane (MMM) is an emerging trend membrane-based separation. Table(3) summerizes the properties of polymeric, inorganic and mixed matrix membranes. Upon comparison, it is obviously noted that MMMs possess very promising properties that have remarkably surpassed that of polymeric and inorganic membranes [95].

Table.3 Comparison of the properties for polymeric, inorganic and mixed-matrix membranes [95]

Properties	Polymeric membrane	Inorganic membrane	Mixed-matrix membrane
Cost	Economical to fabricate	High fabrication cost	Moderate
Chemical and thermal stability	moderate	High	High
Mechanical strenght	Good	Poor	Excellent
Compatibility to solvent	Limited	Wide range	Limited
Handling	Robust	Brittle	Robust

A MMM is a heterogeneous membrane consist of inorganic fillers embedded in a polymeric matrix and can be made into flat sheets and hollow-fiber. Nevertheless, the selection of membrane configuration is greatly dependent on the application and therefore in the preparation of MMMs the choice of configuration is essential to development of this material [96]. MMM combine the superior permeability and selectivity of inorganic membranes with the processability of polymeric membranes. The combination in MMM has resulted in a synergistic effect in which the rigid adsorptive porous type inorganic phase provides superior separation properties, meanwhile the presence of flexible polymer enables the ideal membrane forming hence solving the problem of fragility inherent found in the inorganic membranes [97].

Inorganic materials that have been investigated are metal oxides (e.g., Al_2O_3, TiO_2, SiO_2, ZnO, Fe_2O_3), metals (e.g., Cu, Ag) and carbon-based materials (e.g. graphene and carbon nanotubes) [98]. Introducing inorganic moieties into a polymeric matrix system can offer multifunctionality beyond separation alone and can enhance hydrophilicity, mechanical strength, water permeability, rejection rate, and antifouling properties. This is, in part, because such additives can modify the kinetics and thermodynamics of the formation process of the polymeric membrane such that the membrane surface and pore structure can be altered [99]. These nanoporous materials possess the shape and size selective nature and hence allow molecular sieving discrimination by permitting smaller sized penetrates to diffuse at higher rate than that of larger sized [95]

Various fabrication methods have been developed to incorporate these nanomaterials in a polymer matrix. These include blending, phase inversion methods (resulting in well-mixed nanomaterials in the matrix), interfacial polymerization (resulting in a thin layer of nanocomposite on the surface of the membrane or a thin layer with nanocomposite membrane substrates), self-assembly of nanoparticles, surface coatings, layer-by-layer processing, and surface grafting [100]. Wang et al. recently reviewed the behavior of various nanomaterials in polymeric matrices during the phase-inversion process and their structural performance during filtration [101] Membranes consisting of nanomaterials in a polymer matrix for water treatment were recently reviewed by Goh et al.2000 [102]. Recent developments in thin film composite membranes [103] have received increasing attention as these systems exhibit superior performance compared with asymmetric membranes for desalination and have been reviewed by Lau et al. [104]. Modifying the membranes by blending organic and inorganic materials (especially nanoparticles) may offer advantages such as excellent filtration performance, thermal and chemical stability, as well as membrane forming ability. Widely used polymeric membranes such as PES and PVDF with improved antifouling property were realized by incorporating various inorganic materials. Arsuaga et al. reported the effects of the type, size, and spatial distribution of metal oxide (TiO_2 (485 ± 148 nm), Al_2O_3 (438 ± 131 nm) and ZrO_2 (398 ± 122 nm)) on the properties of composite PES UF membranes (Fig. 4) [105]. They observed a correlation between physico-chemical properties (porosity, hydrophilicity, and permeability of composite membranes) and the spatial particle distribution in the membrane structure. General improvement of water flux and rejection upon incorporation of the particles was seen. Also, the study showed that metal oxide added in the PES membranes exhibited reduced fouling due to increased hydrophilicity of the membrane surface. Metal oxide distribution is a key parameter for membrane fouling reduction, but there is no effect on the rejection potential of the composite membranes.

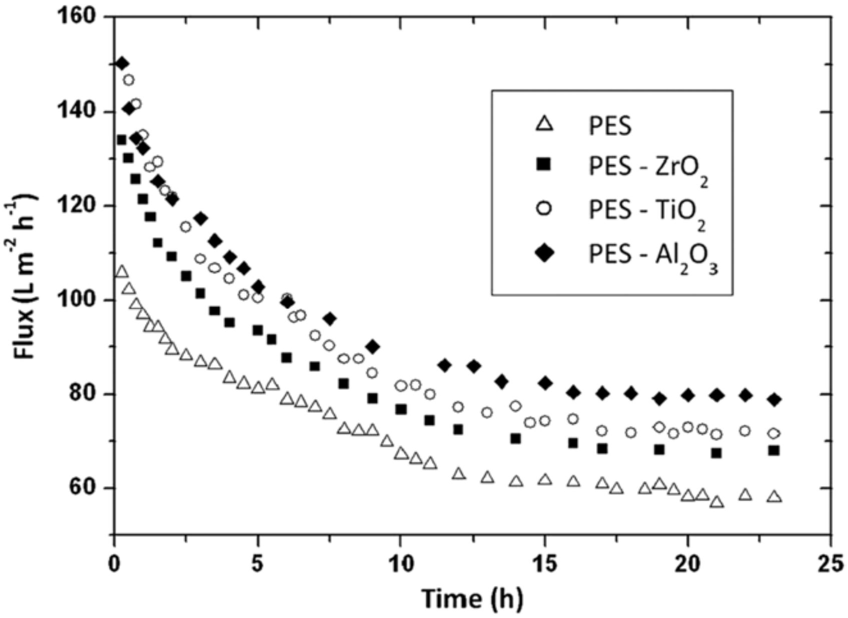

Fig.4. Comparison between flux perfomnce of polymic PES and MMMs [106]

Another interesting materials is the GO nanosheet additives that offer good chemical stability and high surface area. GO-doped PSU polymer matrix exhibits enhanced hydrophilicity, water flux, and salt rejection [107]. There are also reports in which GO nanosheets act as a hydrophilic modifier for polymeric membranes such as PVDF [108], PSF[107], GO/PVP on PVDF [109] as well as enhancing antifouling[107-108] and mechanical strength of MF membrane.

Many studies have reported the MMMs may exhibit substantially increased permeability and selectivity that are far beyond the intrinsic properties of pure polymer membranes [109-110]. To make full use of the advantages of MMMs, the knowledge of permeability variation of a penetrant with the type and concentration of filler materials are required in order to design and operate the separation process of MMMs [114]. In order to achieve a successful and practical implementation of MMMs, certain criteria of the membrane development have to be taken into account. These include the compatibility and properties of polymer-inorganic materials, the development of a defect-free MMM that can be related to the mechanical adhesion and segmental conformance of the matrix at sieve/matrix interface. In addition to that, a sufficiently thin selective membrane layer later is also necessary to provide desirable economically viable flux [115].

There are numerous examples in the fabrication of MMMs. These molecular sieve type fillers used in MMMs are capable of discriminating between different molecules present in the feed mixture, based on the sizes and shapes of the molecules. Zeolite 4A is one of the commonly used zeolites that served as a dispersed phase in MMMs [116]. Besides that, many researchers have reported the performance of MMMs consisting of silica zeolite ZMS incorporated into silicon rubber polymer, such as poly (octyl methyl siloxane) and poly(phenyl methyl siloxane) [117] to form MMMs for separation through pervaporation. In the context of pervaporation, the expected ease of manufacturing, reduced cost and the ability to save energy relative to other conventional processes of zeolite membranes have made these MMMs attractive. Unfortunately, this seemingly simple operation does not always yield the highest performing membranes, in particular for gas separation [118].The majority of gas diffusion occurs through the phase with lower diffusional resistance, resulting in the dominating properties of the high permeability and low selectivity polymer matrix [119].

Although a great deal of effective practical and fundamental studies has been reported, the development of new materials of MMMs is still needed. An interesting example is MMM prepared with carbon nanotubes (CNTs), which is an inorganic filler material that differs substantially from molecular sieves, as well as, other inorganic particles. In membrane separation, matching of pore size to that of the target molecules is critical to achieve improvements in both selectivity and flux. Therefore, it is beneficial to produce a membrane structure with initial pore diameter close to that of the target molecule diameter with small dispersion [59]. During the growth of CNTs, the nanotubes size is controlled by the diameter of the catalyst particles and hence offers a possible route for pore diameter control by varying the size of the catalyst particles with nanometer-scale diameter dispersion, so that there is a potential for porosity tuning in the membrane [60-62].

2.4 Carbon nanotubes

The area of carbon nanotubes (CNT)-polymer composites has been progressing extremely rapidly in recent years. CNTs have the structure of a rolled up graphene sheet [120]. Although CNTs are not formed via the roll up of a graphene sheet, it is nevertheless a useful visualization in understanding nanotube geometry (Fig.6). The degree of "twist" resulting from where the hypothetically rolled up graphene sheet overlaps to form the nanotube determines the chirality of a CNT. Chirality marks the difference in CNTs between zigzag, armchair, and chiral types [121].

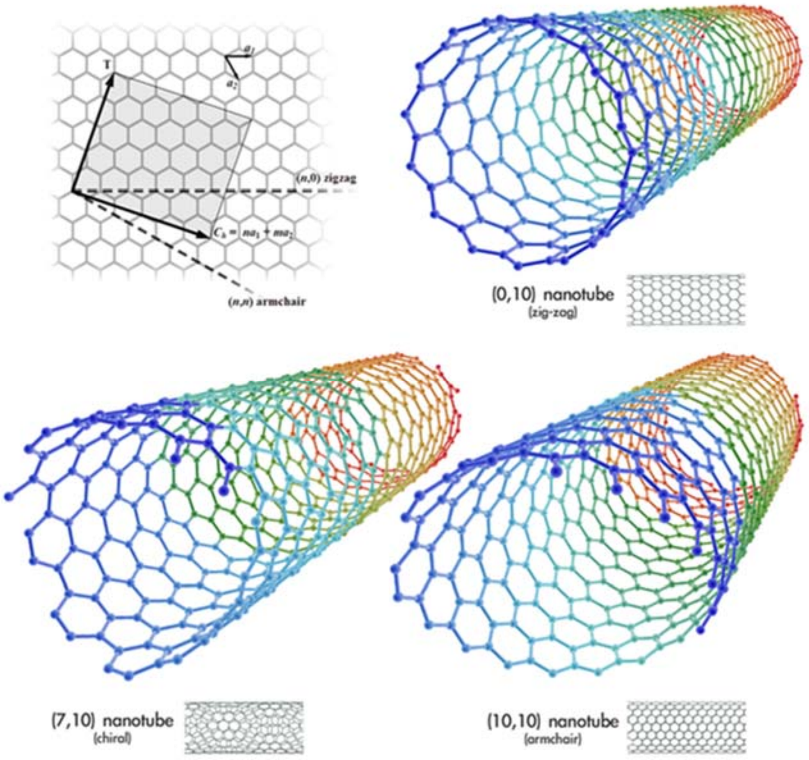

Fig.5 Different chirality of CNTs, zigzag, armchair and chiral [120].

Two types of CNTs, namely single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), (Fig. 6) which differ by the number of carbon atom cylindrical arrays arranged around the hollow nanotube core, were development [122].

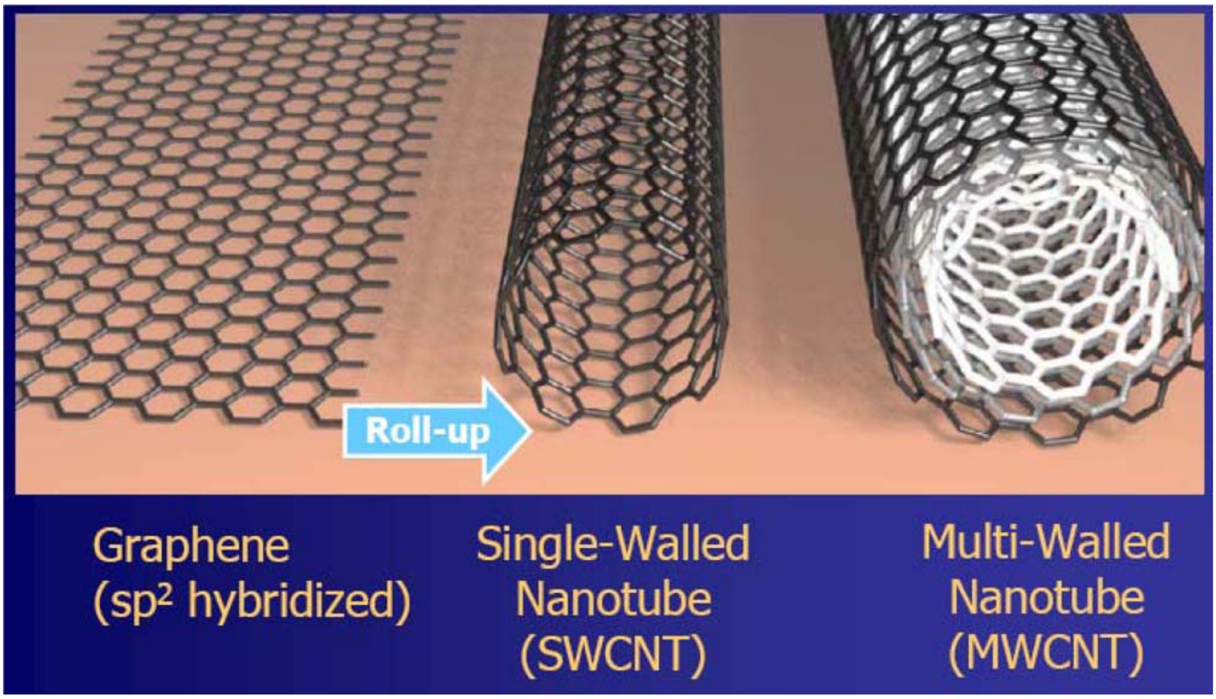

Fig.6 Graphic representation of graphene and two types of CNTs, single-walled nanotubes and multi-walled nanotubes [123].

Nanotubes themselves have remarkable electrical, thermal, and mechanical properties. For example, CNTs theoretically have exceptional mechanical properties such as elastic modulus and strengths 10-100 times higher than the strongest stee. In 2000, Yu et al.[124] measured Young's moduli values for individual MWNT between 0.27-0.95 TPa, strengths in the 11-63 GPa range, and a toughness of 1240 Jg^{-1} [124]. For SWNT, Young's moduli were found to be in the range of 0.32-1.47 TPa and strengths between 10 and 52 GPa with a toughness of 770 Jg^{-1} [124]. CNT also show unique electrical properties and electrical-current-carrying capacity 1000 time higher than copper wire [125]. Frank et al.[126] calculated the conductance of an average nanotube to be 1/12.9 $k\Omega^{-1}$. This combination of properties makes CNTs potentially ideal candidates for the formation of polymer composite with improved mechanical properties and electrical conductivity. CNT-polymer composite have a multitude of potential applications ranging from ultrastrong materials for bullet-proof vests, to flexible displays, and electronic paper [127]. Adding carbon –based fillers to polymers to improve mechanical properties, decrease weight, and act as heat conductors is not a novel idea. Carbon black has been widely utilized to reinforce rubber and plastics, for example, it is extensively used in racing tires to reduce thermal damage. Carbon fibers are also hugely popular industrial materials that are used in cars, airplanes, bicycles, etc. However, the carbon-based polymer additives with the greatest potential are CNTs. The ability to harness the mechanical strengths of CNTs has already given rise to new industrial products [128].

2.4.1 Functionalization of Carbon Nanotubes for polymer-composite preparation

The chemical functionalization of CNTs has been a subject of several reviews[119-126]. It is known that nanotubes solubility, dispersion, and stress transfer must all be maximized to reach optimum mechanical properties. Unless the interface between nanotube and polymer is carefully engineered, poor load transfer between nanotubes, when in bundles, and between nanotubes and surrounding polymer chains may result in interfacial slippage [130]. Therefore, functionalization of nanotubes is extremely important for their processing and potential applications in polymer composites. In general, composites based on chemically modified nanotubes show the best mechanical results because functionalization enables a significant improvement in both dispersion and stress–strain transfer. The treatment of CNTs by chemical functionalization and/or ultrasonication is widely used to increase the dispersion of nanotubes in solvents. In particular, a better dispersion of nanotubes in solvents overcomes the problems of nanotube aggregation in polymer composites processed by the solution casting technique[128-129]. There are two major approaches to nanotube functionalization: covalent functionalization and non-covalent supramolecular modifications [130-131].

- *Covalent functionalization*

The most common and facile method for the surface functionalization of CNTs is nanotube oxidation, which results in the formation of a number of carboxylic acid and oxydrilic groups (COOH, OH) on the surface of the nanotubes. These functionalized nanotubes are much more stable in polar solvents. For example, Feng et al. [135] showed that by treating MWNTs with HNO3/H2O2 and HNO3/H2SO4 functionalized nanotubes formed, which were stable in water at room temperature for more than 100 days. As a result, the water-stable nanotubes can be easily embedded into water soluble polymers such as a poly(vinyl alcohol) (PVA), giving polymer–CNT composites with homogeneous nanotube dispersion [136]. It has been shown that acid functionalization significantly improves the interfacial bonding properties between the CNTs and a polymer matrix [137].The carboxylic functional groups have been shown to give a stronger nanotube–polymer interaction, leading to enhanced values in Young’s modulus and mechanical strength[128]. The presence of active functional groups such as carboxylic acids or amines allows for further covalent functionalization with polymer molecules (polymer grafting). Two main approaches for the covalent functionalization of CNTs with polymers have been reported: ‘‘grafting from’’ and ‘‘grafting to’’ [135-137] The grafting-from approach is based on the initial immobilization of initiators onto the nanotube surface, followed by in situ polymerization with the formation of the polymer molecules bound to the nanotube. However, this method requires a strict control of the amounts of initiator and substrate. [140].

The grafting-to approach is based on the attachment of already preformed end-functionalized polymer molecules to functional groups on the nanotube surface via appropriate chemical reactions. However, the main limitation of grafting-to technique is that initial binding of polymer chains sterically prevents diffusion of additional macromolecules to the surface leading to relatively low polymer loading [141]

- *Non-covalent functionalization*

The non-covalent functionalization of nanotubes normally involves van der Waals, π-π, CH– π-π or electrostatic interactions between polymer molecules and CNT surface [142]. The advantage of non-covalent functionalization is that it does not alter the structure of the nanotubes and, therefore, both electrical and mechanical properties should also remain unchanged. However, the efficiency of the load transfer might decrease since the forces between the wrapping molecules and the nanotube surface might be relatively weak [143]. There are several non-covalent approaches for nanotube functionalization such as surfactant-assisted dispersion, polymer wrapping, plasma polymerization-treatment, and polymerization filling technique (PFT) [133].

2.4.2 Strategies for the fabrication of carbon nanotubes-polymer composite

Common traditional approaches for the fabrication of CNT–polymer composites include: solution processing of composites, melt spinning, melt processing, in situ polymerization, processing of composites based on thermosets, electrospinning, and coagulation spinning for composite fibers. Solution casting processing of composites is one of the most usual methods for making polymer–nanotube composites on a laboratory scale. The nanotubes and polymer are mixed in a suitable solvent before to form a composite film [128-141].

Numerous publications can be found on nanocomposites with many other polymers, such as ethylene-vinyl acetate copolymer [145], polyvinylidene fluoride [146], polyolefins [147], acrylonitrile-butadiene-styrene [148], polyphenylene sulfide[149], poly(ethylene terephthalate) (PET) [150]. The researchers mainly conclude that in order to achieve the true potential of carbon nanotubes, several challenges have to be faced. Carbon nanotubes have to be produced with higher purity, longer lengths, better integrity, in larger amounts, and at lower cost. Moreover, issues such as orientation of the nanotubes, their concentration, interfacial adhesion, distribution, and dispersion have to be overcome. Nevertheless, it is widely understood that a small quantity of nanotubes can significantly increase the electrical properties of composites and reduce the coefficient of thermal expansion[151]. Usually, superior mechanical properties are reported, which comprises many aspects such as tensile strength, compressive and flexural properties, and interlaminar, interfacial and fracture strength.

2.4.3 Transport through CNTs

The tubular structure of CNTs provides structurally perfect and stable nanochannels with variable size, thus the potential application of CNT channel can be manifold [152]. These ambitious applications, in particular membrane separation require the delivery of fluids or gases through the interior of CNTs and therefore these transport phenomena have been the object of widespread research. Generally, as the size of the channel pores approaches the size of the molecules, the interaction between the transported molecules and pores walls become increasingly important.

Furthermore, the thermodynamic state of the molecules in this confined system is also strongly affected by this interaction. As a result, the transport properties and molecular distribution in this nanoporous media may differ from ordinary transport in bulk media [153]. Diffusion is a fundamentals mechanism of molecular transport through a porous media. Two different pure-fluid diffusivities i.e. self-and transport diffusivity are of interest and have become an ever increasingly important topic over the past few years. Self-diffusivity is the diffusion of a single tagged molecule through a fluid whereas transport diffusivity is related to the macroscopic mass transport of molecules in a system where the driving force is the concentration gradient [154].

Transport of fluid through CNTs is of great interest since they have been recognized as a promising material for nanofluidic and membrane technology. The high fluid fluxes reported in the recent publications are contributed by atomic-scale smoothness of the CNT walls and the molecular ordering phenomena inside the nanopores [155]. In order to fully utilize these materials for membrane application, a better understanding of the fluid flow in the cylindrical channel of the nanopores is required. Despite some qualitative similarities of fluid behavior in cylindrical and slit like pores such as in microporous zeolite channel, the transport phenomena taking place in these narrow pores can be more complicated and are different in important details [156]. The transport properties of fluid in nanopores depend strongly on the curvature of the surface and shape of the pore. Solid surfaces have profound influences on the transport properties of as they impart not only normal stresses due to the adsorption potential and the resulting density variation in the direction normal to the interface, but also lateral stresses as demonstrated by Sokhan et al. in their simulation studies of fluid flow in nanotubes [157].

The pore size, molecule-wall interaction and the helicity of CNTs have also made important impacts on the dynamic behaviors and molecular motion of water confined in different nanotubes which in turn determine the transport properties in CNTs [153]. By conducting molecular dynamics (MD) simulation, Sholl and co-workers showed that when simple fluids are simulated within narrow molecular sieves, the fluid diffusion was dominated by concerted event in which multiple molecules move simultaneously [158]. Nevertheless, several theoretical works have suggested that inherent smootheness of the interior CNTs facilitated exceptionally fast diffusion for the molecules of water and simple gases [156-158]. These studies showed evidence that the absorbed water molecules can exist inside the CNT segments and tend to organize themselves into a highly and long lasting hydrogen-bonded network between absorbed water molecules. The smooth and frictionless CNT surfaces resulted in weak carbon-water attractive interaction and hence facilitated the extremely high flow velocity.

2.4.4 Application area

Four many application areas of nanotubes-enhanced membranes are investigated in literature: gas separation, water treatment, drug delivery and fuels cells. These are considered as the areas with the highest potential for implementation. Several have potential in a more distant future but need to be further developed.

One of the most fascinating areas of application of carbon nanotubes in membranes is desalination. Elimelech and Phillip [161] provide a clear evaluation of the current state of the art in desalination, including the potential of carbon nanotubes. They relate the extremely high water fluxes to the molecular smoothness of nanotube wall, the structure that water takes within nanotubes, and the smooth energetic landscape inside nanotubes. However, they also state that none of these mechanisms actually results in a selective rejection of dissolved salts, which means that chemical functionalities to the mouth of the nanotubes pores should provide for that. Alternatively, the nanotube diameter should be small enough to sieve ions from solution based on size, but such membranes do not yet exist. Corry [162] makes a detailed calculation of these effects for nanotubes between 6 and 11 Ǻ. It was shown that ions face a large energy barrier at the pore mouth when the channel is narrow enough. They do not pass through narrow tubes but can pass through the wide and nanotubes. Thus, it can be concluded that more fine tuning in CNT membranes is needed for practical applications of desalination. This is confirmed by Lee et al. [163] who state that such novel materials represent the most likely opportunities for enhanced RO desalination performance in the future, but that a number of challenges remain with regard to their practical implementation.

Nevertheless, carbon nanotubes are nowadays frequently used as additives for membranes in view of improving their performance. Zhao et al. [164] have reviewed procedures for synthesis of membranes with nanotubes incorporated, and suggest that nanofiltration membranes based on vertically aligned CNT are the most promising.

Shawky et al. [170] studied MWCNT/aromatic polyamide (PA) nanocomposite membranes to reject NaCl and humidic acid. They concluded that rejection increased significantly; however, flux decrease [15]. Choi et al. found a higher flux when incorporating MWCNT, but the pore size of the membranes depended on the concentration of nanotubes. The pore size of the blend membrane increased with the concentration of MWCNT up 1.5% and then decreased until it became even smaller than PSf membrane (at 4%). This indicates a clustering effect that may eventually have a negative effect on the flux [165].

Mitigation of membrane fouling is another objective, which has been described by Celik et al.They show that MWCNT/polyethersulfone blend membranes have a better fouling resistance than bare membranes [166]

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Chapter 3: Polyimide based mixed matrix membranes

3.1 Introduction

In the first part of thesis, MMMs with three different poly(imide) (PI) were prepared by NIPS: a homopolymer (Matrimid) and two co-polymers (Lenzing P84 and Torlon) (Fig.1). PI combine an easy processability in the form of membranes, with a high chemical and thermal stability, over a wide range of operative conditions. Membrane made of PIs, have shown excellent transport properties in both gaseous and liquid phase separation[1].

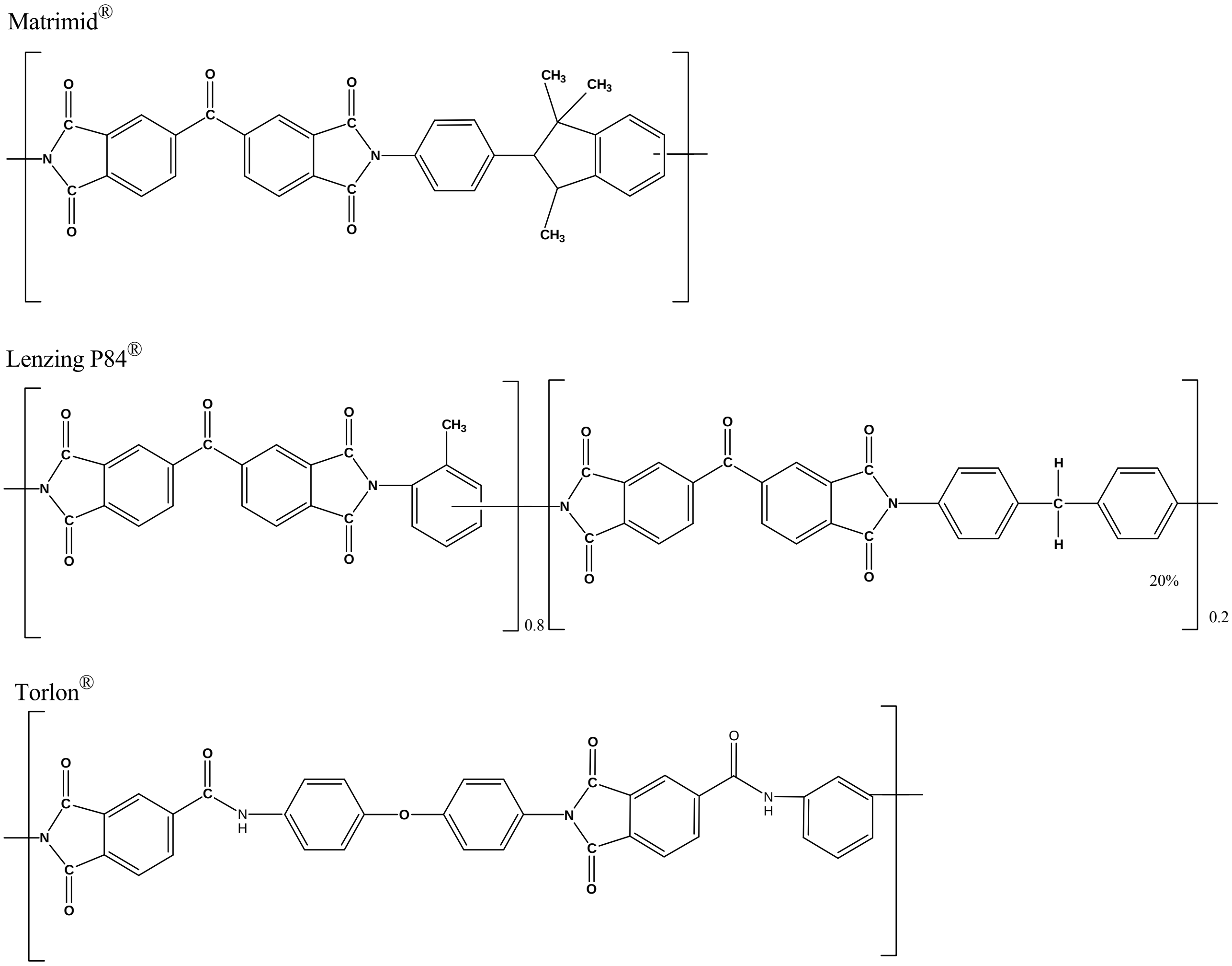


Fig.1 Chemical formula of the poly(imide) (PI) used as membrane materials.

Considering that the presence of dyes in textile industrial wastewater is presently one of the most worrisome ecological problems in recent years, membrane operations were used, because have the advantage to use intrinsically more clean and energy-efficient separation routes, compared to conventional separation technologies.

In fact, numerous textile industrial processes require a large volume of water for treatments, like: dyeing, washing and cleaning, producing a variety of wastewaters in terms of composition and toxicity. In addition to dyes, these industrial effluents have a high content of salts and dissolved solids (organic and inorganic) [2-3]. Many of the dyes present in industrial wastewater are difficult to be eliminated in nature because of their complex structure and synthetic origin.

There are several conventional methods for treating wastewater including: biological treatment, ozonation, coagulation-flocculation, adsorption on powdered activated carbon, electrochemical processes and photocatalysis[4-5]. However, the need for more efficient and environmental friendly wastewater treatments together with the increasingly stringent discharge regulations has attracted the attention of many scientists and environmental engineers towards membrane technology for wastewater treatment [6-3].

The effects of the membrane preparation condition on the membrane morphology and transport properties, were investigated. Moreover, mixed matrix membranes based on co-polyimide P84 and functionalized multiwalled carbon nanotubes (oxidized or aminated MWCNTs), were prepared and compared with literature data obtained with commercial membranes and other laboratory made membranes containing MWCNTs.

3.2 Materials and method

3.2.1 Materials

Co-polyimide Lenzing P84® was purchased from HP polymer GmbH (Austria); the co-poly(amideimide) Torlon® 4000 TF was kindly supplied from Solvay Solexis (Italy); the polyimide Matrimid® 5218 was purchased from Ciba Specialty Chemicals (North America). 1-Methyl-2-Pyrrolidone (NMP), dimethylsulfoxide (DMSO), tetrahydrofuran (THF), Ethanol, Orange II Sodium salt (MW 350,32 g/mol), Safranin O (MW 350,45), Sudan Blue II (MW 350,82 g/mol), NaY zeolite, H2SO4, HNO3, cobal acetate tetrahydrate, iron nitrate nonahydrate were purchased from Sigma-Aldrich. HF was purchased from Carlo Erba.

3.2.2 Preparation of MWCNTs

The synthesis of MWCNTs was carry out at the Department of Chemical Engineering of the University of Calabria by Professor Nagy and Doctor Vuono in framework of the project: King Abdulaziz City for Science and Technology (KACST). The synthesis was carry out by catalytical chemical vapor deposition. The procedure of synthesis was performed as follows:

2.11 g of Cobalt acetate tetrahydrate and 3.62 g of iron nitrate nonahydrate were dissolved in 6.08 ml of distilled water. After manual homogenisation for 5 min, the solution was treated by an ultrasound bath for 1 hour. The solution was mixed with 9 g of NaY zeolite and homogenised (with a spatula for 5 min) to obtain a wet product of uniform colour (red). The product was dried in an air oven, at 130°C for 16 hours. The dried solid was treated by ball milling for 15 min to afford the supported catalyst.

3.2.3 Synthesis, purification and functionalization of MWCNTs

0.25 g of supported catalyst were spread on a 25 cm long quartz boat, made of a half tube of 3 cm in diameter. The boat was introduced into a quartz tube reactor of 4 cm in diameter and flushed with nitrogen (416 ml/min) for 5 min at 25 °C. The reactor was introduced into a furnace preheated at 700 °C (reaction temperature) and the nitrogen flow is maintained for 10 min. A C_2H_4 flow of 800 ml/min is added to the N_2 flow for 20 minutes. The C_2H_4 stream was replaced by a N_2 stream of 416 ml/min, the reactor was removed from the furnace and the N_2 flow was maintained for 10 min. After cooling to 25 °C, the boat was removed from the reactor and the product was collected. The produced MWCNTs were purificated in order to remove residual traces of the support catalyst by immersion in aqueous solution of HF (40 wt%). The resulted suspension was stirred for at least 3 days. The

MWCNTs were filtered with HF and immersed again in an aqueous solution of HF maintaining the stirring for 1 day. Then the product was washed with distilled water until the pH was neutral. The obtained product was dried in oven at 130°C for 18 hours. The purity of the purified MWCNTs was > 99% (estimated by Thermal Gravimetric Analysis (Figure 2-3)). The presence of two different peaks in the DTg curve, at 600°C and 633.41°C respectively, means that the total loss is due to two different effects. The DTA curve can help to understand this phenomenon of combustion. The two exothermal peaks at 606.53°C and 626.41°C, respectively, point out two different combustion degrees (Fig. 3b). This could mean that the purification step has operate a refining effect comparing to the thermal analysis of the as made CNTs. The MWCNTs were characterized by Fourier transform infrared analysis (FT-IR) using a Jasco 430 spectrophotometer. The pellets were prepared mixing the samples with KBr. The oxidation treatment was carried out putting 1 g of MWCNTs in 200 ml of a 0.6 (v/v) ratio HNO_3/H_2SO_4 solution for 24 hours (MWCNT-OX). The NH2 functions were introduced on the MWCNTs by means of a ball mill treatment in vacuum conditions, using a gas flow of NH_3 at 0.5 bar for 6h (MWCNT-NH2). The transmission electron microscopy (TEM) pictures were taken on a Philips CM10 transmission electron microscope using 100V accelerating voltage. The sample preparation relied on the classical method. About 10 mg of CNT were suspended in 3 ml ethanol and the suspension was then deposited on a carbonated Cu-Rh grid.

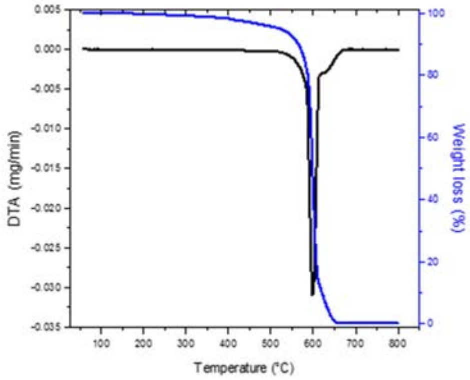


Fig.2 Tg and DTg curves purified sample.

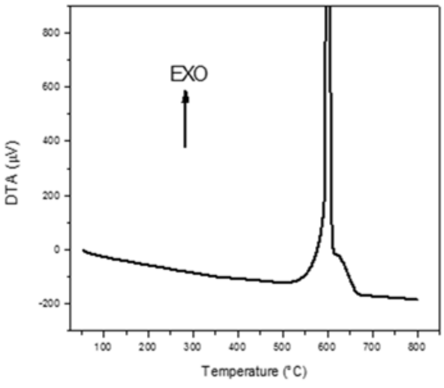


Fig.3 DTA curve of the purified sample.

3.3 Membrane preparation

The polymeric membranes were prepared by NIPS using water as coagulation bath. The polymer was dissolved under stirring at room temperature in organic solvent and the composition of the casting solutions is reported in Table 1. The solutions were cast at 250 μm thickness onto a glass plate by using a casting knife (Elcometer 3700), at 25±3°C and relative humidity 50 ± 10%. The surface in contact with glass was indicated as “down”, while that exposed to air during casting, as “up”. The liquid film was immediately immersed in the water coagulation bath and the membranes were stored in water until their use. The MMMs membranes were prepared following a procedure similar to the polymeric membranes, the only difference was the addition of the MWCNTs in the homogenous polymer solution and successive sonication for 2 hours, before casting. The loading of MWCNTs in the formed membrane was 0.5 wt% (99.5 wt% polymer). The estimated volume fraction of MWCNTs in the membrane was 3.0 v% assuming the bulk density the MWCNTs and of the P84 respectively 0.22 g/cm^3 and 1.34 g/cm^3 [7].

Table 1. Composition of the casting solution used to prepare polymeric and mixed matrix membranes

Membrane code	**Polymer type**	**Polymer wt%**	**Solvent type wt%**		**MWCNTs Type**
P84(N)	Co-polymide P84	18%	NMP	82%	-
P84(N) + MWCNTs(OX)	Co-polymide P84	18%	NMP	81.9%	Oxidized
P84(N) + MWCNTs (Am)	Co-polymide P84	18%	NMP	81.9%	Aminated
P84(D)	Co-polymide P84	18%	DMSO	82%	-
P84(D) + MWCNTs (OX)	Co-polymide P84	18%	DMSO	81.9%	Oxidized
P84(D) + MWCNTs (Am)	Co-polymide P84	18%	DMSO	81.9%	Aminated
Matrimid (N)	Polyimide Matrimid 5218	18%	NMP	82%	-
Matrimid (D)	Polyimide Matrimid 5218	18%	NMP	82%	-
Torlon (N)	co-poly(amide-imide) Torlon 4000 TF	15%	NMP	82%	-
Torlon (D)	co-poly(amide-imide) Torlon 4000 TF	15%	NMP	82%	-

3.4 Membrane characterization

FT-IR analyses in attenuated total reflectance (ATR) was performed using a Perkin Elmer Spectrum One, on the up surface of each membrane. The cross-section and surface morphology of membranes was observed by scanning electron microscopy (SEM) using a FEI Quanta 200 Philips SEM instrument. Cross-sections were prepared by fracturing the membrane in liquid nitrogen. Surface roughness of the up surface was assessed by Nanoscope III atomic force microscope (AFM Digital Instruments, VEECO Metrology Group) in tapping mode AFM images 3 X 3 µm2 squares of the sample surface. Roughness analysis was perfomed by SPIP 6.0 software (Image Metrology), by calculating average roughness. Advancing and receding contact angles were measured by growing/shrinking sessile water drop, with the tangent method [8] using a CAM 200 contact angle meter (KSV Instruments Ltd.) equipped with a microsyringe, automatic dispenser, and software for image acquisition and processing. Advancing contact angle was measured with the increase in the volume of the droplet (initially 3 μL) by adding water with a constant dosing (1 μL/s) up to 8 μL while capturing images. During the entire measurement, the needle remained attached to the drop so that the portion of the needle inside the drop was maintained as small as possible to minimize adhesion of the droplet. Receding contact angle was achieved by reducing the volume of the drop, with the same dosing flow rate used in the advancing contact angle measurements. Contact angles were calculated as the average of five different measurements.

The mean pore diameters was measured by a capillary flow porometer (PMI, Porous Materials Inc.Ithaca, NY) using a wetting liquid 3M Fluorinert Electronic Liquid FC-40.

Membrane total porosity was measured by the gravimetric method, determining the weight of water contained in the membrane pores. The porosity ε, was calculated by the following equation:

$$\varepsilon = \frac{(w_2 - w_1)/D_w}{(w_2 - w_1)/D_w + (w_1/D_p)} \tag{1}$$

where w_1 is the weight of the dry membrane, w_2 the weight of the wet membrane, Dw the water density (0.997 g/cm^3) and D_p is the polymer density (1.34 g/cm^3) or polymer + MWCNTs density estimated considering the volume fraction of each component and their density (1.342 g/cm^3).This method was used to determine the density of dense part of membranes considering also the presence of MWCNTs without the porous part.

3.1.5 Membrane permeation and retention test

The membranes were tested by pure solvent permeation test using a SteriltechTM HP4570 dead-end stirred cell having an active membrane area of 14.6 cm2, pressurized by air and operating at room temperature (25 ± 3°C). After about one hour of stabilization, permeate sample were collected at regular time intervals in order to determine the flux (J) and Permeance (Pe) as reported in the following equations:

$$J = \frac{V_p}{t * A} \tag{2}$$

$$P_e = \frac{J}{TMP} \tag{3}$$

Where V_p (L) is the permeate volume; t (h) is the permeation time, A (m2) is the active membrane area and TMP (bar) is the transmembrane pressure difference. The TMP applied was 1 bar for the P84 and Matrimid membranes; TMP of 30 bar was used for Torlon membranes.

Three different dyes having similar molecular weight (MW 350 g/mol) but different charge (Orange II Sodium salt, Safranin O and Sudan Blue II), were used for retention test at a concentration of 0.1 g/L in water or ethanol (Table 2). Orange II Sodium salt and Safranin O were solubilized in water; in the case of Sudan Blue II the solvent used was ethanol because this molecule was not soluble in water. Phenol (MW 94.11 g/mol) in water (0.01 g/L) was also used as a model of neutral organic pollutant in rejection test. A new membrane disc was used for each rejection test. The membrane rejection (R) was calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_r}\right) * 100 \tag{4}$$

Where C_p and C_r represent permeate and retentate concentrations, respectively. The mass balance was used to check solute adsorption/absorption on/in membrane during the experiment.

$$Mass\ balance\ (\%) = \left(\frac{V_p * C_p + V_r * C_r}{V_f * C_f}\right) * 100 \tag{5}$$

Where C_f represents the concentrations of the feed and Vf, Vp and Vr are the volumes of feed, permeate and retentate, respectively. In the rejection test, 100 mL of feed solution was used and 50 mL of permeate were collected under constant transmembrane pressure. The feed was continuously stirred by means of a Teflon coated magnetic stir bar to reduce concentration polarization. The concentration of the solute in the feed, retentate and permeate was analyzed by UV spectrometer (Lambda 650S UV-vis spectrometer, PerkinElmer).

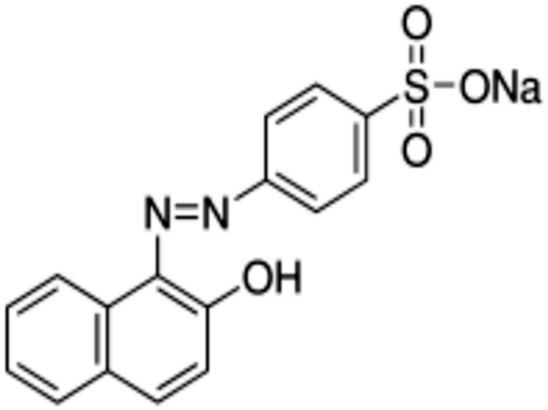
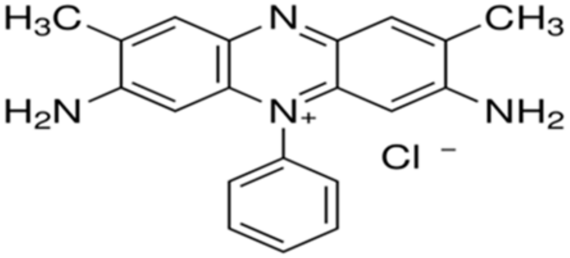
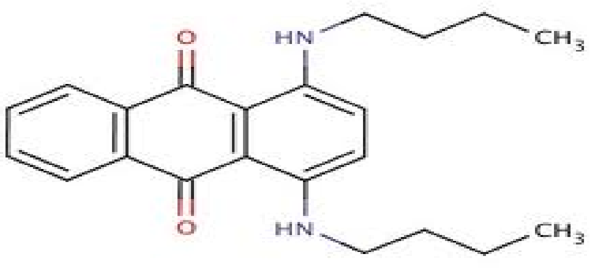
The wavelengths for solute spectrophotometric analysis were: 486 nm for Orange II sodium salt, 525 nm for Safranine O, 648 nm for Sudan Blue II and 270 nm for phenol. The concentrated samples were diluted when necessary.

After retention test the membrane were characterized again by pure solvent permeation (water or ethanol) to measure the relative flux (J_r) defined as follow:

$$J_R = \frac{J_2}{J_1} \tag{6}$$

Where J_1 and J_2 are, respectively, the pure solvent flux before and after rejection test. The relative flux can be used to have an indication about the membrane fouling: more J_R is close to 1, less the membrane is fouled.

Table 2. Solute used in the rejection test.

Molecule	Molecular weight (g/mol)	Chemical structure	Charge
Orange II sodium salt	350.22		Negative
Safranine O	350.45		Positive
Sudan Blue II	350.82		Neutral
Phenol	94.11		Neutral

3.6 Result and discussion

3.6.1 MWCNTs

The morphology of the purified MWCNTs was assessed by TEM analysis (Figure 4).

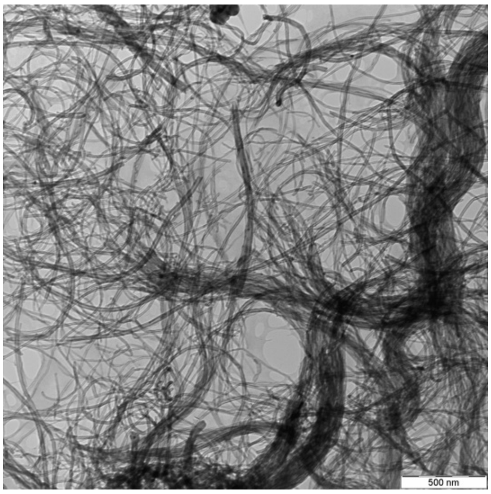


Fig.4 TEM images of the purified MWCNTs

The product seemed to grow organized in bundles. The length of single MWCNTs was about 20 μm, while the diameter was between 15 and 20 nm. One of the major problems in the incorporation carbon nanotubes in membranes prepared by casting methods, is their low dispersion in most of the solvents used for polymer solubilization, and their high tendency to aggregate because of van der Wall interactions. In this work, the dispersion of the purified MWCNTs was promoted by surface functionalization following two different procedures indicated as oxidation and amination. The pristine (not functionalized) MWCNTs were poorly dispersed in polar solvents like NMP and DMSO because of the essentially hydrophobic properties of the MWCNTs. However, the introduction of functional groups on their surface improved the dispersion by the formation of hydrogen bonds between the functional groups (OH, C=O, NH2, etc.) and the solvent. Moreover, the compatibility between the MWCNTs and polymer matrix was also improved allowing to obtain membranes with a homogeneous distribution of the additive, as can be easily appreciated already by a visual observation of the samples (Figure 5).

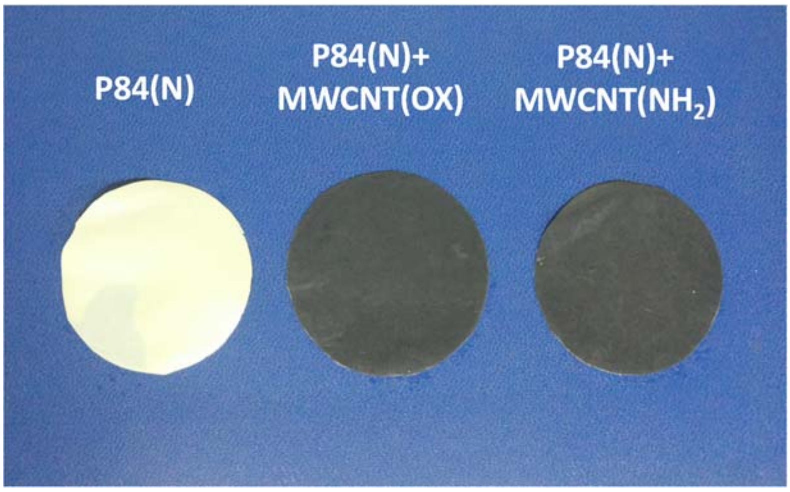


Fig.5 Photo of polymeric and mixed matrix P84 membranes

The FT-IR spectra the MWCNTs samples presented an intense strong band at 1639 cm^{-1} attributed to the stretching of the conjugated C=C bonds (Figure 6).

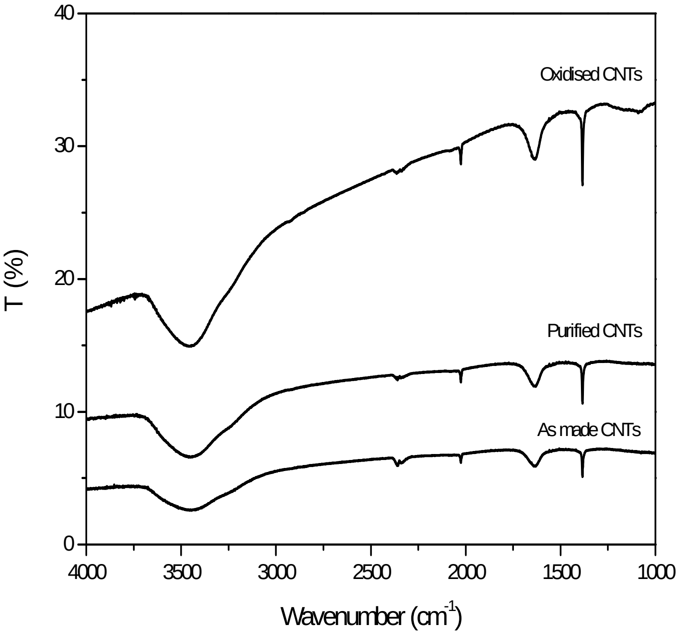


Fig.6. FTIR spectra of the not purified, purfied and oxidized MWCNTs

Moreover, a broad band was observed at 3450 cm^{-1}. This band is due to the stretching of the OH groups. It is interesting to note that this band was present in all the samples but increased of intensity going from the not-purified, to the purified and oxidized. This means that already in the not-purified sample some OH groups are present probably because of the presence of the hydrophilic support catalyst. In this form the system does not disperse well. On the contrary, during the purification, the acid treatment induce an attack of graphitic system acid-catalized with the possibility to induce the formation of polar groups continent oxygen. This system is disperse well. Moreover, the oxidation reaction, introduced a higher number of oxygen containing groups on the MWCNTs.

The FT-IR spectra of the MWCNTs treated by NH_3 gas presented at 1558 cm^{-1} a new band ascribed to the bending of the N-H groups, thus confirming the successful introduction of amino groups (Figure 7).

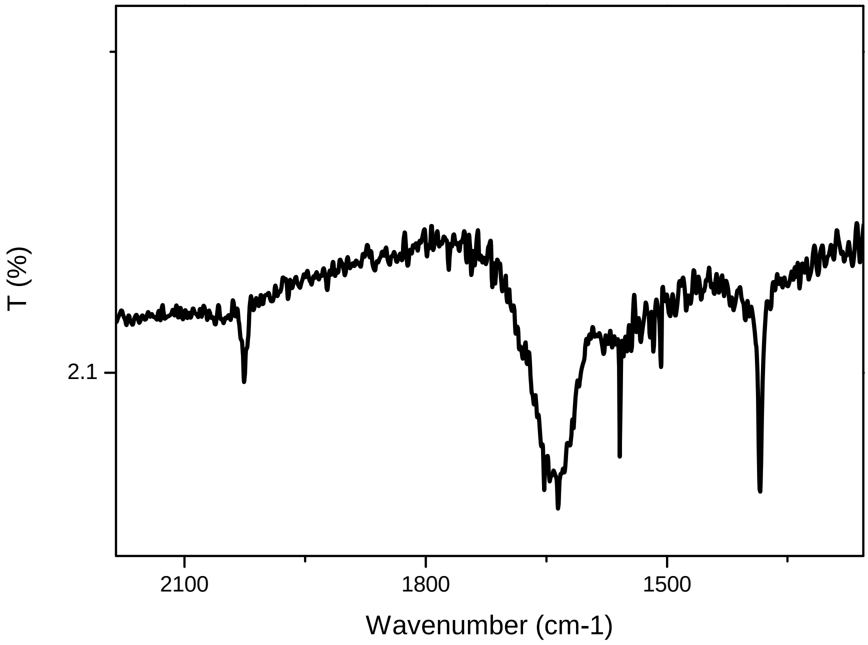


Fig.7. FT-IR spectra of the aminated MWCNTs

Mixed matrix membranes were prepared using the functionalized MWCNTs (aminated and oxidized) and P84; moreover, P84 polymeric membranes were prepared. All the P84 membranes showed an asymmetric porous structure (Figure 6), but the morphology was strongly influenced by the solvent used.

3.6.2 Effect of solvent on membrane morphology

The P84 membranes cast from NMP solution were characterized by the presence of finger-like macrovoids (Figure 6 A1-A2). On the contrary, using DMSO as casting solvents, a sponge-like structure under a tighter and thicker skin layer, with some macrovoids in the bottom part of the cross-section, was the morphology (Figure 6 B1-B2). The results indicated that the phase separation process was faster in the case of the NMP solution (formation of finger-like macrovoids) and it was slower in the case of DMSO (sponge-like structure) [43]. The different rates of the phase separation can be explained considering the different affinities between the two solvents with respect to the polymer, using their solubility parameters (Table 3). The cohesive energy ($E_{cohesive}$) of a substance in a condensed state is defined as the increase in internal energy (ΔU, variation of internal energy) per mole of substance if all the intermolecular forces are eliminated [44]. The $E_{cohesive}$ is related to the solubility parameter and molar volume (V_{molar}) by the following relation:

$$\delta = \sqrt{\frac{E_{cohesive}}{V_{molar}}} \tag{6}$$

The comparison of the solubility parameters of a polymer and a solvent provides the basis for the evaluation of the polymer-solvent interactions, because materials with similar $E_{cohesive}$ (or also similar solubility parameter) should be miscible [9]. The DMSO has the solubility parameters more closer to P84 in comparison with the NMP, this means that the DMSO is a better solvent for the polymer than the NMP and it delays the phase separation, moreover, DMSO is also characterized by a lower diffusion coefficient in water in comparison with NMP, contributing to the delaying the mass transfer during the phase separation process [9-10].

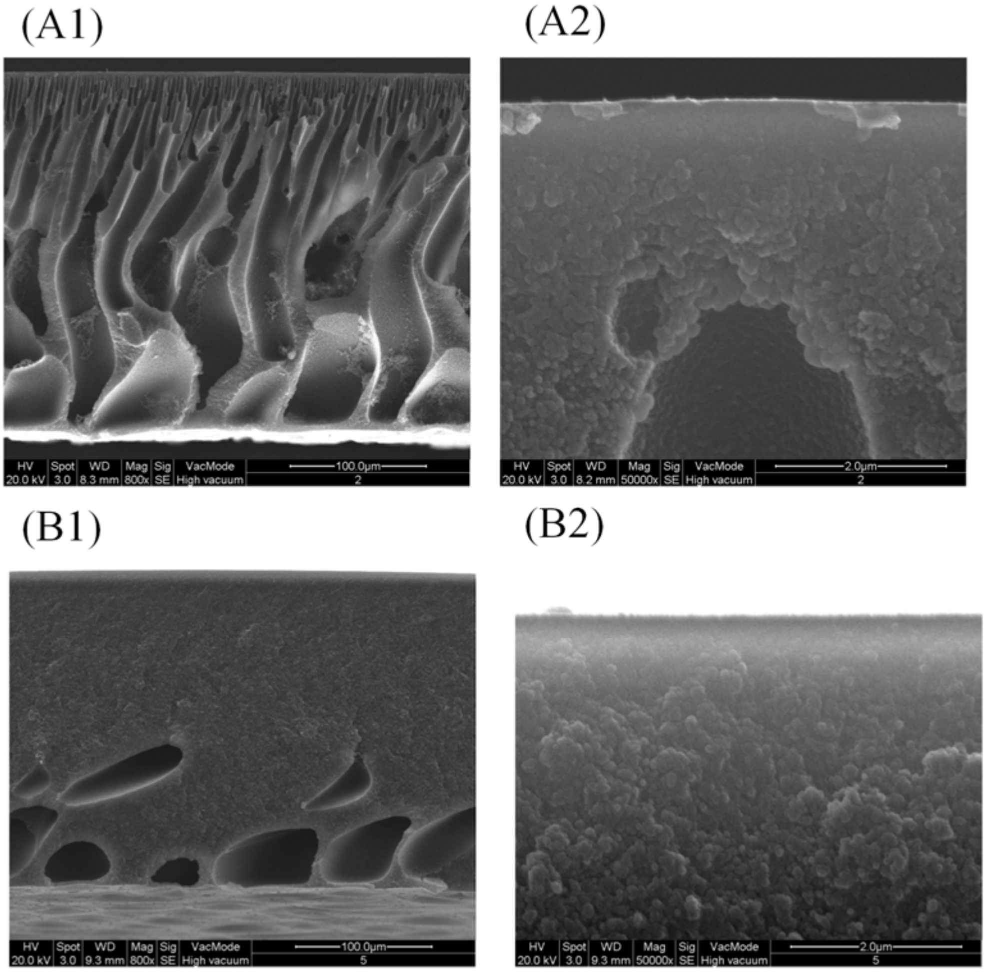


Fig.8 SEM images of the polymeric co-polyimde P84 membrane cast fron NMP: (A1: cross-section, A2: particular of the top layer) and from DMSO solution (B1: cross-section, B2: particular of the top layer)

In the case of the co-poly(amide-imide) Torlon 4000 TF membrane, the use of THF as co-solvent was necessary because of the not complete solubility of the polymer in pure NMP at room temperature and concentration ≥ 15 wt%, despite the quite close solubility parameters reported for the polymer [12] and the solvent [9] (Table 3).

Table 3. Solubility parameters of polymers and solvents

Material	*Solubility parameter* $[(Jcm^{-3})^{1/2}]$	*Refs.*
P84	26.8	[45]
Torlon	26.28	[48]
Matrimid	22.0	[49]
NMP	22.9	[44]
DMSO	26.6	[44]
THF	19.5	[44]
Ethanol	26-26.5	[44]
Water	48	[44]

Like in the case of the co-polyimide P84, also with the Torlon, the DMSO had a macrovoids suppressing effect with respect to the NMP (Figure 9).

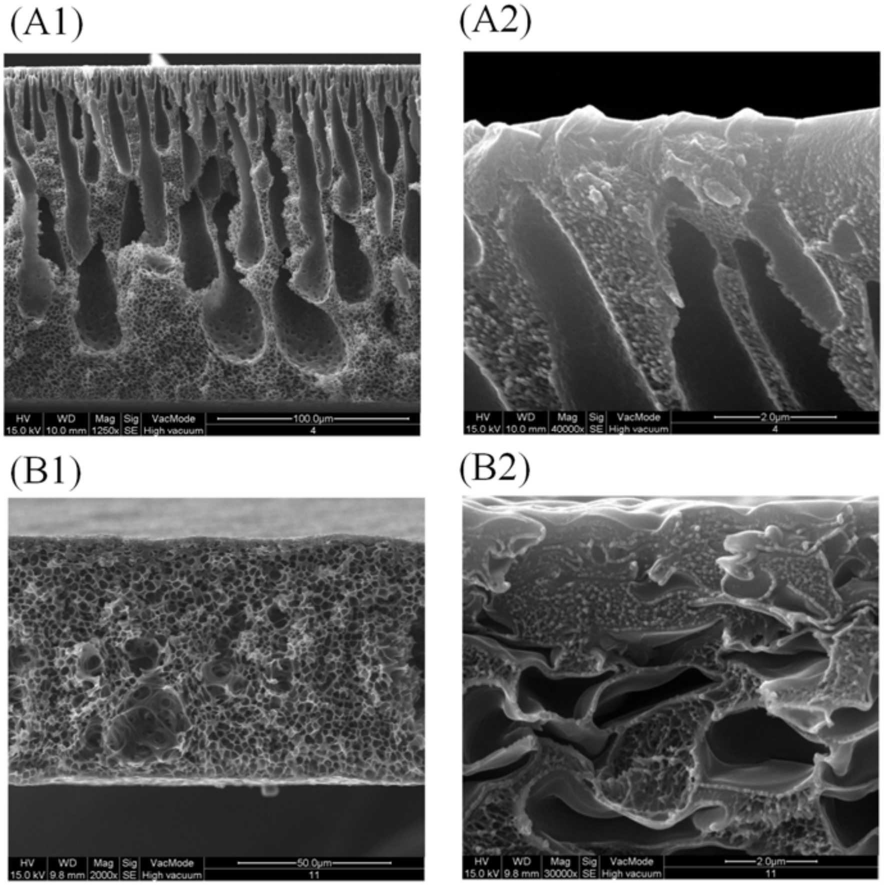


Fig.9 SEM images of the polymeric co-poly(amide-imide) Torlon membranes cast from NMP/THF (70/30 wt%) (A1: cross section; A2: particular of the top layer) and from DMSO/THF (70/30 wt%) solution (B1: cross section; B2: particular of the top layer).

The Torlon membranes had a cellular morphology with not completely interconnected pores. A dense skin layer was formed because of the partial evaporation of the volatile co-solvent (THF) in the short, but inevitable, time interval between casting and immersion in the coagulation bath (boiling point of THF: 65°C; NMP: 202 °C; DMSO: 189 °C[9]). Moreover, the phase separation was delayed due to the low affinity between the co-solvent and the water (Table 3).

The homopolymer Matrimid 5218 solubilized in NMP gave asymmetric membranes with a dens skin layer over a porous sub-structure characterized by finger like macrovoids (Figure 8 A1-A2). Also with this polymer the DMSO delayed the phase separation giving a denser morphology in comparison with NMP (Figure 8 B1-B2), despite the fact that NMP had a solubility parameter closer to the polymer with respect to DMSO (Table 3). However, it is necessary to point out that the homopolymer Matrimid is a semicristalline polymer[13] and in the solubility parameters calculation the contribution of the melting enthalpy is not included [9]. This can cause a strong deviation between the experimental results and those expected. Moreover, as reported above, the diffusion coefficient of the DMSO in water was lower than that of the NMP[10][11].

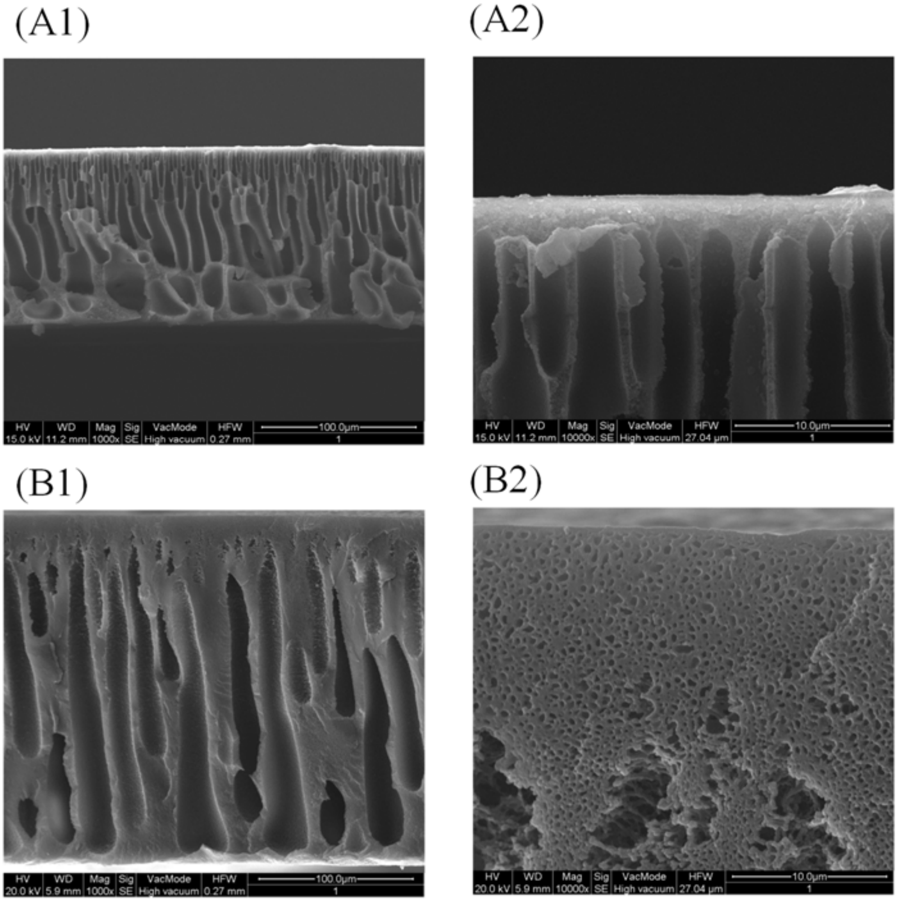


Fig.10 SEM images of the polymeric Matrimid membrane cast from NMP (A1: cross section; A2: particular of the top layer) and from DMSO solution (B1:cross section; B2: particular of the top layer)

The P84 membrane prepared from NMP solution (P84(N)) was characterized by a higher water permeance in comparison with the membranes cast from DMSO solution (Table 4). These differences were due to the diverse morphology and structure of the two membranes: the membrane cast from DMSO solution was characterized by a tighter and thicker skin layer in comparison with the membranes cast from NMP; the first membranes had basically a sponge like structure versus a finger like macrovoids structure of the second one (Fig.8).

The co-poly(amide-imide) Torlon membranes were characterized by a lower permeance in comparison with the P84 membranes (Table 4) because of the formation of a thicker and denser skin layer induced by the presence of the volatile co-solvent THF (Figure 9).

A permeance intermediate between the P84 and the Torlon membranes, was observed with the Matrimid membranes (Table 4).

Table.4 Water permeance of polyimide and co-polyimide membranes. Temperature:25°C; transmembrane pressure: 1bar for P84 and Matrimid membrane; 30 bar for Torlon membranes.

Membrane	**Water permeance (L/(hm^{2}bar))**
P84(N)	254
P84(D)	207
Matrimid(N)	18.4
Matrimid(D)	3.5
Torlon(N)	0.25
Torlon(D)	0.03

The transport properties of the P84(N) and P84(D), were compared in the reject of phenol in water (0.01 g/L) obtaining higher solution permeance and rejection for the first membrane (Figure 11), indicating the NMP as a better casting solvent than DMSO for this application.

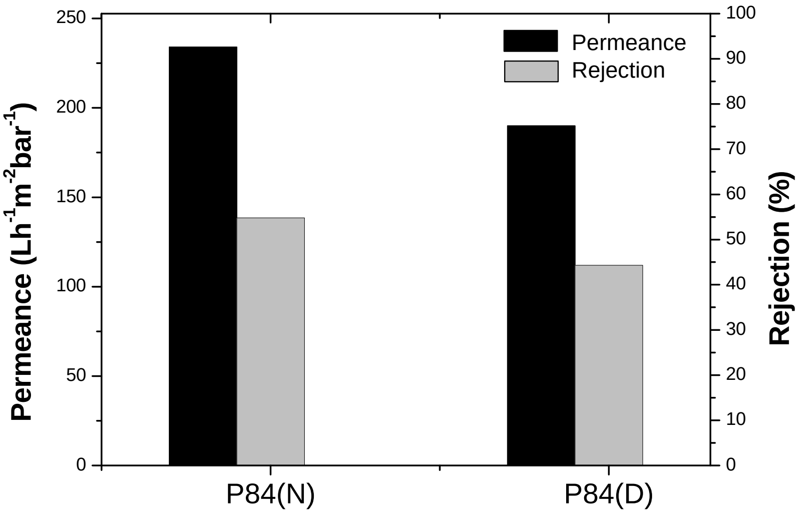


Fig.11 Permeance (black bar) and rejection (grey bar) of the polymeric P84 membranes cast from NMP and DMSO solution (respectively P84(N) and P84(D)). Solution composition: phenol in water (0.01 g/L), TMP 1 bar, temperature 25°C.

Polymeric membranes cast from NMP solution were compared in the rejection of Safranine O in water (0.1 g/L) showing superior performance for the P84 membrane in comparison with Torlon and Matrimid based membranes: the solution permeance for the P84(N) was 160 $Lh^{-1}m^{-2}bar^{-1}$a rejection of 99.4% versus a permeance of 4.08 $Lh^{-1}m^{-2}bar^{-1}$ with a rejection of 49.2% for the Matrimid(N) and a permeance of 0.19 $Lh^{-1}m^{-2}bar^{-1}$ with a rejection of 88.5% for the Torlon(N) (Fig. 12).

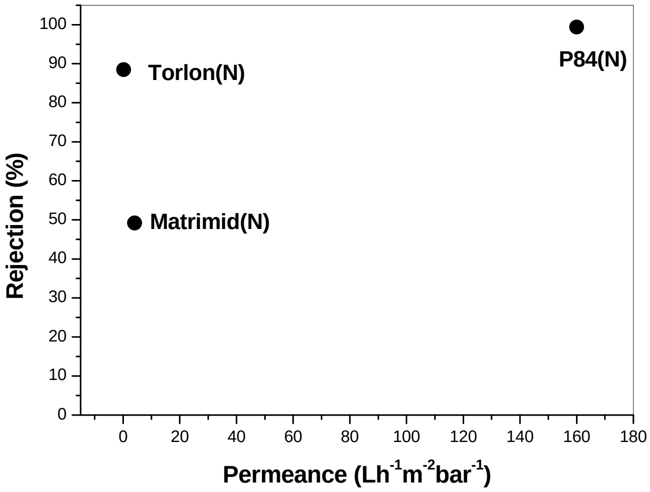


Fig.12 Rejection versus permeance of Safranine O in water (0.1g/L; 25°C) through polymeric membranes cast from NMP solutions or NMP/THF mixture (for Torlon) solution.

3.6.3 Mixed matrix membranes-morphology characterization

P84 was selected as polymeric material and NMP as solvent for the preparation of mixed matrix membranes containing MWCNTs. The P84 MMMs were characterized by an asymmetric structure with finger-like macrovoids without relevant differences, appreciable by SEM observation, between the membranes containing oxidized and aminated MWCNTs (Figure 13).

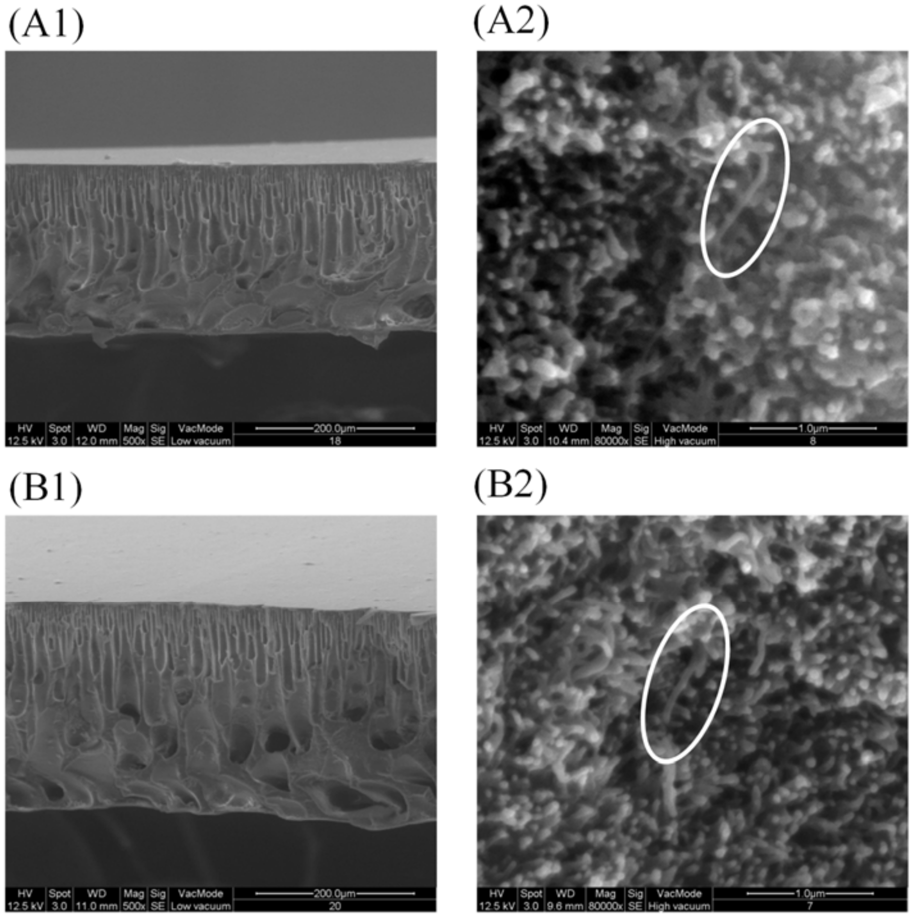


Fig.13 SEM images of the mixed matrix mmbranes containing oxidized (A1: cross section; A2: particular at higher magnification) and aminated MWCNT (B1: cross section; B2: particular at higher magnification).

The presence of the MWCNTs increased the viscosity of the casting solution and delayed the mutual diffusion between, solvent in the coagulation bath, and non-solvent in the liquid cast film, and partially reduced macrovoids formation in comparison with the polymeric membranes (Figure 8 and 13). The MWCNTs were observed by high resolution SEM images (Figure 13 A2 and B2). They were quite homogenously distributed in the polymeric matrix membranes in the form of bundles with a medium diameter of 75±10 nm which tended to be oriented in the direction of solvents diffusion (the same direction of macrovoids development).

The P84 MMMs were characterized by similar mean pore size and total porosity with respect to the P84 polymeric membrane (Table 5).

Table 5 Structural and surface properties of polymeric and mixed matrix membranes

Membrane code	Mean pore diameter (μm)	Total porosity (%)	Average roughness (nm)	Advancing water contact angle (°)	Reciding water contact angle (°)
P84(N)	0.026 ± 0.004	83 ± 2	8.6 ± 0.7	73 ± 0.8	28 ± 3
P84(N)+MWCNTs(OX)	0.020 ± 0.003	84 ± 1	8.3 ± 0.5	96 ± 1	71 ± 4
P84(N)+MWCNts(Am)	0.021 ± 0.002	81 ± 2	4.7 ± 0.6	71 ± 1	34 ± 3
Matrimid (N)	-	-	2.9 ± 0.4	65 ± 2	35 ± 0.4
Torlon (N)	-	-	6.1 ± 0.6	71 ± 0.5	26 ± 2

The presence of oxidated MWCNTs did not change significantly the surface roughness in comparison with the polymeric P84, but the water contact angles resulted to be increased because of the hydrophobic nature of the MWCNTs, despite the presence of the hydrophilic functional groups (Table 5). For the P84(N)+MWCNTs(Am) membrane, the expected increase in hydrophobicity due to the presence of the hydrophobic MWCNTs was counterbalanced by the reduction in surface roughness, so that the resulting water contact angles were substantially unchanged with respect the polymeric P84 membrane (Table 5).The explanation of this result is the polar interaction between the basic groups of MWCNTS and the polymeric chains that are different respect to the interaction with acid groups.

This wetting behaviour is in agreement with the Cassie-Baxter model which predicts that a hydrophilic rough surface can increase its hydrophilicity with the reduction of roughness [14]. The surface topography differs strongly between the homopolymer (Matrimid) and the co-polymers (P84 and Torlon). The membrane made of the homopolymer was characterized by a smoother surface in comparison with the membranes made of co-polymers (Table 5). However, all the polymeric membranes showed hydrophilic behavior, confirming the interest towards the use of polyimide membranes in aqueous separations.

Finally, the total thickness of asymmetric membranes prepared was measured by a micrometre. It is not possible to determine the exact thickness of skin layer in this type of membranes because SEM images don’t have a sufficient resolution to obtain this measure and also because during the SEM analysis the membrane is in the dry state that change the morphology.

Table 6. Thickness of membranes prepared

Membrane	Spessore µm
P84(N)	185 ±5.4
P84(N)+MWCNTs(OX)	218± 1.3
P84(N)+MWCNts(Am)	242 ± 1.3

Despite all membranes have been cast at the same initial eight (250 µm), the final total thickness of the polymeric and MMMs are different (Table 6). The MMMs are characterized by ah higher total thickness, in comparison with the polymeric sample, as a consequence of the presence of MWCNTs that work as a non solvent for the polymer increasing the rate of precipitation and reducing the compaction time.

3.6.4 Mixed matrix membranes-rejection test

The polymeric and mixed matrix P84 membranes were used in the rejection of dyes having the same molecular weight (350 g/mol) but different charge, in order to investigate the effect of the solute charge on membrane rejection (Table 7). It is worth to note that the Safranine O rejection in water was higher than the Orange II sodium salt rejection in the same solvent, despite the two molecules have the same molecular weight. The large difference in the rejection values indicate that these molecules are retained not only by a sieve mechanism, but also charge effect has a decisive role in determining the membrane retention mechanism.

Table 7 Comparison of the performance obtained in the rejection of dyes with the membranes prepared in this work with commercial membranes and literature data. Dyes concentration: 0.1g/L; Pe: solution permeance; R: rejection; MB: mass balance; Jr: relatice flux.

membrane	**Safranine O**				**Orange II sodium salt**				**Sudan II blue in ethanol[this work] or methanol [54]**				**Ref.**
	P_e(L/hm^2(bar)	*R(%)*	MB(%)	J_r(-)	P_e(L/hm^2(bar)	*R(%)*	MB(%)	J_r(-)	P_e(L/hm^2(bar)	*R(%)*	MB(%)	J_r(-)	
P84(N)	160	*99.4*	38.6	0.79	198	55.8	80.5	0.95	174	17.7	89.0	0.98	This work
P84(N)+MWCNTs(Ox)	201	99.1	50.8	0.94	222	31.4	89.8	0.92	184	17.8	100	0.95	This work
P84(N)+MWCNTs(Am)	190	99.6	51.5	0.97	222	49.1	80.0	0.95	196	20.9	87.0	1.0	This work
UTC-20	3.5	100			3.5	100			0.17	79			[15]
MPF-44	1.13	100			0.8	100			0.18	85			[15]
DESAL-5	3.6	96			4.8	95			6.2	28			[15]
DESAL-DR	2.73	98			3.6	97			0.086	49			[15]
PESCNT-3	3.81^a	67											[16]

P84 membranes have a negative surface charge at pH > 3.75 [51]. As a consequence, the negatively charged Orange II sodium salt was rejected by electrostatic repulsion (Donnan exclusion [17]) from the membrane, which was also negatively charged at the pH of the solution used (about 6). Surprising, the positively charged Safranine O was rejected at higher level than the negatively charged dye, with a quite complete solution discoloration (Table 7 and Figure 14 A). These results can be explained considering the relevant dye adsorption on the P84 surface also by electrostatic interaction, as can be easily appreciated by a direct visual observation of the membrane surface after rejection test (Figure 14B). Moreover, the lower relative flux and mass balance obtained with this dye in comparison with Sodium Orange II salt, confirmed the higher fouling impact of the positively charged dye (Table 7).

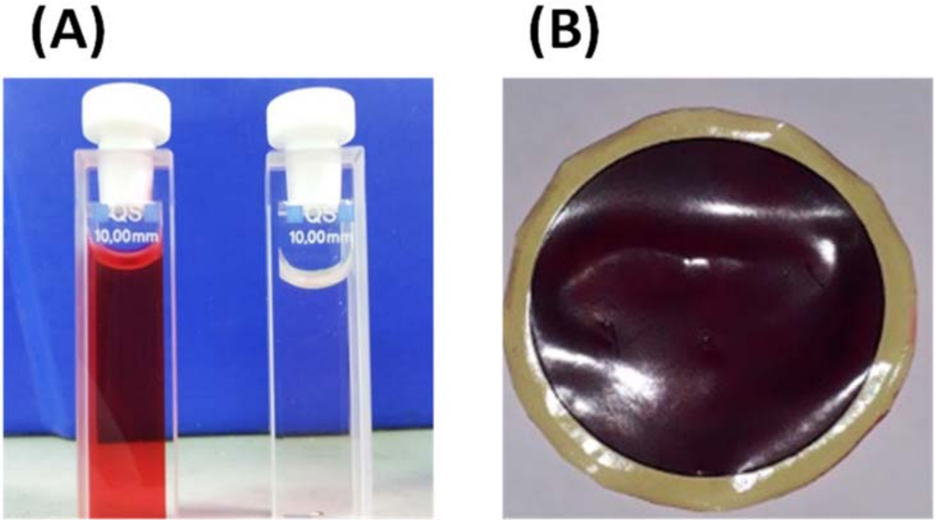


Fig 14. Photo of the Safranine O feed and permeate through the P84(N) membrane (A) and up surface of the same membrane after filtration.

Considering the chemical formula of the Safranine O, containing two amino functionalities (Table 2). It is possible to speculate the chemical reaction of the imido groups of the polymer (Fig.1) with the amino groups of the dye with a formation of covalent amide bonds [18]. This reaction can be efficiently monitored by FT-IR analyses following the disappearing of the typical imide bands around 1780 cm^{-1} (asymmetric stretch of C=O imide group), 1720 cm-1 (symmetric stretch of C=O imide group) and 1365 cm-1 (C-N stretch), while increasing the typical signals of the amide groups at 1640 cm-1 (C=O stretching) and 1535 cm-1 (C-N stretch). FT-IR in ATR mode carried out on the fouled P84 membranes, both polymeric and MMMs, excluded the formation of a covalent bond between the amino groups of the Safranine O and the imidic functionalities of the membranes. The typical imide bands of the P84 polymer were visible, and new bands ascribable to amidic bonds were not identified in the spectra (Figure 15). For what concern the increased transmittance after dye solution filtration, this was due to the presence of the layer of absorbed dye, which is characterized by a lower absorbance in the region of the FT-IR spectra considered, in comparison with the polymer.

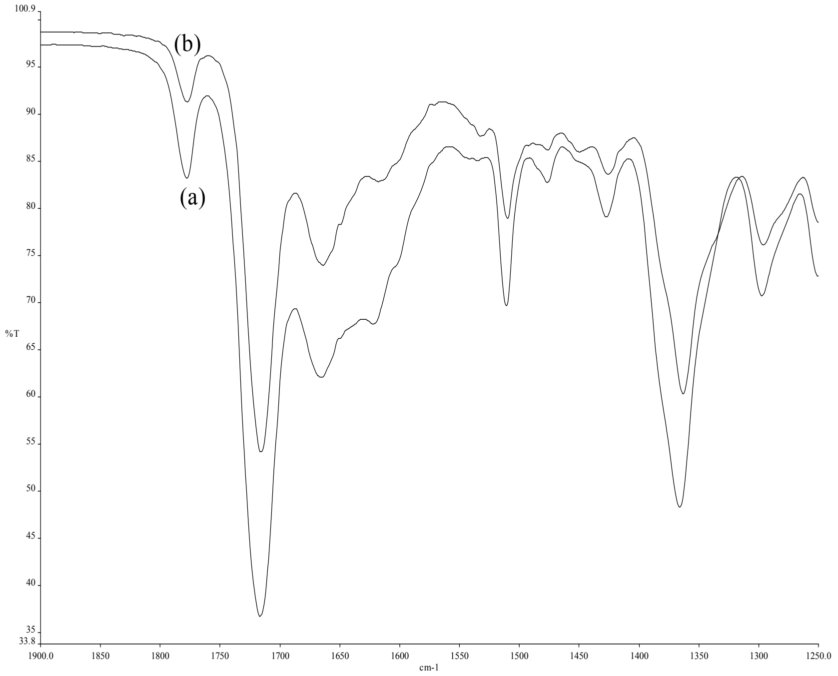


Fig.15. FT-IR spectra in ATR mode of the P84(N) membrane before (a) and after (b) safranine rejection.

3.6.5 Mixed matrix membranes-effect of MWCNT

The solution permeance of all the P84 membranes was lower than the pure solvent permeance; moreover, the dyes solution filtration had an adverse effect on pure solvent permeation (lower relative flux) because of concentration polarization and membrane fouling in the presence of the dyes (Table 6). These phenomena were more evident in the case of the Safranine O filtration which was strongly adsorbed on the P84 membrane surface hindering the permeation (relative flux 0.79; Table 6). However, the presence of the MWCNTs in the membrane, was found to increase solution permeance with respect to the polymeric sample, despite the similar mean pore size (Table 5). A possible explanation is the formation of low-resistance pathways for solvent transport between the MWCNTs and the polymeric chains. Moreover, the MWCNTs reduced membrane fouling increasing the relative flux with Safranine O with respect to the polymeric membrane (0.94 and 0.97, respectively for MMMs containing oxidized and aminated MWCNTs versus 0.79 obtained with the polymeric sample; Table 7), probably by a screening effect of the attractive electrical interactions between the negatively charged membrane and the positive charged solute. The lower fouling tendency of the MMMs in comparison with the P84 polymeric membrane, was more evident with the membrane containing aminated MWCNTs which was more smooth and hydrophilic in comparison with the membrane containing oxidized MWCNTs (Table 5). Moreover, the amines functionalities of the MWCNT-Am are expected to shift the surface charge of the P84 membrane to less negative values compared to the polymeric membrane or MMMs containing oxidized MWCNTs. It is also interesting to note that the dyes rejection of the P84 MMMs was similar or higher than the rejection of the polymeric membrane, with the only exception of the values obtained for the Orange II sodium salt (negatively charged dye rejected by size and Donnan exclusion mechanism).

A separate discussion is necessary for the rejection of the Sudan II blue in ethanol. The rejection of the Sudan Blue was lower in comparison with the charged dyes (Table 7) because of its neutral charge (no charge effect on reject). Moreover, the complexation of ethanol molecules with the neutral dye is expected to be lower with respect to the water complexation with the charged dyes, increasing less the effective solute size in the first case. The pure ethanol, as well as ethanol solution permeance, were lower in comparison with the water and water solutions permeance. This was due to the higher viscosity and molar volume of the first solvent in comparison with the second one (1.074 cP at 25°C and 58.40 cm3mol-1 for ethanol; 0.894 cP at 25°C and 18.00 cm3mol-1 for water [9]). The solvent permeance was also influenced by the mutual affinity between the solvent and the polymeric matrix. The ethanol has a high affinity for the P84 (Table 3) and this solvent can swell the porous P84(N) membrane reducing the effective pore size and, as a consequence, the permenace.

3.6.6 Mixed matrix membranes-comparison with commercial membranes

The polymeric and mixed matrix P84 membranes performance in the rejection of dyes were also compared with litterature data obtained with commercial and other laboratory made mixed matrix membranes in Table 6.

Yang et al. [15] used four commercial nanofiltration membranes UTC-20 (Toray), MPF-44 (KOCH), Desal-5 and Desal-DR (Osmonics), for retention of the same molecules used in this work (the only difference was the use of methanol instead of ethanol as solvent in the rejection of Sudan II blue). The rejection of Safranine O in water was also tested by Roy et al.[16] using a laboratory made thin film composite polyamide membrane containing MWCNTs in the selectivity layer (PESCNT-3).

Only the UTC-20 and MPF-44 membranes showed a higher Safranine O rejection in comparison with our membranes (100% vs. 99.1-99.6 %). However, the permeance of the P84 membranes were significantly higher. It is imporatnt to highlight the low molecular weight of the dyes used (350 g/moles). These type of molecules are usually retained by nanofiltration membranes characterized by permeances around 1.4-12 [L/(hm2bar)]. On the contrary, the P84-based membranes prepared in this work were in the range of the microfiltration (permeances > 50 [L/(hm2bar)]).

In order to separate the effect of dye adsorption from the membrane rejection, the membrane containing aminated (P84 (N) + MWCNT-Am) as used in 15 consecutive rejection test with Safranine O, without applying a cleaning procedure between the different runs. The adsorption sites of the membrane were completely saturated after about 7 cycle as confirmed by the reaching of a plateaux in the mass balance (fig. 16). In parallel also the membrane rejection reached a plateaux with a rejection value obtained at the 15th run of 58% and a permeance of 88 L/(hm^{2}bar).

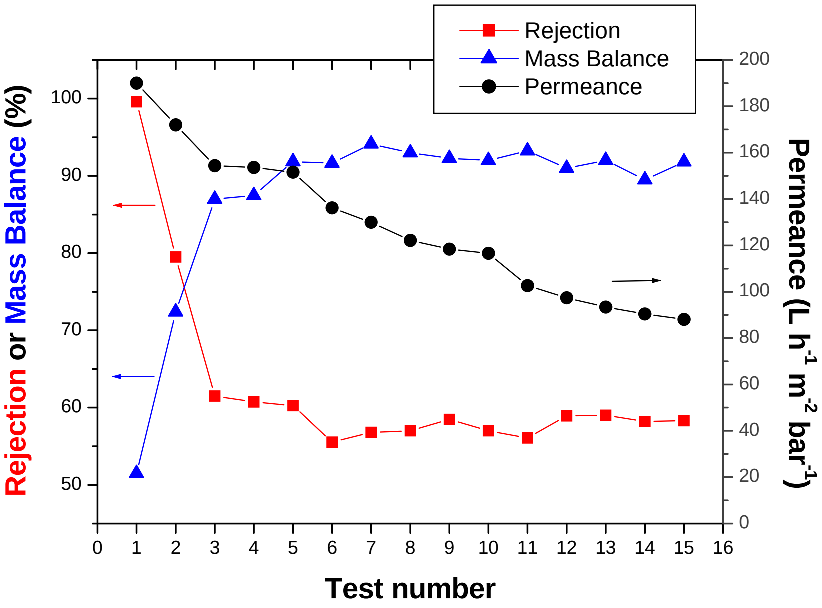


Fig. 16. Rejection, permeance and mass balance of the mixed matrix membrane containing aminated MWCNTs (P84(N) + MWCNT-Am) used in 15 consecutive rejection test with Safranine O (0.1 g/L; TMP 1bar; temperature 25°C).

The rejection of the Orange II sodium salt and Sudan II blue with the P84 membranes were lower in comparison with the commercial NF membranes, however, considering the high permeance of the P84 membranes, their performance result competitive for example for wastewater pre-treatment in order to reduce the dyes content a low transmembrane pressure.

3.7 Conclusions

Porous asymmetric polyimide membranes were prepared by NIPS technique for liquid phase separation process. The effect of the casting solvent (NMP or DMSO) on membrane morphology and transport properties, was investigated using three polyimide polymers: a homopolymer (Matrimid) and two co-polymers (P84 and Torlon). NMP was the most convenient solvent to obtain high flux membranes, while DMSO can be used to have sponge-like structure, more appropriate for high pressure applications. The different polymeric membranes were compared in the rejection of organic dyes showing superior performance (higher permeance and rejection) in the case of the co-polyimide P84. Using dyes having same molecular weight but different charge, relevant ―charge effects‖ on membrane rejection were observed: Donnan exclusion for the negatively charged dye, electrostatic adsorption for the positively charged dye and higher rejection for the charged dyes in comparison with the neutral dye. Mixed matrix P84 membranes were also prepared using functionalized MWCNTs (aminated or oxidized). The MWCNTs functionalization improved their dispersion in the casting solution and, as a consequence, in the formed membrane. The presence of the MWCNTs in the polymeric matrix improved membrane performance for the rejection of dyes (enhanced flux and reduced fouling, with similar or higher rejection), with respect to reference polymeric membranes (without MWCNTs). This behaviour was probably due to the formation of low-resistance pathways for solvent transport at the interface between the MWCNTs and the polymeric chains. Moreover, the MWCNTs reduced the severe membrane fouling caused by the absorption of the positively charged dye with respect the polymeric matrix, by a screening effect of the attractive electrical interactions. The polyimide membranes prepared showed competitive performance in comparison with NF commercial membranes and other laboratory made mixed matrix membranes.

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Chapter 4: PVDF based membranes

4.1 Introduction

Fluoropolymers are an important class of materials with interesting properties. These polymer have high thermal stability, improved chemical resistance, and low surface tension because of the low polarizability and the strong electronegativity of the fluorine atom, its small van der Waals radius (1.32 A), and the strong C-F bond (485 KJ mol^{-1}) [1-2].

Homopolymer of PVDF are semicrystalline and long chain macromolecules which contain 59.4% fluorine and 3% hydrogen [3]. They typically have a crystallinity of 35-70% depending on the various conditions [2]. The crystalline phase of PVDF has three different molecular conformations and five distinct crystal polymorphs. The three molecular conformations are TGTG', TTT and TTTGTTTG'. The crystal polymorphs are named α (phase II), β (phase I), γ (phase III), δ, and ε. [4]. Van der Waals radius of the fluorine atom (1.32 A) versus that of the hydrogen one (1.20 A) determine the polymorphism of PVDF [2].

For the α-phase, the polymeric chains are nonpolar, with helix-type structure. This structure it is produced by the hydrogen and fluorine atoms alternation in a regular way on both sides of the chains. For the β-phase with zig-zag conformation, the most polar form, the orientation of the strong dipole in the $–CH_2CF_2$- base units along the polymer chain given the fluoropolymer its piezo-, pyro- and ferro-electric properties [4]. It has found that β-phase PVDF has some specific properties such as polarity and higher mechanical strength compared with α-phase. Each different polymorph exhibit specific properties. PVDF crystal with a desired polymorph can be formed from melts, non-solvents, and temperature change. The α-phase can be obtained from melt, solvent, or by thermal method. The β-phase is usually obtained from homopolymer including additive [5], from solution under appropriate conditions [6].

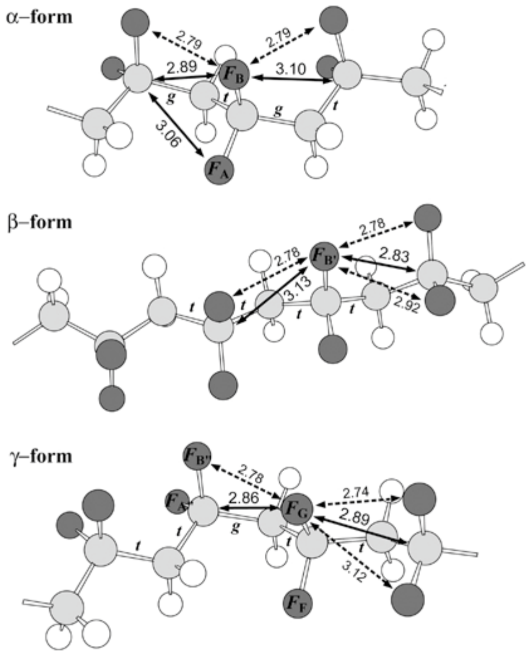

Fig.1 Three crystalline polymorph of PVDF [7]

PVDF membrane are widely employed in the process industry and have been used in UF/MF, MD, PV. The main preparation method pf PVDF porous membranes are non-solvent induced phase separation (NIPS) and thermal induced phase separation (TIPS). For the NIPS process, PVDF is dissolved in a proper solvent close to room temperature and non-solvent is employed to reduce phase separation. For this method, selecting suitable solvents/diluents is very important for the morphologies, structures, properties, and performances of the resulting PVDF membranes [2].

As reported in literature [8] [9][10], solvent type seems to attract more attention in the crystalline phase formation. Dipolar interaction between polymer chain and solvent molecules is being used to explain the results. It is generally believed that solvents with higher polarity led to the production of β-phase [11][12][13]

The use of additive in the polymeric solution as a pore former to improve the permeation performance of the PVDF membranes is an interesting field. The additive can be categorized in: a) polymeric additive such as poly(vinyl pyrrolidone) (PVP)[14] [15] [16] and poly(ethylene glycol) (PEG) [17][18]; b) low-molecular-weight chemicals, including salts such as lithium chloride (LiCl) [19] and lithium perchlorate (LiClO4) [20], and inorganic acids (acetic acid, phosphoric acid)[21] and organic acids (propionic acid) [22].

As reported in literature, the presence of pore forming additives in the casting solution, LiCl and PVP, induced relevant variations of the membranes morphology and transport properties. PVP and LiCl, at specific percentage, work both as nonsolvents, reducing the thermodynamic miscibility of the casting solution (thermodynamic effect), and inducing the enhancement liquid-liquid phase separation [23]. Practically, when the polymeric film is immersed in the coagulation bath, the poreforming, with high affinity for water, go outside of polymeric film forming the pore inside the membrane.

In this work PVDF MMMs were prepared. Three-different type of functionalized MWCNTs (oxidized(OX), aminated(Am) and amidated(AMD)) were dispersed in polymeric membranes made of polyvinylidenefluoride (PVDF). Based on our previous investigation, the optimized loading of the carbon nanotubes in the polymeric film was fixed at 1 wt% (99wt% polymer) and the best solvent for MWCNTs dispersion and polymer solubilization was the dimethylformamide (DMF) [24].

The effects of the additive such as poreforming on the membranes performance was investigate. Also membrane preparation condition on the membrane morphology and transport properties, were analyzed. In particular, the MWCNTs effect on the permeance performance of PVDF membranes was investigate.

4.2 Materials

PVDF (Solef 60/10) was purchased from Solvay and was used as base polymer in the membrane casting solution. Reagent grade DMF was used as solvent. Lithium Chloride (LiCl) and Poly(vinylpyrrolidone) (PVP) were used as a pore-forming and Multiwalled Carbon nanotubes (MWCNT) functionalized (-Am, -OX, AMD) were used as additives in the casting solution. A protein bovine serum albumine (BSA) were used to rejection test.

4.2.1 Synthesis of MWCNTs

In this work, the interface chemistry of multiwalled carbon nanotubes (MWCNTs) was tailored by chemical functionalization of their sidewall surface by oxidation, amidation and amination procedure. The aim was to optimize the interaction with a polymeric matrix made of PVDF in order to realize high performing composite film with improved performance.

MWCNTs were synthesized by catalytic chemical vapor deposition using ethylene as carbon source and a cobalt/iron catalyst supported on zeolite, as describe in the previous chapter. The MWCNT-AMD were synthetized started by MWCNT-OX, that were also further modified by reaction with thionyl chloride and successively by reaction with dibuthylamine in order to convert carboxylic groups in amidic ones.

4.3 Membrane preparation

The polymeric membranes were prepared by NIPS using water as coagulation bath. The polymer was dissolved under stirring at 50°C as temperature in organic solvent and the composition of the casting solutions is reported in Table 1. The solutions were cast at 350 μm thickness onto a glass plate by using a casting knife (Elcometer 3700), at 25±3°C and relative humidity 50 ± 10%. The surface in contact with glass was indicated as “down”, while that exposed to air during casting, as “up”. The liquid film was immediately immersed in the water coagulation bath and the membranes were stored in water until their use. The MMMs membranes were prepared following a procedure similar to the polymeric membranes, the only difference was the addition of the MWCNTs in the homogenous polymer solution and successive sonication for 2 hours, before casting. The loading of MWCNTs in the formed membrane was 1 wt% (99 wt% polymer).

Table1. Composition of the casting solution used to prepare PVDF-based polymeric and mixed matrix membranes

Membrane code	**Polymer wt%**	**Solvent type wt%**		**Poreformer wt%**		**MWCNTs type**
PVDF	13%	DMF	87%	-	-	-
PVDF_LiCl	13%	DMF	85%	LiCl	2%	-
PVDF_PVP	13%	DMF	85%	PVP	2%	-
PVDF_LiCl (Ox-MWCNTs)	13%	DMF	84.87%	LiCl	2%	Oxidized 0.13%
PVDF_LiCl (Am-MWCNTs)	13%	DMF	84.87%	LiCl	2%	Aminated 0.13%
PVDF_LiCl (AMD-MWCNTs)	13%	DMF	84.87%	LiCl	2%	Amidated 0.13%

4.4 Membrane characterization

The type and concentration of functional groups present on the MWCNTs synthesized were determined by titration method [25]. The tritation method proposed by Boehm was used to estimate the number of acidic and basic groups. The MWCNTs were immersed in the following solutions: NaHCO3, Na2CO3, NaOH, HCl. The amount of acidic functional groups was estimated under assumption that NaHCO3 neutralizes only carboxyl groups; NaOH neutralizes carboxyl, phenolic hydroxyl and lactone groups. The amount of the hydroxyl groups was estimated from the amount of HCl that reacted with the MWCNTs. After continuous stirring for 24h, the solutions were filtered and analysed by pH analysis.

The cross-section and surface morphologies of the films were observed by a FEI Quanta 200 Philips SEM instrument. Cross-sections were prepared by fracturing the film samples in liquid nitrogen.

Fourier transform infrared spectroscopy (FT-IR) analyses in attenuated total reflectance (ATR) was performed using a Perkin Elmer Spectrum One, on the up surface of each film.

Raman spectra were recorded using a Jasco NRS-5100 micro Raman Spectrometer. The spectra were acquired in the back-scattering geometry. The 532 nm line of the laser with attenuated power of 0.3 mW, was focused on the sample by means of an 100X objective.

The mean pore diameters was measured by a capillary flow porometer (PMI, Porous Materials Inc. Ithaca, NY) using as wetting liquid 3MFluorinert™ Electronic Liquid FC-40.

The total porosity of the film was measured by the gravimetric method at 25°C, determining the weight of water contained in the porous part of the film. The porosity ε, was calculated by the following equation:

$$\varepsilon = \frac{(w_2 - w_1)/D_w}{((w_2 - w_1)/D_w) + (w_1/D_p)} \tag{1}$$

where w_1 is the weight of the dry sample, w_2 the weight of the wet sample, D_w the water density (0.997 g/cm3) and D_p is the polymer density (1.78 g/cm3) for polymeric film, or polymer/MWCNTs density estimated considering the fraction of each component and their density (density of the MWCNTs assumed equal to 2.1 g/cm3).

4.5 Membrane permeation and fouling test

The membranes were tested by pure solvent permeation test using a cross-flow cell having an active membrane area of 3.79 cm2, operating at room temperature (25 ± 3°C). The multicycles test is carry out in the following way: half hour of stabilization, permeate sample collected at regular time intervals (5min), in order to determine the flux (J) and Permeance (Pe) as reported in the equations (2)-(3) (chapter 3)

Table 3. Procedure for filtration test

Step	Solution	Time (min)	TMP (bar)
1°	Water	30	1
2°	Water	60	1
3°	BSA (1g/L)	60	1
4°	Water	30	1
5°	Back-washing	5	0.5
6°	Water	30	1
7°	BSA (1g/L)	60	1
8°	Water	30	1
9°	Back-washing	5	0.5
10°	Water	30	1

The membrane rejection (R) and the mass balance (MB) were calculated using the equation (4)-(5) (chapter 3):

The concentration of the solute in the feed, retentate and permeate was analyzed by UV spectrometer (Lambda 650S UV-vis spectrometer, PerkinElmer). Thw BCA method was used to prepare the samples. BCA Protein Assay is a detergent-compatible formulation based on bicinchoninic acid (BCA) for the colorimetric detection and quantitation of total protein. This method combines the well-known reduction of Cu+2 to Cu+1 by protein in an alkaline medium (the biuret reaction) with the highly sensitive and selective colorimetric detection of the cuprous cation (Cu+1) using a unique reagent containing bicinchoninic acid.1 The purple-colored reaction product of this assay is formed by the chelation of two molecules of BCA with one cuprous ion. This water-soluble complex exhibits a strong absorbance at 562nm.This procedure requires a smaller volume (10-25µL) of protein sample [26].

4.6 Result and discussion

4.6.1 Characterization of MWCNTs

The type and concentration of functional groups present on the MWCNTs synthesized were summarized in table 4.

MWCNTs	**Carboxylic (mmol g^{-1})**	**Phenolic (mmol g^{-1})**	**Lactonic (mmol g^{-1})**	**Aminic (mmol g^{-1})**	**Total (mmol g^{-1})**
Pristine	0	0	0.86±0.02	0	0.86±0.02
OX-CNTs	0.230±0.003	1.40±0.02	1.35±0.05	0	2.98±0.07
AMD-CNTs	0	1.83±0.02	0.61±0.06	0	2.44±0.08
Am-CNTs	0	0.143±0.004	1.34±0.03	9.04±0.18	10.5±0.2

MWCNT-OX presented on the external walls oxygenated species: carboxylic, phenolic, and lactonic groups, with acid properties. On the contrary, the aminated MWCNTs were characterized by the presence of an high content of aminic functionalities with basic properties, but also by the occurrence, at lower concentration, of phenolic and lactonic groups. Lactonic groups were present already on the purified MWCNTs, probably formed at level of the defects and vacancies of the graphitic structure [27].

However, it is interesting to note that the total concentration of the functional groups in the pristine sample was substantially lower in comparison to the functionalized MWCNTs. In the MWCNT-AMD all the carboxylic groups present on the MWCNT-OX were converted by an amidation reaction with dibuthylamine. Moreover, part of the lactonic groups of the MWCNT-OX were opened during the treatment with the diamine (lactone is less reactive than the acyl chloride), increasing in parallel the concentration of the phenolic groups.

Raman spectroscopy was used to estimate the quality of the functionalized samples via the ratio of intensity of G and D band (I_G/I_D).

Raman spectra of the pristine and functionalized MWCNTs, present the two characteristic bands of the MWCNTs, indicated as D-band and G-band (1335-1345, 1565-1584 cm^{-1}, respectively, Figure 2 (a)). Moreover, a weak shoulder of the G-band was evident, indicated as D' band (1600-1620 cm^{-1}). The D and D' bands are attributed to the presence of amorphous or disordered phase in the carbon nanotubes [28]. The G-band relates to the in plane tangential stretching of the carbon-carbon bonds in the graphene sheets.

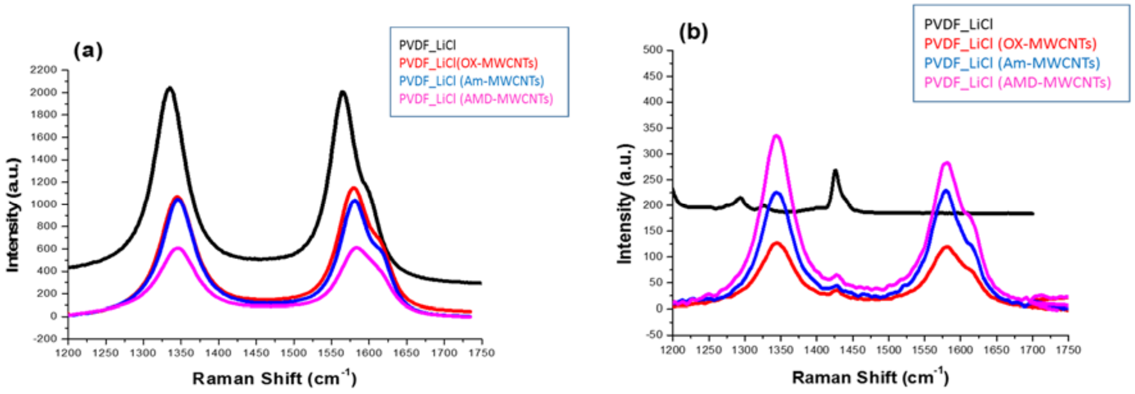

Fig 2. (a) Raman spectra of the pristine (black line), oxidized (red), amidated (blue) and aminated (purple) MWCNTs. (b) Raman spectra of the PVDF polymer (black line) and composite membranes containing oxidized (red), amidated (blue) and aminated (purple) MWCNTs.

However, it is possible to observe a blue shift of characteristic signals of the functionalized carbon nanotubes (MWCNT-OX; MWCNT-AMD and MWCNT-Am) in comparison with the pristine ones (Table 5). Molecular vibration are sensitive to their local environment and it is possible to attribute the different features of the spectra to electron acceptor–electron donor interactions of the polar functional groups present on a MWCNT with the π-system of another one. The presence of blue shift indicates that the π-system acts as electron donor and the functional groups as electron acceptors [29].

Table 5. Main Raman signals of the pristine (purified) and functionalized MWCNTs.

MWCNTs	**Powder**			**Entrapped**		
	D-band (cm-1)	G-band (cm^{-1})	D'-band (cm-1)	D-band (cm-1)	G-band (cm^{-1})	D'-band (cm-1)
Pristine	1335	1565	1596	-	-	-
MWCNT-OX	1345	1580	1614	1345	1580	1613
MWCNT-AMD	1345	1582	1617	1343	1579	1614
MWCNT-Am	1345	1584	1618	1343	1579	1614

In the Raman spectra of the composite films (indicated as M-OX, M-AMD and M-Am for the samples containing oxidized, amidated and aminated MWCNTs, respectively) it was possible to clearly distinguish D, G and D' bands (Figure 2 (b)). This confirms that the membrane manufacturing process does not compromise the structural integrity of the carbon nanotubes. The band at 1430 cm-1 in the spectra of the composite membrane was characteristic of the PVDF polymer. The others Raman bands of the PVDF polymer at 1294 and 1327 cm-1 were covered by the more intense D-band of the carbon nanotubes.

The position of the Raman bands of the oxidized MWCNTs entrapped in PVDF films are similar to the value of the corresponding nanotubes not included in membrane (Table 5).

On the contrary, the composite films containing AMD-CNTs and Am-CNTs show a small red shift of the D-, G- and D’-band (Table 5 and Figure 2b) indicating the formation of a charge transfer complex with the PVDF polymer [29].

4.6.2 PVDF polymorphism: effect of additive

PVDF membranes were prepared by nonsolvent induced phase separation and during the process, a homogenous polymeric solution is initially demixed into two liquid phase because of the exchange of the solvent and nonsolvent. The phase with the higher polymer concentration form the solid membrane; the phase with a lower polymer concentration form the pores of the membrane [23]. The polymer molecules may rearrange their structure until the solidification (vitrification or crystallization) of the concentrated phase occurs.

The effect of additives, LiCl, PVP and MWCNTs, on polymorphism of PVDF-based membranes was investigated.

Multy-type electron donor/electron acceptor interactions between the PVDF and the functionalized MWCNT are possible. The C-F bonds of the PVDF are polar and the highest dipole moment is obtained with the alignment of all dipoles of the polymer in the same direction, corresponding to the β-phase of the PVDF.

All membranes produced in this work crystalize in the β-form as conformed by ATR-FT-IR. The PVDF can theoretically interact with the π-system of the carbon nanotubes as electron donor (interaction by the negative part of the polymer dipole, i.e. C-F bonds) or electron acceptor (interaction by the positive part of the dipole, i.e. C-H bonds). The red shift of the D- and G-band in the composite membranes containing MWCNT-AMD and MWCNT-Am indicates that PVDF polymer acts as electron donor towards the π-system of the carbon nanotubes [29].

In parallel, the functional groups can form hydrogen bonds with the positive part of the dipole of the polymer by the electrons lone pairs present on the heteroatoms (nitrogen and/or oxygen). The Figure 3 a-c schematized the formation of charge complexes between the PVDF and the functionalized MWCNTs. For clarity reasons, only the functional groups peculiar for each type of MWCNTs are reported (i.e. carboxylic for MWCNT-OX; amidic for MWCNT-AMD and aminic for MWCNT-Am). However, it is necessary to keep in mind that also phenolic and lactonic groups, present on all the three types of MWCNTs, can give similar interactions. Moreover, it is possible also the formation of hydrogen bonds in which the functional groups works as electron acceptors using their hydrogen atoms bond to heteroatoms.

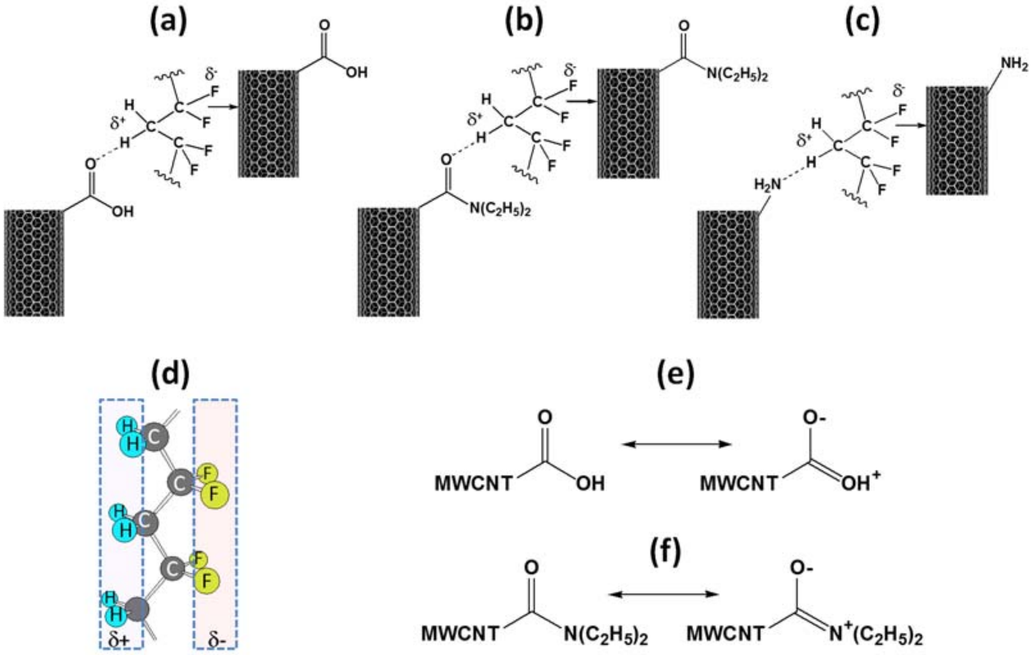

Fig.3 Electron donor/electron acceptor interactions between the PVDF and the functionalized MWCNTs: MWCNT-OX (a); MWCNT-AMD-s (b), MWCNTs-Am (c); and schematization of the structure and dipole moment of the PVDF in β-phase (d) and resonance formula of the characteristic functional groups of MWCNT-OX- (e) and MWCNT-AMD (b).

Fourier transform infrared spectroscopy (FT-IR) analyses in attenuated total reflectance (ATR) and in transmittance (Figure 3) were performed on the PVDF membranes to observe the crystalline structure. Commonly, in the PVDF membrane is present a mixture of α and β phase. By FT-IR, the mixture α/β phase was observed for PVDF membrane without additive; while the only β-phase was observed in the membranes prepared with LiCl and mixture LiCl/PVP and MWCNTs additives. To confirm the presence of β-phase not only in the top surface layer but also in all membrane structure, the FT-IR analysis were carry out both in attenuated total reflectance and in transmittance. The comparison of FT-IR spectra of membrane with and without additives confirm the presence of only β-phase for membrane with LiCl. The typical bands of α-phase (1383-1211-975-853-797-762 cm^{-1}), present in the PVDF membrane without additives, disappeared completely in the spectra of PVDF with LiCl.

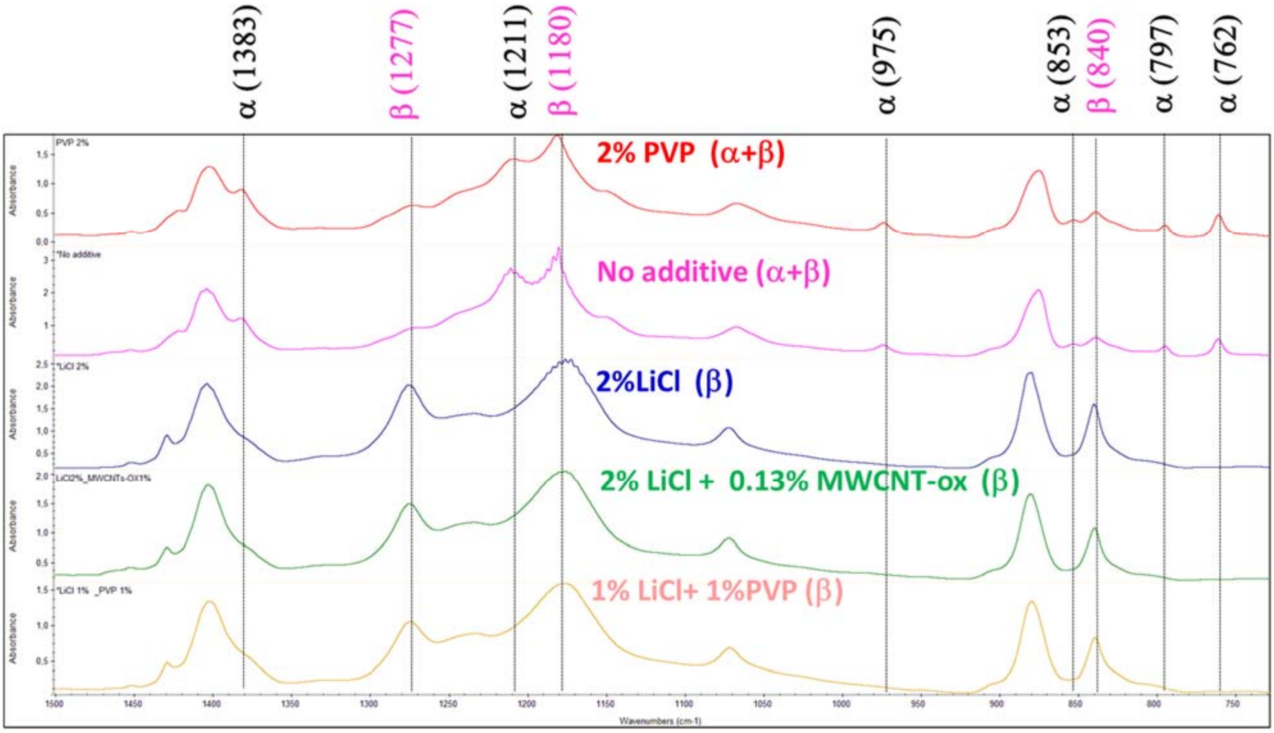

Fig. 3. FT-IR spectra of PVDF membrane with and without additives.

These results can be explained considering the PVDF structure. Considering that the PVDF in the α-phase has apolar structure while the β-phase has a polar structure. The presence of ions LiCl it determined better orientation packing of CF_2-CF_2 dipoles and the consequential TTT conformation referring to β-phase.

This additive is soluble both in DMF and water and is leached out of from the casting solution into the coagulation bath. In fact, this additive, work as pore former agents, because, when go out from the liquid improve pore formation during phase separation (Figure 4) (table 6).

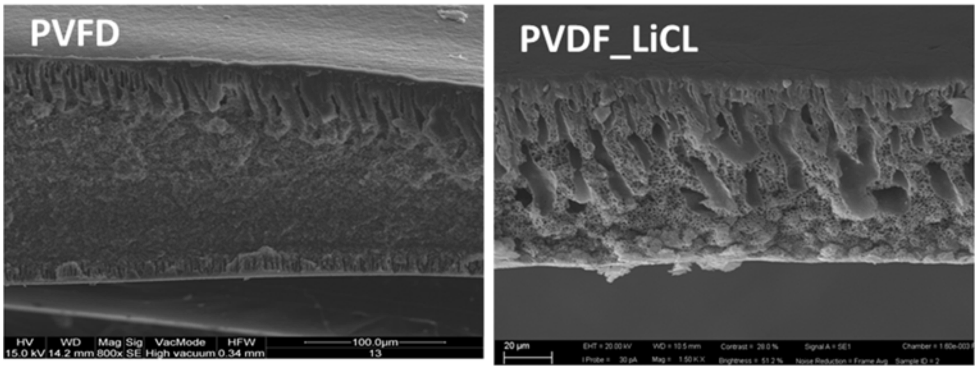

Fig.4. SEM images of PVDF membrane with and without LiCl

The presence of pore structures on membrane skin layer formed with LiCl was confirmed by images SEM (Figure 4), a difference of membrane without LiCl that have the dense skin layer. As expected, the PVDF membrane with PVP, that have higher molecular weight respect to LiCl, are characterized by higher mean pore size diameter and porosity. By these characterizations, LiCl was selected as poreformer for the preparation of PVDF mixed membrane membranes containing MWCNTs.

The presence of MWCNTs did not change significantly the mean pore size diameter and total porosity respect to the polymeric membrane (PVDF_LiCl). Also, the water contact angle did not change in the mixed matrix membrane. Therefore, the presence of oxidated MWCNTs reduce the hydrophobicity because, probably of the presence of the hydrophilicity functional groups.

Table 6. mean pore size diameter, total porosity and water contact angle of PVDF membranes.

Membrane code	**Mean pore size diameter (μm)**	**Total porosity (%)**
PVDF	0.029 ± 0.001	76 ± 0.02
PVDF_LiCl	0.036 ± 0.0002	86 ± 0.01
PVDF_PVP	0.13 ± 0.007	93 ± 0.02
PVDF_LiCl_PVP	0.05 ± 0.008	91 ± 0.004
PVDF_LiCl (Ox-MWCNTs)	0.037 ± 0.001	82 ± 0.02
PVDF_LiCl (Am-MWCNTs)	0.035 ± 0.004	82 ± 0.003
PVDF_LiCl (AMD-MWCNTs)	0.039 ± 0.003	84 ± 0.02

The good distribution of MWCNTs was appreciated already by a simply visual observation of the composite film (Figure 5) but also confirmed by microscopy techniques (Figure 6). They were quite homogenously distributed in the polymeric matrix in the form of bundles

Fig.5 Images of composite film made with PVDF with 1% of MWCNTs

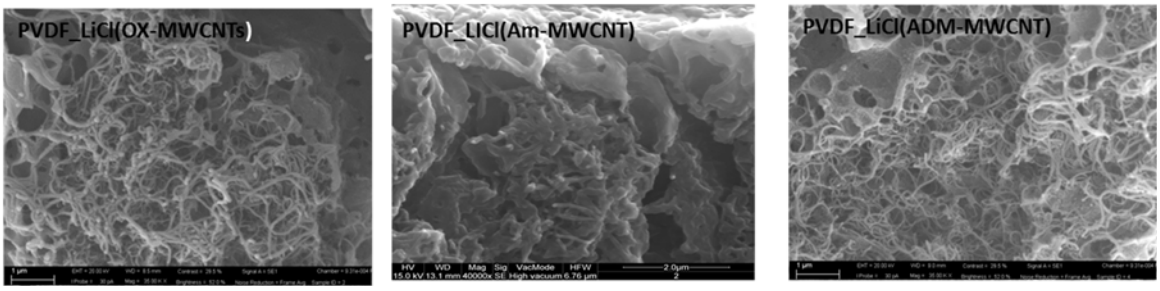

Fig.6 SEM images of the PVDF mixed matrix membrane containing oxidized, aminated and amidated functionalized MWCNTs.

The composite membranes were characterized in order to observe the effect of the MWCNTs functionalization on their thermal, mechanical and transport properties, as a result of specific chemical interactions with the polymer and compared with a polymeric sample prepared under similar conditions but without carbon nanotubes.

The total thickness of membranes prepared was measured by micrometer and the resulst obtained are reported in table 7. It is possible to observe that when LiCl is present in the vesting solution the membranes have a low thickness. These results can be explained considering the higher viscosity of these solutions which reduced the rate of phase separation increasing the time available for film compaction.

Table 7. Thickness of membranes prepared

Membrane	Thickness µm	Viscosity (cP)
PVDF	146± 3.9	280 ± 3.5
PVDF_LiCl	100 ± 2.8	649 ± 9.9
PVDF_(Ox-MWCNTs)	114 ±3.1	689 ± 6.3
PVDF_(Am-MWCNTs)	107 ± 5.4	630 ± 7
PVDF_(AMD-MWCNTs)	112± 1.7	530 ± 4.5

By mechanical test, the properties of composite membrane were analyzed and compared with the polymeric membranes. The composite film was thoroughly characterized in order to further highlight the effect of the MWCNTs on membrane properties. Mechanical and thermal properties of the composite membranes were compared with a polymeric sample prepared under similar conditions but without carbon nanotubes (Figure 7). The composite films are characterized by higher ultimate tensile strength (or tensile stress at break) and elongation at break than the polymeric sample (Figure 7). In particular the MWCNT-AMD-and, at minor extend, the MWCNT-Am, are more effective than MWCNT-OX in enhancing the membrane toughness because of favored chemical interaction between the carbon nanotubes and the PVDF matrix, assisted by the functional groups [

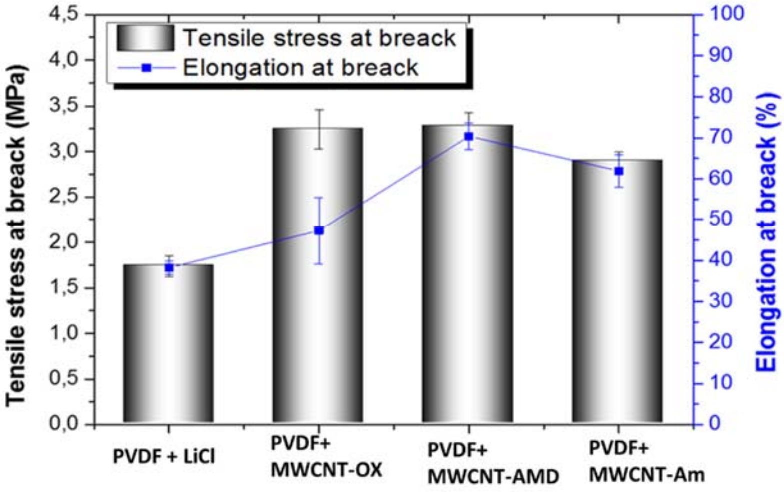

Fig.7 Tensile stress and elongation at break of PVDF membranes with and without MWCNTs.

The polymeric and mixed matrix PVDF membranes were used in filtration and rejection of BSA (Bovine serum albumin). The Figure 5 shows the results obtained by the test. An increased flux of membranes with MWCNTs respect to the polymeric membrane were observed. The presence of MWCNTs in the membrane, was found to increase water flux with respect to the polymeric sample, despite the similar mean pore size (Table 6). A possible explanation is the formation of well-defined interfacial structure formed by the functionalized MWCNTs leads to an improved mass transport and realizes a high performing membrane. Despite the gap of permeance between composite and polymeric membranes it has been reduced during the test, the volume permeate with composite membrane was higher in the same time.

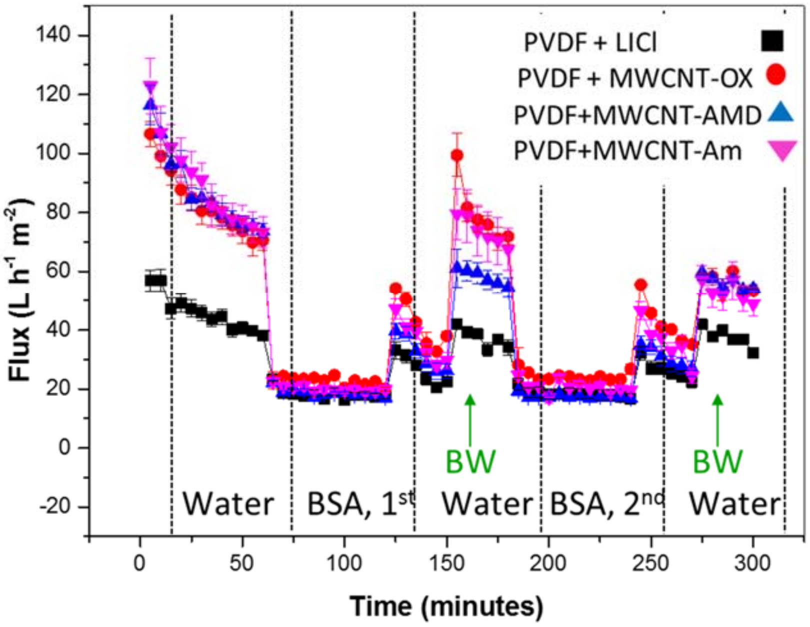

Fig. 5. Time-depend flux of polymeric and mixed matrix membranes with two cycle of BSA solution and back-washing

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The Figure 6 show a similar rejection values for all PVDF membranes despite the higher flux for composite membranes.

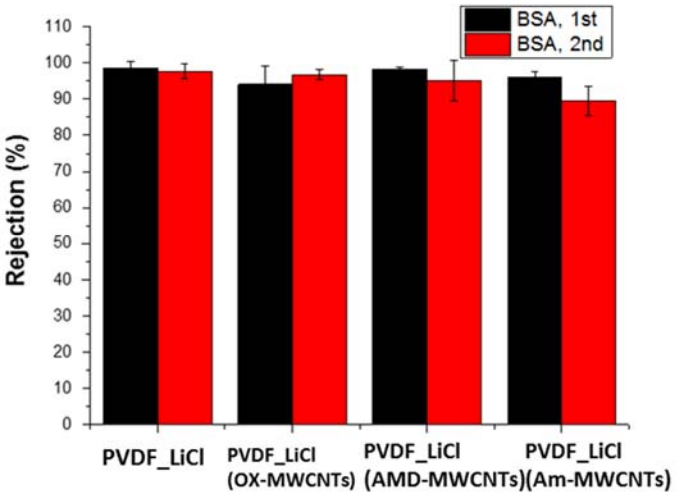

Fig. 6. BSA rejection in the first and second cycle of polymeric and mixed matrix membranes.

4.7 Conclusions

Porous asymmetric PVDF membranes were prepared by NIPS technique. The effect of pore-forming additives on PVDF polymorphism was investigate using two compound: Lithium chloride (LiCl) and poly(vinylpyrrolidone) (PVP). From a point of view of membrane morphology, these additives increased membrane pore size and total porosity. From a point of view of PVDF polymorphism, the influence of LiCl and mixture LiCl/PVP on the crystalline phase of PVDF, was observed. The presence of LiCl ions induce the formation of only β-phase in the PVDF membrane. This because the PVDF in the β-phase has a polar structure and the interaction with LiCl ions is favored, on the contrary using only PVP.

LiCl was select for the PVDF mixed matrix membranes using functionalized MWCNTs (oxidized, aminated and amidated).

The functionalization of MWCNTs improved the dispersion of MWCNT in polymeric membrane.

Multy-type electron donor/electron acceptor interactions between the PVDF and the functionalized MWCNT are possible.

By Raman analysis, a good graphitization degree of the materials produced was observed. Also, in the Raman spectra of the composite films containing the functionalized MWCNTs it was possible to clearly distinguish typical bands of MWCNTs. These results confirmed that the membrane manufacturing process did not compromise the structural integrity of the carbon nanotubes.

The Raman results support a better interaction of the PVDF polymer with the MWCNTs functionalized with nitrogen containing groups (aminated and amidated) than with oxidized sample.

The MWCNTs were observed by high resolution SEM images and they were quite homogenously distributed in the polymeric matrix membrane in the form of bundles. The different PVDF mixed matrix membrane were compared in the mechanical test, showing superior tensile stress and elongation at break respect to polymeric membrane.

The different PVDF membranes were compared by water and BSA filtration test. The presence of the MWCNTs in the polymeric matrix improved membrane performance (enhanced flux). Despite the similar mean pore size diameter and total porosity, the mixed matrix membrane flux was enhanced. The superior transport properties of the mixed matrix membranes was probably due to the formation of low-resistance pathways for solvent transport at the interface between the MWCNTs and the polymeric chains.

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5. General conclusions

In this work, the effect of MWCNTs as additive in the polymeric membrane were investigated.

Was demonstrated that, a relevant effect can be observed using small amount of MWCNTs (0.1%) to prepare mixed matrix membranes with improved performance, respect to polymeric membranes.

In the case of P84 based membranes, the presence of MWCNTs in the polymeric matrix improved membrane transport and rejection performance (enhanced fouling with similar rejection or higher rejection) with respect to polymeric membranes prepared without MWCNTs. This behaviour was probably due to the formation of low-resistance pathways for solvent transport at the interface between the MWCNTs and the polymeric chains. This hypothesis is confirmed by mean pore size distribution and total porosity results. In fact, the presence of MWCNTs did not change the means pore size and the total porosity of the mixed matrix membranes in comparison with polymeric membranes, but the flux was higher.

The different membranes were compared in the rejection of organic dyes showing superior performance respect to polymeric membranes. Using dyes having same molecular weight but different charge, relevant “charge effects” on membrane rejection were observed: Donnan exclusion for the negative charge dye, electrostatic adsorption for the positively charged dye and higher rejection for the charged dyes in comparison with the neutral dye.

In the case of PVDF based mixed matrix membranes, to evaluate the transport and antifouling properties, Bovine serum albumin (BSA) was used in filtration test. Enhanced flux and high rejection were observed in comparison with polymeric membrane.

Also, the presence of MWCNTs in the PVDF membrane improved mechanical properties. Tensile stress and elongation at break of mixed matrix membrane were increased in comparison with polymeric membranes. This result was due to the formation electron donor/acceptor interactions between the functionalized MWCNTs and the polymeric matrix, as confirmed by Raman analyses.

This work demonstrated as the chemical functionalization of MWCNTs by oxidation, amination and amidation was necessary, not only for the good dispersion in the casting solvent and in the polymeric matrix, but also for the interactions with polymeric chains.

Furthermore, this work demonstrated that, the choice of functional group of MWCNTs is related to the characteristic of the polymer used for membrane preparation. In fact, was tested as, in the case of P84 membrane, the amminic functionality of MWCNTs has improved membrane performance. On the contrary, in the case of PVDF membrane, the amidic functionality has awarded better membrane performance.

This work demonstrated as, a small amount of functionalized MWCNTs, can be excellent additives to prepare mixed matrix membrane with improved performance.

List of publications

1. V. Grosso, D.Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E.Fontananova, “POLYMERIC AND MIXED MATRIX POLYIMIDE MEMBRANES”, Sep. Pur.Technol. 132 (2014) 684-696.
2. E. Fontananova, V. Grosso, S. A. Aljlil, M. A. Bahattab, D. Vuono, F. P. Nicoletta, E. Curcio, E. Drioli, G. Di Profio, “EFFECT OF FUNCTIONAL GROUPS ON THE PROPERTIES OF MULTIWALLED CARBON NANOTUBES/POLYVINYLIDENEFLUORIDE COMPOSITE MEMBRANES”, Journal of membrane Science, In Press, Accepted Manuscript, DOI: http://dx.doi.org/10.1016/j.memsci.2017.07.002

Conference proceedings

1. V. Grosso, D.Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E.Fontananova. “Preparation of Mixed Matrix Membrane containing functionalized multiwalled carbon nanotubes”.XXX EMS Summer School on Membrane Technology, Essen (Germany) from 22 to 27 Jul 2013 (POSTER PRESENTATION)
2. V. Grosso, D.Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E.Fontananova “Preparation of polyimide mixed matrix membranes containing functionalized multiwalled carbon nanotubes” XXXI EMS Summer School on “ Innovative Membrane Systems”, Cetraro (CS)- Italy from September 28 to October 3, 2014. (POSTER PRESENTATION)
3. V. Grosso, D.Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E.Fontananova” High flux mixed matrix membranes for wastewater treatment”, ITM seminar DAYS , Rende (CS), Italy December 18- 19 , 2014 (POSTER PRESENTATION)
4. V. Grosso, D.Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E. Fontananova, ”PVDF-MWCNTs nanocomposite membranes with tailored properties” EUROMEMBRANE 2015 Aachen Germany, September 06-10.2015 (PITCH POSTER PRESENTATION)
5. V. Grosso, D. Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E.Fontananova “Preparation of polyimide mixed matrix membranes containing functionalized multiwalled carbon nanotubes” XXV Congresso Nazionale della Società Chimica Italiana-SCI Rende September 7-12 2014 (ORAL PRESENTATION)
6. V. Grosso, D.Vuono, M.A. Bahattab, G.Di Profio, E.Curcio, S.Al-Jilil, F.Alsubaie, M.Alfife, J.B.Nagy, E.Drioli, E.Fontananova “Study of different polymers for mixed matrix membranes preparation containing functionalized carbon nanotubes for water treatment” ITM Seminar DAYS Rende (CS) Italy, November 25-26.2015 (ORAL PRESENTATION)
7. E. Fontananova,V. Grosso, D. Vuono, M. A. Bahattab, G. Di Profio, E. Curcio, S. A. Al-Jilil, F. A. M. Alfife, J. B.Nagy, E. Drioli, Mixed matrix membranes containing functionalized carbon nanotubes

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8. E. Fontananova, M.A. Bahattab, S. A. Al-Jilil, M. Alowairdy, V. Grosso, G. Rinaldi, G. Di Profio, D. Vuono, J. B. Nagy, E. Drioli, Polymeric and mixed matrix PVDF membranes with tailored properties, “9th Italy-Korea Workshop”, Ravello (SA), Italy, June 28 - July 1, 2015

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