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Effect of multi wall carbon nanotube on vacuum membrane distillation performance of microporous polyvinylidene flouride membranes

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Abstract

Membrane technology has gradually become a popular separation technology over the past few decades. There are many significant advantages to use membranes for industrial processes. MWCNT possible locations for small molecules are absorbed. Since the transmission properties of CNTs is always the key issue is to improve the properties of polymeric membranes to separate the CNTs are able to transfer the molecules studied. MWCNT/PVDF membranes were fabricated using solution casting method. The synthesized membranes were structurally characterized using Fourier transform infrared spectroscopy, scanning electron microscope and thickness of membrane. The membrane performance was tested by vacuum membrane distillation setup. SEM images showed appropriate distribution of multi wall carbon nanotubes within polyvinylidene fluoride matrix. FTIR analysis showed a physically linking between the nanoparticles and the polymeric matrix of the membrane. Thickness of membranes wasabout 40,50 µm. The MD performance of neat PVDF and MWCNT/PVDF flat sheet membranes with the approximate contact area of 32 cm^2 was examined in a vacuum membrane distillation setup. The pure water flux for PVDF/MWCNT and neat PVDF membranes was 8.44 ,11.25(kg/m^2h), Respectively. Pure water flux test showed that increasing the nanoparticle, pore wetting is reduced. so, the hydrophobicity is increased.

Keywords : *Polyvinylidene fluoride, Multi wall carbon nanotubes, Nano composite membranes, water permeation, polymeric membrane*

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1- Introduction

Membrane technology has gradually become a popular separation technology over the past few decades. There are many significant advantages to use membranes for industrial processes. membrane technology has been widely applied to various fields such as water treatment, gas purification, food processing, pharmaceutical industry and environmental protection [1-6]. Polyvinylidene flouride (PVDF) is a semicrystalline polymer with repeated unit of $–(C_2H_2F_2)n–$.It exhibits high mechanical strength, good chemical resistance and thermal stability as well as excellent aging resistance, which are very important for the actual application of separation membranes. Moreover, PVDF shows good processability to prepare flat sheet, hollow fiber or tubular membranes. PVDF is soluble in some common solvents such as N,N-dimethyl acetamide (DMAc), dimethyl formamide (DMF) and N-methyl-2-pyrrolidone (NMP). Consequently, PVDF membranes can be produced by conventional non-solvent induced phase separation (NIPS) process. Thermally induced phase separation (TIPS) was a technique developed since 1980s [7] the PVDF membranes can be also fabricated by vapor induced phase separation (VIPS), solution casting and electro-spinning, etc. The preparation methods and influencing parameters of PVDF membranes were discussed in detail in a recent review [7]. So far, there have been a lot of articles reporting on the application fields of PVDF membranes, including microfiltration (MF), ultrafiltration (UF), membrane bioreactor (MBR), membrane distillation, gas separation and stripping, pollutants removal from water (e.g., boron, volatile organic compounds and ammonia), recovery of biofuels, separator for lithium ion battery, ion exchange process and others[8]. Water treatment is a major application area of PVDF membranes nowadays. There have been many articles published reporting on the preparation, characterization and applications of PVDF membranes in water treatment such as MF, UF and MBR, etc. Moreover, some membrane manufacturers also developed a variety of PVDF membrane products for water purification in recent years[9,10].

Carbon Nano Tubes (CNTs) with mechanical and electronic remarkable, that this effect is due to the close relationship between the CNT and graphite, and the next one that appears to enable the potentially scales small electronic and mechanical are usable. In addition, the thermal properties and optical properties of CNT can be expanded as well. From the perspective of their use as a dispersed phase in the blend membranes, it is important to know that CNTs have high mechanical strength. Excellent mechanical properties of the material due to the presence of carbon-carbon bonds in the layer of graphite, which is probably the strongest bond known in nature. This link is very high hardness and strength eventually nanotube axis, and of course, this material is expected to have a potentially important role in reinforcing composites.

As shown in Figure 1, nanotubes can be synthesized by a variety of sizes and shapes, about 1nm carbon single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) for 10nm and taking into account their hollow structure for use in molecular separation permeability nanostructured fillers have been proposed.

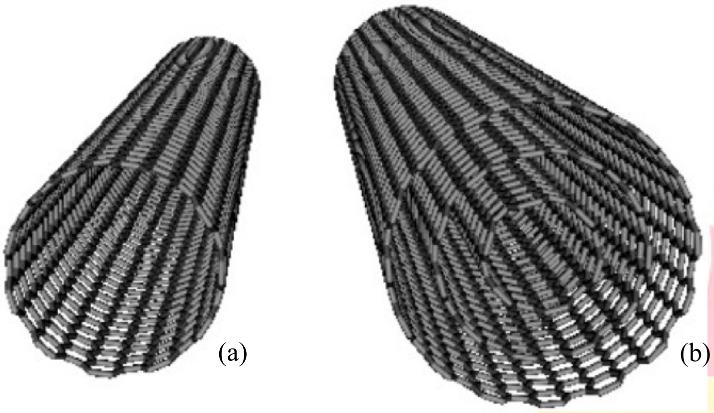

Figure 1: A schematic of the structure of a) single-walled carbon nanotubes b) multi-walled carbon nanotubes

New techniques has provided the opportunity to get organized and row layout CNTs in a polymer matrix to do. This is potentially a new window to the wider application of membrane separation of gas, liquid and vapor leaks alike. SWCNTs are attracting multiple locations, such as network channels and locations with high binding energy is very high porosity and surface area. In addition, the interlayer spaces MWCNT possible locations for small molecules are absorbed. Since the transmission properties of CNTs is always the key issue is to improve the properties of polymeric membranes to separate the CNTs are able to transfer the molecules studied [11].

2- Experimental

2-1- Materials

PVDF powders was purchased from Kynar® (the grad of 761) was used for flat sheet membrane. The solvent used to dissolve PVDF were dimethyl formamide (DMF). Carbon nanotubes (multi-walled carbon nanotubes, outer diameters < 8 nm) were obtained from Neutrino Co. and distilled water were used as solvent and nonsolvent for the casting solution.

2-2- Preparation of neat PVDF and PVDF/MWCNT membrane

A 12 wt% PVDF polymer was weighed and dried at 70 for at least 24h before use. The dried polymer was prepared by dissolving a pre-weighted PVDF in a mixture of DMF(85 wt% in casting solution) The dope solution was stirred mechanically for at least 1 day at 50 degree. The homogenous dope solution was then cooled down and degassed at room temperature for overnight. The solution was cast onto a glass plat. The thickness of knife was 150 micro meter. The nascent membrane was immersed in a room temperature tap water coagulation bath for 1 day. PVDF/MWCNT were prepared by the same method where MWCNT at 1 wt% of PVDF dosage were dispersed into the solvent and stirred for a predetermined period of time and. Then the MWCNT suspension was added to the polymeric solution and sonicated for 30 min to ensure a good dispersion. Polyvinylidene fluoride/multi wall carbon nanotube membrane films were prepared.

2-3- Characterization of neat PVDF and PVDF/MWCNT membrane

The morphology of films and the presence and proper dispersion of MWCNT in PVDF matrix were studied by scanning electron microscopy (SEM). The properties of MWCNT have also been expressed.

For comparison membrane bonds with nanoparticles and nanoparticle membrane without IR spectroscopy has been used in the investigation of the German broker FTIR Vector22 model was used. Both with and without nanoparticles in membrane thickness was measured with a micrometer.

3- Results and discussion

3-1- Characterization of MWCNT

The morphology of nano particle were studied by SEM. Fig.2 showed the SEM image of MWCNT powder. The Transmission Electron Microscopy (TEM) image of MWCNT was showed in Fig.3. Review and analyze the data obtained in Raman spectroscopy can be used to determine the structure of CNTs. Fig.4 was showed The Raman spectrum of MWCNT. To assess the quality of the analysis of X-Ray Diffraction (XRD) nanoparticles have been used. Fig.5 was showed the XRD analysis of MWCNT. To evaluate the thermal stability of a substance and its purity is used Thermogravimetric analysis (TGA). The TGA analysis was showed in Fig.6. Other Specification of MWCNT was explained in Table.1.

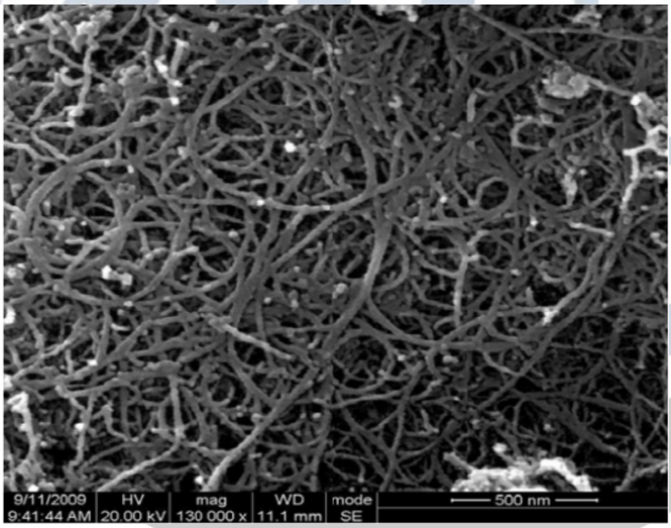

Figure 2: SEM image of multi wall carbon nanotube

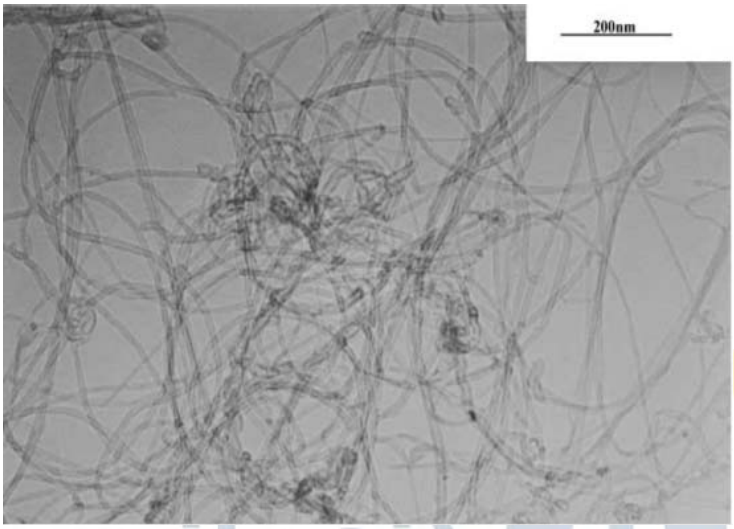

Figure 3: TEM image of multi wall carbon nanotube

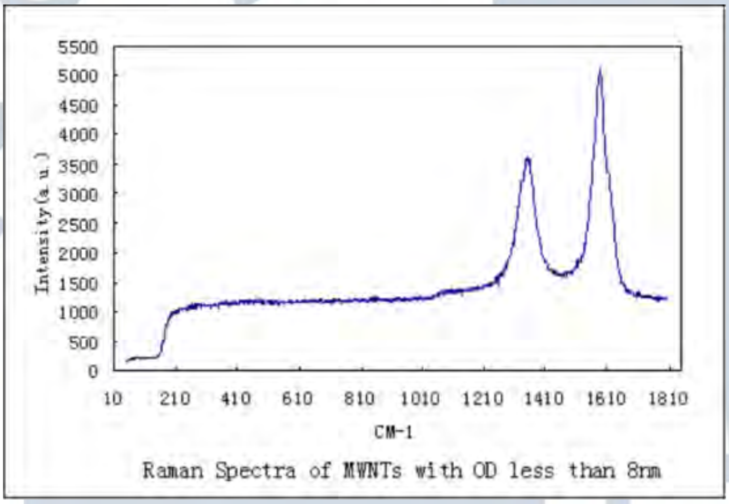

Figure 4: The Raman spectrum of multi wall carbon nanotube

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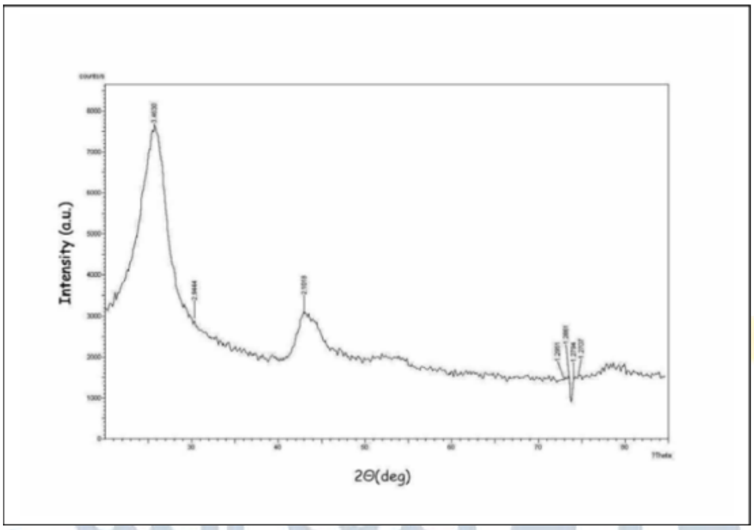


Figure 5: The XRD of multi wall carbon nanotube

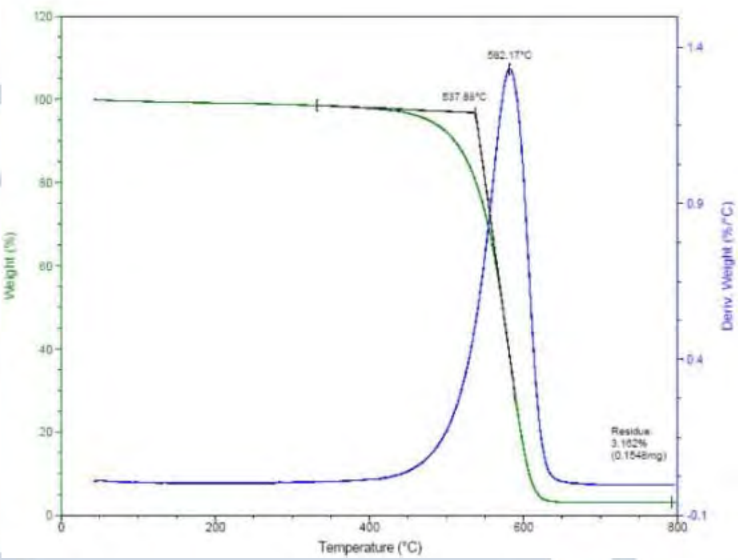


Figure 6: The TGA of multi wall carbon nanotube

Table 1: The Specification of multi wall carbon nanotube

Purity	>95%
Outer Diameter (OD)	<8 nm
Inner Diameter (ID)	2-5 nm
Length	>10 µm
Special Surface Area (SSA)	>500 m^2/g
Color	Black
Tap density	0.27 g/cm^3
True density	~2.1g/cm^3
Electric Conductivity (EC)	100 s/cm

3-2- Fourier transform infrared spectroscopy (FTIR) analysis

Almost all organic compounds or minerals that are covalently, different frequencies of electromagnetic radiation in the infrared region of the spectrum, they are attracted to. Each link has a certain natural vibration frequency, as well as a special bond between the two molecules are located in two different environments, so no two molecules with different structures, have similar infrared spectrum. The FTIR analysis of neat PVDF and MWCNT/PVDF membrane are shown in Fig. 7. As seen in the figure, the peaks in both spectra are identical, the same peaks in both spectra show that carbon nanotubes or PVDF have only physical link. So, there is no chemical bond between carbon nanotubes and PVDF.

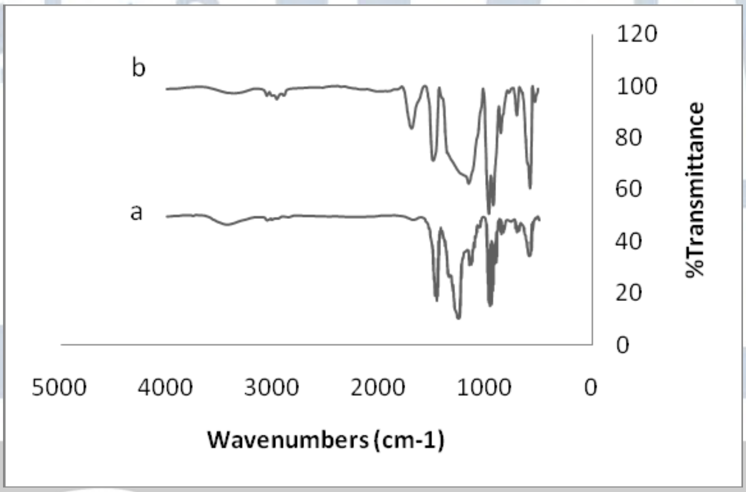


Figure 7: FTIR of a) neat PVDF membrane and b) MWCNT/PVDF membrane

3-3- SEM investigations

The SEM images for neat PVDF and MWCNT/PVDF membranes are presented in Fig.8. The presence and nano metric distribution of MWCNT in Polyvinylidene fluoride matrix are evident from the SEM micrographs. Obviously, the blend membrane displayed better surface morphology than pristine membrane, PVDF/MWCNT blend membrane have bigger pores but lower pore density than PVDF blend membrane (shown in Fig. 8 a and b). It can be seen that both of the membranes showed a typical asymmetric porous structure with a skin layer and a finger-like porous sublayer. The finger-like pores for PVDF/MWCNT membrane were much wider than the PVDF membrane (Fig. 8 c and d). These results indicated that the addition of nano materials plays an important role in the membrane formation process due to the surface properties of MWCNT such as surface charge and active site concentrations, to such an extent as to modify the membrane microstructure.

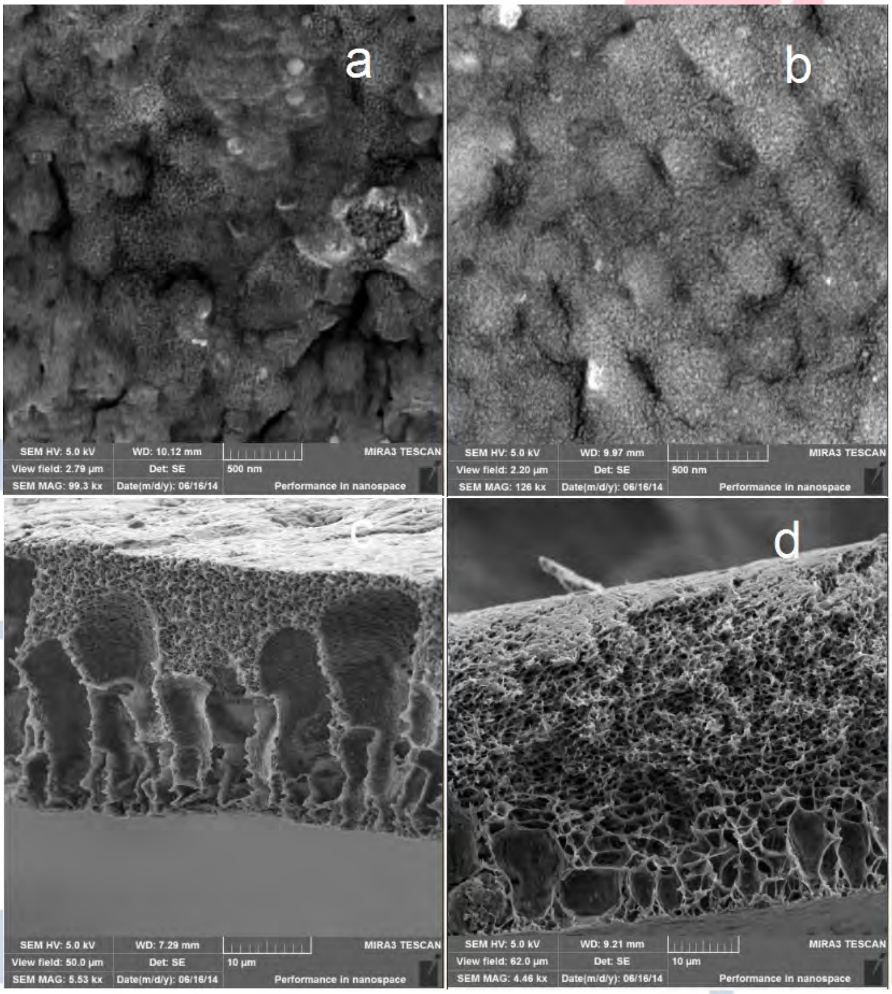


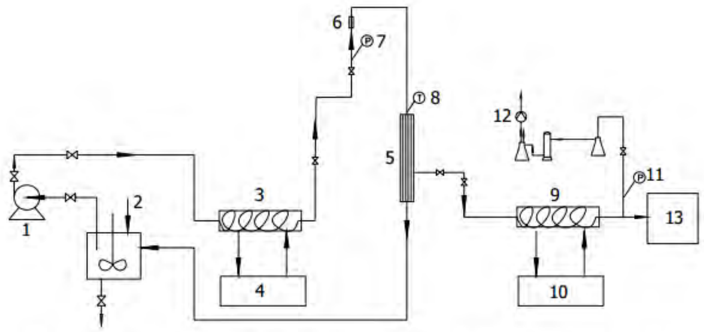
Figure 8: SEM micrographs of PVDF membranes: a,b represented surface of PVDF, PVDF/MWCNT membranes. c,d represented cross-sectionof PVDF, PVDF/MWCNT membranes.

3-4- Thickness of membranes

As occurred in other membrane separation processes, the permeate flux in MD is inversely proportional to the membrane thickness. Membrane thickness plays a significant role in dictating the resistance to mass transfer. To obtain a high MD permeability, the membrane should be as thin as possible. On the contrary, to achieve better heat efficiency the membrane should be as thick as possible due to the fact that in MD heat loss by conduction takes place through the membrane matrix. Using a micrometer thickness of the membrane was measured neat PVDF and PVDF/MWCNT. The thickness of neat PVDF and PVDF/MWCNT was 40 µm and 50 µm, Respectively.

3-5- Membrane performance in a vacuum membrane distillation (VMD) process

The MD performance of neat PVDF and MWCNT/PVDF flat sheet membranes with the approximate contact area of 32 cm^2 was examined in VMD setup. Fig.9 showed a schematic diagram of VMD experimental setup. Pure water is used for feed solution. The vapor was removed from the shell side of the module by the suction of a vacuum pump. Cold traps refrigerated by liquid antifreeze were used to condense and recover the permeated vapors. Table 2 shows the operating parameters used during the MD experiments. The pure water flux for PVDF/MWCNT and neat PVDF membranes was 8.44 ,11.25(kg/m^2h), Respectively. The results show that the addition of nano particle flux decreases. The more hydrophobic membrane flux decline due to increasing nanoparticle more hydrophobic membrane and decline of pore wetting, the flux decreases.



1. Pump 2. Storage tank 3. Heat exchanger 4. Heat thermostat 5. Membrane module
6. Flow meter 7.Pressure meter 8. Temperature meter 9. Cold exchanger
10. Cold thermostat 11. Vacuum meter 12. Vacuum pump 13. Permeate collector

Figure 7: a schematic diagram of VMD experimental setup

Table 2: operational parameters of VFD setup

Parameters	The values
Feed inlet temperature	60 C°
Vacuum pressure	0.2 bar
Feed flow rate	1300 L/hr

4- Conclusions

The effect of MWCNT on pure water permeation of microporous PVDF membrane was investigated in this study. Neat PVDF and MWCNT/PVDF were prepared by solution casting method. The structure of samples was characterized using FTIR, SEM and thickness of membranes. The obtained results from SEM show appropriate distribution of multi wall carbon nanotubes nanoparticles in the prepared membrane. FTIR analysis showed that there is no chemical bond between carbon nanotubes and PVDF. Thickness of membranes showed that the optimum thickness has been estimated to 50 micron. Pure water flux test showed that increasing the nanoparticle, pore wetting is reduced. so, the hydrophobicity is increased. Therefore flux is reduced .

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