Hydrophilicity, pore structure and mechanical performance of CNT/PVDF materials affected by carboxyl contents in multi-walled carbon nanotubes

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Abstract. Poly (vinylidene fluoride) (PVDF) membranes have been prepared by loading different type of MWCNTs-COOH as the dispersed phase via phase inversion method. The chemically functionalized MWCNTs with increasing carboxyl content were chosen for achieving a better dispersion in PVDF and altering the membrane hydrophilicity. The effect of the carboxyl content in MWCNTs on crystal structure, thermal behavior, membrane morphology, hydrophilicity, and water flux of blended membranes were investigated. Due to the addition of carbon nanotubes, various performances of the hybrid membrane had obvious changes. The most prominent was that thermal stability could be enhanced and the pore morphology was more preferable, also that the hydrophilicity were improved, further that water flux could be increased to some extent.

1. Introduction
PVDF is a semi-crystalline polymer [1], which exhibits more hydrophobic and can easily dissolve in common solvent [2]. The application of PVDF membranes have been extensively reported since the 1980[3], the remarkable progress has been made in achieving higher performance of the PVDF membrane for diverse applications [4]. Despite of the many advantages, the PVDF materials are easily fouled due to its hydrophobicity. Many efforts have been made in improving the hydrophilicity and anti-fouling performance by different methods such as surface coating [5, 6], the addition of hydrophilic additives [7] and inorganic material [6]. Among these materials, carbon nanotubes were regarded as ideal nanofillers for polymeric ultrafiltration membranes as they could provide extraordinary mechanical and thermal properties, improved water flux as well as anti-fouling behavior. However, the poor dispersion of CNTs in solvent and polymer has restricted its application. Therefore, some tactics were taken by surface modified such as carboxylation and hydroxylation to improve their hydrophilicity and the dispersion of CNTs in the polymer membranes. Moreover, the CNTs with different content of functional groups may result complicated effects on the resultant hybrid membranes, thus it is necessary to further study the unknown effect. In this study, three carboxylated MWCNTs with carboxyl content of 0.49, 2, 3.86 wt% and pristine MWCNTs were introduced to prepare PVDF/MWCNTs blended membranes by the phase inversion method. The characterization means included scanning electron microscopy (SEM), static contact angle, DSC. The synergism effects of carboxyl content of MWCNTs in membranes on the crystallization, surface morphology, hydrophilicity, and thermal properties were elaborated in details.
2. Experimental

2.1 Materials
Powdered polyvinylidene fluoride (904, Mw=450KDa) was purchased from Arkema Inc. N,N-dimethylformamide (DMF, purity ≥99.5%) used as solvent was supplied by Tianjin Guangfu technology development co., LTD. Pristine multi-walled carbon nanotubes (p-MWCNTs, length 10-30 μm) and MWCNT-COOH (carboxyl content 0.49 wt.%, length 0.5-2μm, 2 wt.% and 3.86 wt.%, length 10-30 μm) were obtained from Chengdu institute of organic chemistry.

2.2 Preparation of membranes and Membranes characterization
A certain amount of MWCNTs was dispersed in 30 ml DMF for 40 min by ultrasound assisted (KQ3200DB) until achieving a uniform dispersion. PVDF powder was dried at 60°C for 2h prior to use and then dissolved in DMF at 70°C for approximately 4 h to form a homogeneous casting solution, which was then cooled down and stored at room temperature overnight to remove the trapped air bubbles. The degassed solution was cast onto a glass plate by a rod with thickness 300 μm and dried for 7 min, which was immersed into a DI water coagulation bath at room temperature by a water/DMF exchange. After coagulation, the membranes were transferred to fresh DI water bath and stored for 2 days to remove the residual solvent. Finally, the membranes were dried in air at room temperature and stored. The PVDF/MWCNT blended membranes were prepared via phase inversion and labeled that contained carboxyl 0.49wt.%, 2wt.%, 3.86wt.% as F1-PVDF, F2-PVDF and F3-PVDF, respectively. The functional groups and crystalline structure of membranes were analyzed by wide angle X-ray diffraction (WXRD). The thermal behavior of the membranes and the effects of carbon nanotubes contained different carboxyl content on the glass transition temperature (Tg) were analyzed by differential scanning calorimetry (DSC, Perkin-Elmer, U.S.). The surface and cross-section morphology of the prepared membranes were investigated by scanning electron microscopy (SEM, Hitachis-4800, Hitachi Limited, Japan). The hydrophilicity of membrane was analyzed via water contact angle measurements (DSA-100), using the sessile drop method of water on dry membranes. And the measurement method of the pure water flux of the prepared membranes can be found in ref [8].

3. Results and discussion

3.1 Membrane properties
In order to determine crystal structure of prepared membranes and measure the phase qualitatively, we studied the five types of membranes by wide angle X-ray diffraction. Figure 1 (left) presents the XRD spectra for pure PVDF and all prepared MWCNTs/PVDF blended membranes. Two major diffraction peaks at 2θ values of 18.4° and 26.3° are observed in all membranes, which correspond to PVDF characteristic α-phase (020) and (021), respectively. A diffraction peak at 20.4° presents to the (110) and (200) of β-phase. For MWCNTs/PVDF membranes, the diffraction peak at 20.3° enhances, which hints that the incorporation of MWCNTs in PVDF matrix slightly alters the crystal transformation of PVDF. The formation of β-polymorph was induced by the interaction between carboxyl groups presented in MWCNTs and the -CF₂ segments in PVDF molecular chains. This further proves a better dispersibility of MWCNTs-COOH in PVDF membranes.

Differential scanning calorimetry was performed to distinguish the effect of adding various types of MWCNT to PVDF matrix on the Tg. A series of TG/DTG curves of pure PVDF membrane and four different MWCNTs/PVDF membranes tested were obtained, as shown in Figure 1.(right). The pure PVDF membrane starts to decompose at 450 °C, whereas, the decomposition temperatures of the other membranes shift to around 455 °C. The enhanced thermal stability of PVDF membranes contained MWCNTs is attributed to the presence of MWCNTs regardless of the type of MWCNTs and the carboxyl content in MWCNTs, in this case, as the variation of carboxyl content in MWCNTs is too small to dramatically change the overall thermal stability of the membranes. In comparison to p-MWCNTs/PVDF membranes, the slightly decreased thermal stability of all MWCNTs-COOH/PVDF blended membranes is directly correlated to the attached carboxyl, which
actually lowers the decomposition temperature. A significant decrease is observed in the composite with 3.86 % MWCNTs.

![Figure 1. XRD spectra (left) and TGA/DTG curves (right) of blended membrane PVDF, p-PVDF, F1-PVDF, F2-PVDF and F3-PVDF.](image)

3.2. Membrane morphology

The surface and cross-section morphologies of the various membranes were investigated by SEM, as shown in Figure 2. Three carboxylated MWCNTs with carboxyl content as 0.49, 2, and 3.86 wt% were selected for a comparison. It can be viewed from surface morphologies of all membranes that the type of MWCNTs has predominant effect on the porous structure. The membranes appear more macrovoids and aggregates on the surface, probably due to the fast phase separation process caused by higher evaporation speed of lower viscose solution. Compared with surface morphology of pure PVDF, more aggregates present on the surfaces of p-PVDF, which caused by worse dispersibility of p-MWCNTs, whereas, the surface morphologies of F1-PVDF exhibits rather smooth surface only a few macrovoids are found. The same tendencies are also observed in the blended membranes with higher carboxyl content in MWCNTs. These results verify that the hydrophilic carboxyl content in MWCNTs can actually promote its dispersibility in PVDF, enhance water diffusion, and thus inhibits the aggregation.

To the cross-section images, the membranes display a typical asymmetric structure with a thinner top-layer and a thicker sub-layer. The formation of such asymmetric structure originates from the solvent diffusivity in the membranes and water in the coagulation bath. For the membrane with different carboxyl content of MWCNTs, obvious discrepancies in cross-section morphology as follows: the pure PVDF membranes possess finger-like structure due to the low solution viscosity, but the membranes of p-PVDF, F2-PVDF and F3-PVDF have wider finger-like structures than pure PVDF. Besides, the finger-like pores of F1-PVDF membrane were obviously more homogeneous and shape more regularly. In order to explain the pore distribution, the membranes were characterized by BET method. From the analysis data of the bar graph, the major concentration of pore size distributed in 0-20nm, and pore structure of PVDF, F1-PVDF, F3-PVDF membranes was more concentrated and smaller than the other two, and the number of pores in F1-PVDF, F2-PVDF, F3-PVDF membranes had been on the rise, therefore, the MWCNT-COOH can enhance the formation of pore structures.
Surfaces and cross-sections morphologies of PVDF, p-PVDF, F1-PVDF, F2-PVDF, and F3-PVDF membranes (left). The pore size distribution of five membranes analyzed by BET is shown in the right column.

3.3. Hydrophilicity of membrane

To characterize the hydrophilicity of the different types of membranes, water contact angles on the membrane surfaces were measured and plotted in Figure 3.(A). All of the membranes exhibit a similar contact angle around 80°. With the increases of carboxyl content in MWCNTs, the hydrophilicity of membranes shows a trend of rising, which proves that the carboxyl content in MWCNTs affect the hydrophilicity of the MWCNTs/PVDF membranes to some extent. However, an exception is observed for the membrane with 2 wt.% carboxyl in MWCNTs. It has a water contact angle of above 90°, which displays slightly increase compared to the other membranes. Therefore, the membranes hydrophilicity is determined by not only the carboxyl contents of MWCNTs, but also the surface roughness of membranes. Permeability of the prepared membranes was characterized by measuring pure water flux, as presented in Figure 3.(B). Many factors may determine water flux, for example, morphologies of the membranes, pore properties and the dispersion of MWCNT. Compared with the water flux of PVDF membrane, the data of p-PVDF, F1-PVDF and F3-PVDF membranes were significantly enhanced, especially, the water flux of F1-PVDF membrane reached the maximum about 342 L/m²*h. However, the exception was also F2-PVDF membrane, the water flux abnormally reduced, which might be caused by hydrophilicity.

Figure 2. Surfaces and cross-sections morphologies of PVDF, p-PVDF, F1-PVDF, F2-PVDF, and F3-PVDF membranes (left). The pore size distribution of five membranes analyzed by BET is shown in the right column.

Figure 3. Water contact angle analysis and Water flux of PVDF, p-PVDF, F1-PVDF, F2-PVDF and F3-PVDF membranes
4. Conclusion
Carboxyl MWCNTs/PVDF flat hybrid membranes were prepared via the phase inversion method. The various performances of blended membranes had been markedly improved due to the addition of MWCNT-COOH. The crystal structure of F1-PVDF membrane enhances significantly, such as the diffraction peak at 18.4° and 26.3° more strengthen. It is observed the highest degradation temperature was 477 ℃ for the p-PVDF on account of the presence of MWCNTs. For the SEM, the p-PVDF and F2-PVDF membranes showed more large pores and aggregates, which made the pore size reduced and the pore distribution expanded. As for cross-section morphologies, all membranes presented both finger-like pores and dense sponge-like pores around the finger pores except for pure PVDF, which are attributed to the addition of MWCNT. Besides, adding MWCNTs-COOH to the membranes can indeed promote hydrophilicity of membranes and the present of carboxyl can enhance the binding forces between MWCNTs and PVDF matrix. The water flux of p-PVDF, F1-PVDF and F3-PVDF membranes were also significantly improved, especially, the water flux of F1-PVDF membrane reached the maximum.

5. References
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Acknowledgements
The research was supported by the Science and Technology Plans of Tianjin (No.15YFXQGX00070 and 15PTSYJC00240)