

Improved surface hydrophilicity of polyvinylidene fluoride ultrafiltration membranes

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A novel modification approach involves blending with polyvinyl alcohol and carboxylated multiwalled carbon nanotubes.

In recent years, polymeric membranes have become widespread in engineering applications and scientific usage.¹ Such membranes include polyamide,² polycarbonate,³ polyacrylonitrile,⁴ polytetrafluoroethylene,⁵ polysulfone,⁶ and polyethersulfone.⁷ In addition, polyvinylidene fluoride (PVDF) is typically regarded as a polymeric membrane material with outstanding characteristics, e.g., being acid-proof, alkali-proof, corrosion-resistant, and having excellent mechanical properties. PVDF has been applied widely in membrane bioreactors, water treatment, gas separation, and pollutants.^{8,9} The strong surface hydrophobicity of the PVDF, however, leads to lower permeability, susceptibility to pollutants, and increased maintenance costs.

To avoid these drawbacks, a blending method has been adopted by many researchers to improve the hydrophilicity of PVDF ultrafiltration (UF) membranes. For example, a PVDF UF membrane that was prepared by blending with graphene oxide exhibited improved antifouling properties.¹⁰ In addition, a PVDF UF has been developed with a hydrophilic polymer (cellulose acetate).¹¹ With this membrane, increased permeability and antifouling ability were achieved. Nonetheless, PVDF UF membranes still have unsatisfactory permeability and weakened mechanical properties, and there is thus still some room for improvement.

In our work¹² we propose a novel modification approach that involves a phase inversion method (where deionized water is used as the coagulation bath), to improve the surface hydrophilicity and other properties of PVDF UF membranes. In our methodology we blend hydrophilic polymer polyvinyl alcohol (PVA) and carbon nanomaterial, i.e., carboxylated multiwalled carbon nanotubes (MWCNT-COOHs) with the PVDF membranes. After preparation of our PVDF/PVA/MWCNT-COOH UF composite membranes, we conducted scanning electron microscopy (SEM) and atomic force microscopy (AFM) to study their morphology and topography,

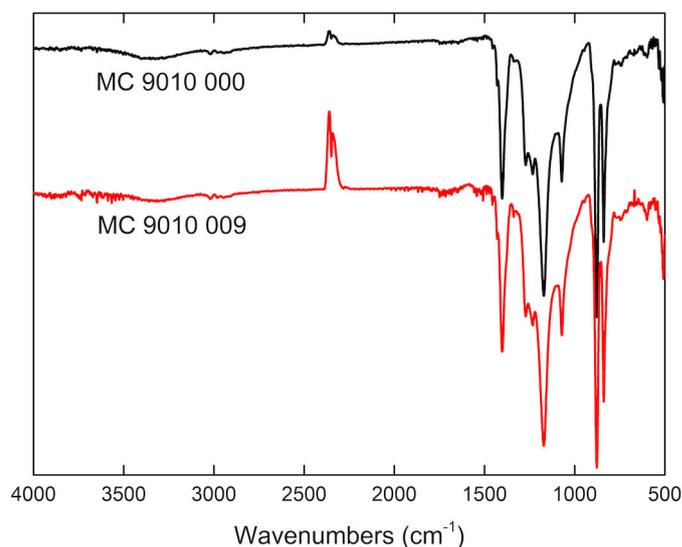


Figure 1. Fourier transform IR spectra of a polyvinylidene fluoride/polyvinyl alcohol (PVDF/PVA) membrane (MC 9010 000) and a PVDF/PVA membrane with 0.09wt% carboxylated multiwalled carbon nanotube (MWCNT-COOH) content (MC 9010 009).¹²

respectively. In addition, we conducted Fourier transform IR spectroscopy (FTIR), in the 500–4000cm⁻¹ range, to investigate the functional groups and chemical composition of the membrane. We also tested the performance and hydrophilicity of the modified membranes through a variety of measurements, i.e., pure water flux (PWF), flux recovery rate (FRR%), fouling resistance, as well as the rejection of polyethylene glycols and Dextran 600k. Lastly, we evaluated the porosity, pore size distribution, molecular weight cutoff, and the mechanical properties of our samples.¹³

From the FTIR spectra of our modified PVDF/PVA membrane samples (with MWCNT-COOH content of 0.00–0.15wt%),¹⁴ we observe weak, but wide, absorption bands in the 3100–3600cm⁻¹ wavelength

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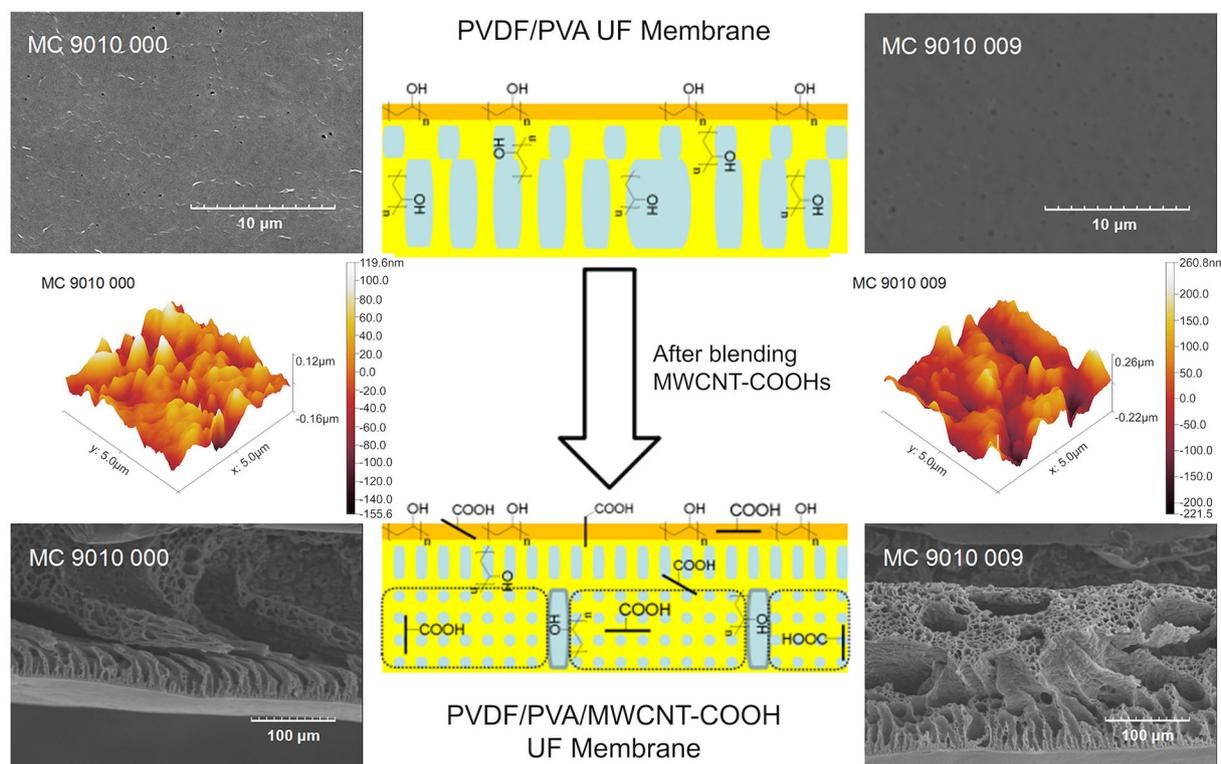


Figure 2. Scanning electron microscope (SEM) images of the external surfaces of two PVDF/PVA ultrafiltration (UF) membranes (MC 9010 000 and MC 9010 009) are shown in the top left and right, respectively. SEM images of the same samples's cross sections are shown in the bottom row. Atomic force microscope images of the modified membranes are also shown (center row). A schematic diagram of the structural transformation that occurs during the modification process is provided in the center column. The condensed structural formula of polyvinyl alcohol is used to present its long chains and dispersion in the membrane structure, where n is the degree of polymerization.¹²

range (see Figure 1). These bands correspond to oxygen–hydrogen absorption, which we ascribe to the presence of PVA acting as a pore-forming agent. All the spectra from the modified membranes also exhibit a stretching vibration at 1730cm^{-1} that is caused by the strengthening of carbon–oxygen double bonds. This vibration signature is strong evidence for the enhancement of the surface hydrophilicity of our modified membranes, which is caused by the increased COOH concentration.

SEM and AFM images, as well as the structural transformation of our modified membranes, are displayed in Figure 2. We find that all the membranes have a traditional asymmetric structure that consists of a compact skin layer and a variational sublayer. This sublayer can be further divided into an ‘upper part’ (a finger-like structure) and an ‘under part’ (a sponge-like structure). With increasing MWCNT-COOH content in the membrane matrix, the under part becomes denser and improves the mechanical properties of the modified membranes. From the SEM images, we identify macrovoid structures that are the

result of increased PWF. One particular membrane (MC 9010 009, i.e., with MWCNT-COOH content of 0.09wt%) has the most porous structure (porosity of 82.4%) we observe. It also has a rougher topography than the pristine PVDF/PVA membrane (i.e., which contains fewer macrovoid structures). This membrane thus has an enlarged effective filtration area and the best hydrophilicity of all our modified membranes.¹⁴

We also measured the PWF, FRR%, and fouling resistance of our modified composite membranes so that we could evaluate their hydrophilic performance. Our experimental results (see Figure 3) indicate that the PWF of the different samples clearly increased after blending. We observe a maximum PWF ($126.61\text{m}^{-2}\text{h}^{-1}$) when the MWCNT-COOH content reached 0.09wt% (i.e., for sample MC 9010 009). The high porosity value of this sample also illustrates the effects of PVA and MWCNT-COOH. In addition, this sample exhibits the peak FRR%

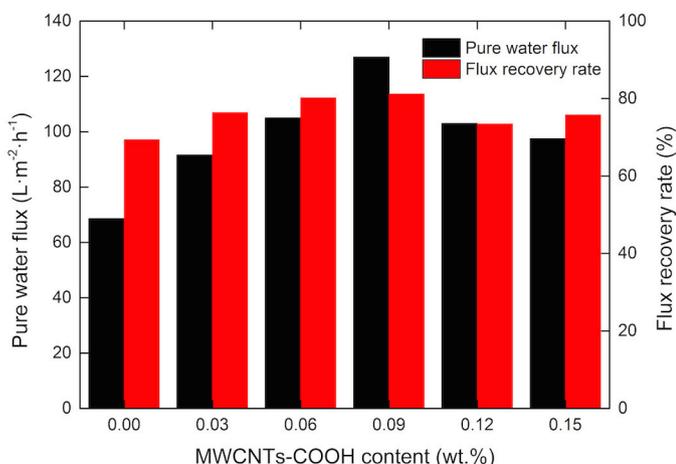


Figure 3. The relationship between MWCNT-COOH content, pure water flux, and flux recovery rate of the PVDF/PVA UF membranes.¹²

value that we observe (81.2%), which is about 17% greater than the sample containing no MWCNT-COOH. With such enhancements of surface hydrophilicity, it is easy to wash out pollutants from the membrane surface. We also find that the fouling resistance ratio of the samples changes in the same way as for the FRR%. MC 9010 009 thus has the highest reversible fouling ratio and the lowest total fouling ratio, which represents the best membrane surface antifouling ability of all our modified composite membranes.¹⁵ Moreover, dynamic contact angle measurements indicate that the introduction of MWCNT-COOH into our composite membranes may also improve the surface hydrophilicity. For instance, the contact angle of the unmodified PVDF/PVA membrane is 60.1°, but after blending for 30 seconds (to produce MC 9010 009), the angle reaches a minimum value of 38.9° (the contact angle remains steady for longer blending times/higher MWCNT-COOH content).

In summary, we have successfully developed a novel hydrophilic PVDF UF membrane preparation approach in which we blend the hydrophilic polymer with carbon nanomaterial. Our experimental results indicate that the inclusion of PVA and MWCNT-COOH into the membrane can substantially improve the surface hydrophilicity. The enhanced performance of our PVDF/PVA/MWCNT-COOH UF membranes is caused by their porous surface structure and denser sublayer, and they thus exhibit excellent performance in a Dextran 600k aqueous solution (0.5g/l), i.e., with separation and rejection of up to 91.0%. In our future work, we will aim to realize further improvements to the performance of PVDF UF membranes obtained with our method. For instance, it may be beneficial to use more compatible hydrophilic polymers (e.g., polyvinyl butyral) and novel carbon materials in more optimal conditions.

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References

1. J. Yin and B. Deng, *Polymer-matrix nanocomposite membranes for water treatment*, **J. Membrane Sci.** **479**, pp. 256–275, 2015.
2. J.-G. Gai, X.-L. Gong, X. Zhang, W.-L. Kang, and W.-W. Wang, *Key role of hydrates in determining ion rejection by polyamide membrane*, **Polym. Eng. Sci.** **55**, pp. 466–473, 2015.
3. Y.-J. Fu, J.-T. Chen, C.-C. Chen, K.-S. Liao, C.-C. Hu, K.-R. Lee, and J.-Y. Lai, *Characterization of morphology and gas separation performance of dry-cast polycarbonate membranes*, **Polym. Eng. Sci.** **53**, pp. 1623–1630, 2013.
4. N. A. M. Nazri, W. J. Lau, A. F. Ismail, T. Matsuura, D. Veerasamy, and N. Hilal, *Performance of PAN-based membranes with graft copolymers bearing hydrophilic PVA and PAN segments in direct ultrafiltration of natural rubber effluent*, **Desalination** **358**, pp. 49–60, 2015.
5. S. Y. Park, J. W. Chung, and S. Y. Kwak, *Regenerable anti-fouling active PTFE membrane with thermo-reversible ‘peel-and-stick’ hydrophilic layer*, **J. Membrane Sci.** **491**, pp. 1–9, 2015.
6. S. M. Mousavi, E. Saljoughi, Z. Ghasemipour, and S. A. Hosseini, *Preparation and characterization of modified polysulfone membranes with high hydrophilic property using variation in coagulation bath temperature and addition of surfactant*, **Polym. Eng. Sci.** **52**, pp. 2196–2205, 2012.
7. M. L. Méndez, A. I. Romero, V. B. Rajal, E. F. Castro, J. I. Calvo, L. Palacio, and A. Hernández, *Properties of polyethersulfone ultrafiltration membranes modified with polyethylene glycols*, **Polym. Eng. Sci.** **54**, pp. 1211–1221, 2014.
8. J. A. Kharraz, M. R. Bilad, and H. A. Arafat, *Simple and effective corrugation of PVDF membranes for enhanced MBR performance*, **J. Membrane Sci.** **475**, pp. 91–100, 2015.
9. G.-D. Kang and Y.-M. Cao, *Application and modification of poly(vinylidene fluoride) (PVDF) membranes—a review*, **J. Membrane Sci.** **463**, pp. 145–165, 2014.
10. C. Zhao, X. Xu, J. Chen, and F. Yang, *Effect of graphene oxide concentration on the morphologies and antifouling properties of PVDF ultrafiltration membranes*, **J. Environ. Chem. Eng.** **1**, pp. 349–354, 2013.
11. M. H. Razzaghi, A. Safekordi, M. Tavakolmoghadam, F. Rekabdar, and M. Hemmati, *Morphological and separation performance study of PVDF/CA blend membranes*, **J. Membrane Sci.** **470**, pp. 547–557, 2014.
12. G.-E. Chen, S.-J. Xu, Z.-L. Xu, W.-W. Zhu, Q. Wu, and W.-G. Sun, *Preparation and characterization of novel hydrophilic PVDF/PVA UF membrane modified by carboxylated multiwalled carbon nanotubes*, **Polym. Eng. Sci.**, 2016. First published online: 19 April. doi:10.1002/pen.24325
13. P.-Y. Zhang, Z.-L. Xu, X.-H. Ma, H. Yang, W.-Z. Wu, Y.-M. Wei, and Y.-D. Liu, *Fabrication and characterization of PVDF hollow fiber membranes employing in-situ self-assembly modulation concept*, **J. Membrane Sci.** **486**, pp. 119–131, 2015.
14. Y.-J. Tang, L.-J. Wang, Z.-L. Xu, Y.-M. Wei, and H. Yang, *Novel high-flux thin film composite nanofiltration membranes fabricated by the NaClO pre-oxidation of the mixed diamine monomers of PIP and BHTM in the aqueous phase solution*, **J. Membrane Sci.** **502**, pp. 106–115, 2016.
15. X. Shen, X. Yin, Y. Zhao, and L. Chen, *Antifouling enhancement of PVDF membrane tethered with polyampholyte hydrogel layers*, **Polym. Eng. Sci.** **55**, pp. 1367–1373, 2015.