Study on surface adhesion of Plasma modified Polytetrafluoroethylene hollow fiber membrane

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Abstract. Polytetrafluoroethylene (PTFE) is popular membrane material because of its excellent thermal stability, chemical stability and mechanical stability. However, the low surface energy and non-sticky property of PTFE present challenges for modification. In the present study, plasma treatment was performed to improve the surface adhesion of PTFE hollow fiber membrane. The effect of discharge voltage, treatment time on the adhesion of PTFE hollow fiber membrane was symmetrically evaluated. Results showed that the plasma treatment method contributed to improve the surface activity and roughness of PTFE hollow fiber membrane, and the adhesion strength depend significantly on discharge voltage, which was beneficial to seepage pressure of PTFE hollow fiber membrane module. The adhesion strength of PTFE membrane by plasma treated at 220V for 3min reached as high as 86.2 N, far surpassing the adhesion strength 12.7 N of pristine membrane. Furthermore, improvement of content of free radical and composition analysis changes of the plasma modified PTFE membrane were investigated. The seepage pressure of PTFE membrane by plasma treated at 220V for 3min was 0.375 MPa, which means that the plasma treatment is an effective technique to improve the adhesion strength of membrane.

1. Introduction

Polytetrafluoroethylene (PTFE) porous membrane was an attractive membrane material, due to its outstanding chemical stability, superior heat resistance, strong hydrophobicity, and high fracture toughness [1]. These properties make it ideally suited for a variety of liquid and gas separation applications, especially for membrane distillation, gas-liquid absorption and industrial flue gas filtration in the strong acid, or corrosive condition [2, 3]. However, due to its highly symmetrical nonpolar linear configure ration, PTFE has low surface energy and inert surface properties, such as poor wettability and poor adhesion property [4], and it is thus difficult to modify PTFE membranes because the forces between the chained molecules are very strong. So it is necessary and challenging to modify the adhesion property of PTFE.

In recent years, several approaches have been developed to prepare hydrophilic or anti-fouling PTFE material, including wet-chemical method with sodium naphthalene [5], deposition [6,7], corona
charging [8,9,10], graft copolymerization and irradiation grafting. However, most of these attempts were complicated, and tried on PTFE flat membranes or PTFE micropowder. Few studies have dealt with surface adhesive bonding properties of PTFE hollow fiber membrane. Therefore, for some industrial applications, it is highly demanded to find a simple route to effectively enhance the wettability and adhesion of PTFE hollow fiber membranes under moderate operation conditions.

Herein, we propose a plasma treatment approach to modify PTFE hollow fiber membrane for strong adhesion property. The plasma treatment was performed with different discharge voltage, treatment time at the same discharge current and electrode distance on the PTFE hollow fiber membrane. The effects of plasma treatment on the morphology and adhesion properties were investigated. The plasma treated PTFE membrane was made into membrane module and was applied in seepage pressure test. Adhesion improvement comparison was also made with traditional wet-chemical-method-modified membrane. The membranes were characterized using Electron-spin resonance spectrometer, Energy Dispersive X-Ray Spectroscopy and Optical Profiler, and the relationship between the adhesion performances of membrane module and the plasma treatment parameters was also discussed.

2. Experimental

2.1. Materials
Polytetrafluoroethylene hollow fiber membrane (PTFE) was obtained from Zhejiang DD Water Industry Co., Ltd; Epoxy adhesive CYD-128 was purchased from Sinopec Baling Branch Company;

Plasma generator.: CTP-2000A, Nanjing Suman Electronics Co., Ltd.

2.2. Modification of PTFE hollow fiber membrane
PTFE hollow fiber membrane was put in Plasma generator at atmospheric pressure with axial rotation, and then the effect of process parameters including discharge current, treatment time, and discharge voltage on the surface properties of the PTFE membrane was systematically studied.

3. Characterization
The content of free radical in modified PTFE hollow fiber membrane was measured by electron-spin resonance (ESR) spectrometer (FA-200, Bruker, Germany).

Composition analysis of the PTFE membrane was characterized by using field emission scanning electron microscopy (SEM) (Nano SEM 430, FEI, USA) and Energy Dispersive X-Ray Spectroscopy (EDX).

The surface profile and roughness of the PTFE hollow fiber membrane was measured by Optical Profiler (Contour GT-K, Bruker, Germany).

The adhesion strength of the PTFE hollow fiber membrane, the original length of which was 100 mm, was investigated by measurements with an Instron apparatus (Instron 5965 U1570-500N, Environmental Chambers 3119-609, Instron Corporation, USA) at 25°C and 65% RH. For the tension load between the membrane and the resin adhesive, the sample was clamped at top end and pulled out of the resin adhesive at a constant elongation rate of 250 mm/min referencing China Standard of GB/T 2790-1995.

The seepage pressure of PTFE hollow fiber membrane module was tested by self-designed water pressure test equipment. Increasing of water pressure slowly, the seepage pressure was tested when the water seep from the joint between the membrane and the resin adhesive.

4. Results and discussion

4.1. Free radical amount/surface activity of PTFE hollow fiber membrane
ESR was used to characterize the surface activity of the samples. Figure 1 showed the ESR spectra of PTFE hollow fiber membrane with different plasma treatment time. As can be seen from Figure 1, no
signal could be observed in the pristine membrane. With increasing the treatment time from 1 to 3 min, the signal strength was significantly improved. However, when further increasing the treatment time, signal strength was gradually decreased. This observation indicated that a best free radical level and the surface activity of membrane were obtained for the membrane treated for 3min.

![Figure 1. ESR spectra of PTFE hollow fiber membrane with different plasma treatment time](image)

**Figure 1.** ESR spectra of PTFE hollow fiber membrane with different plasma treatment time

4.2. **Effect of voltages on average roughness of PTFE hollow fiber membrane**

Figure 2 shows the variation of roughness of the membrane surface at different voltages and treatment times, it was clear that when discharge voltage was 140V, 160V, 180V, 200V respectively, there is no obvious change on membrane surface average roughness with increased treatment time; the membrane surface roughness at 220V was much higher than that at other four voltages with the same treatment time; and it increased with prolonged treatment time. This is because plasma power between electrodes will increase as voltage rises, the energy increasing over the bond energy of C-F or C-C when the discharge voltage increased to 220V, this makes the C-F or C-C bond of the membrane surface open gradually. The impact frequency of filamentous micro-discharge increases, then the plasma streamer impacts the surface of the membrane materials, and therefore the surface morphology became rougher with the increase of voltage.

![Figure 2. Surface roughness of PTFE membrane at different voltages and treatment times](image)

**Figure 2.** Surface roughness of PTFE membrane at different voltages and treatment times
The surface morphology changes on the plasma-modified PTFE hollow fiber membrane can be seen from Figure 3. It could be seen that the pristine PTFE hollow fiber membrane has the microstructure of nodes interconnected by fibrils. The surface of membrane became “ditch” like morphology when plasma treatment time increased over 3 min. Porous PTFE hollow fiber membranes were prepared through stretching mechanical operation with node-fibril surface characteristics. The fibril was easily damaged with increasing degree of plasma treatment. It is indicated that the C-F or C-C bond of the membrane surface open thoroughly with excessive treatment energy and time, resulting in the break of hollow fiber membrane ultimately.

Figure 3. Surface morphology of the PTFE hollow fiber membrane (a. pristine membrane b. plasma-1min c. plasma-3min d. plasma-10min).

4.3. Elemental composition of PTFE hollow fiber membrane
Figure 4 shows the ratio of C/F and oxygen amount of PTFE membrane at different voltages and treatment times. It can be seen that at 200 V discharge voltage, C/F increased from 0.25 to 0.55, and content of oxygen atoms increased from 0% to 1.15%. At 220 V discharge voltage, C/F increases from 0.25 to 1.52, content of oxygen atoms increases from 0% to 17.36%. This observation indicated that the C-C and C-F bond were broken and new Oxygen free radicals or groups were generated at 220 V discharge voltage. This observation was also in good agreement with that found in ESR (as shown in Figure 1).
Figure 4. Ratio of C/F and oxygen amount of PTFE membrane at different voltages and treatment times

4.4. Stretching adhesive strength of PTFE hollow fiber membrane module
Figure 5 illustrates the effect of discharge voltage on the tensile load between the plasma-PTFE hollow fiber membrane and epoxy adhesive. Remarkably, with increasing the voltage, the tensile load increased significantly. The tensile load was 12.7 N without treatment, however, when increasing the discharge voltage to 140V, the tensile load increased to 34.6 N. When further increasing the discharge voltage to 220V, the tensile load increased to 86.2 N. The reason for this observation was that the energy of plasma was higher at higher discharge voltage, resulting in higher surface activity of the membrane. As a result, better adhesion between membrane and epoxy adhesive could be obtained.

Figure 5. Stretching adhesive strength of PTFE hollow fiber membrane module at different voltage

4.5. Seepage pressure of PTFE hollow fiber membrane module
The effects of plasma modification on seepage pressure of PTFE hollow fiber membrane were shown in Table 1. The epoxy adhesive was used as adhesion to prepare all the membrane modules. The seepage pressure of Module-P (membrane module prepared with pristine membranes) was 0.10MPa. With increasing the discharge voltage, the seepage pressure of Module-plasma (membrane module prepared with plasma treated membranes) were increased correspondingly. At 220 V discharge voltage, a seepage pressure of 0.375 MPa was achieved. This value was about 3 times higher when compared to the pristine module, indicating that plasma treatment could effectively improve the interfacial adhesion between the epoxy adhesive and PTFE hollow fiber membrane.
Table 1. Results of seepage pressure test

| Sample Description | Membrane treatment method | Treatment Parameter | Adhesion | Seepage pressure (MPa) |
|--------------------|---------------------------|---------------------|----------|-----------------------|
| Module-P pristine membrane | — | | Epoxy adhesive | 0.10 |
| Module-plasma Plasma-1 | 140V, 3min, 4A, 8cm | | Epoxy adhesive | 0.325 |
| Module-plasma Plasma-2 | 160V, 3min, 4A, 8cm | | Epoxy adhesive | 0.335 |
| Module-plasma Plasma-3 | 180V, 3min, 4A, 8cm | | Epoxy adhesive | 0.335 |
| Module-plasma Plasma-4 | 200V, 3min, 4A, 8cm | | Epoxy adhesive | 0.350 |
| Module-plasma Plasma-5 | 220V, 3min, 4A, 8cm | | Epoxy adhesive | 0.375 |

5. Conclusion
In this study, the plasma treatment was performed to improve the surface adhesion of PTFE hollow fiber membrane. It was found that the content of free radical and surface activity was enhanced by the plasma treatment. The plasma treatment voltage has significantly change the improvement of surface roughness of the PTFE membrane, which was verified with Optical Profiler observations, and strongly affected the adhesion strength between the membranes and epoxy adhesive. The plasma treatment effectively enhanced the adhesion property of the PTFE hollow fiber membrane and thus an improvement of the seepage pressure was achieved for the membrane module. This study showed that plasma treatment could effectively improve the interfacial adhesion between the epoxy adhesive and PTFE hollow fiber membrane, and thus greatly improve performance of membrane.

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References
[1] Xiaoqun Wang, Jiecai Han, Shanyi Du. A novel crystalline structure Poly (tetrafluoroethylene) spherulitic crystal and its crystallization kinetics. Macromolecular Symposia, 148 (1999) 455-461.
[2] Hailin Zhu, Hongjie Wang, Feng Wang, Yuhai Guo, Huapeng Zhang, Jianyong Chen. Preparation and properties of PTFE hollow fiber membranes for desalination through vacuum membrane distillation. Journal of Membrane Science, 446 (2013) 145-153.
[3] Dhananjay Singh, Kamalesh K. Sirkar. Desalination of brine and produced water by direct contact membrane distillation at high temperatures and pressures, Journal of Membrane Science, 389 (2012) 380-388.
[4] E. David, A. Lazar, A. Armeanu, Surface modification of polytetrafluoroethylene for adhesive bonding, Journal of Materials Processing Technology, 157-158 (2004) 284-289.
[5] Yan Qin, Jinrong Jia, Zhixiong Huang, PTFE treated with sodium naphthalene solution and low temperature radio frequency plasmas, Engineering Plastics Application, 39 (2011) 4-7.
[6] Sikuai Xue, Chengcai Li, Jiuming Li, Hailin Zhu, Yuhai Guo. A catechol-based biomimetic strategy combined with surface mineralization to enhance hydrophilicity and anti-fouling property of PTFE flat membrane, Journal of Membrane Science, 524 (2017)409-418.
[7] Zahira Ghalmi, Masoud Farzaneh. Durability of nanostructured coatings based on PTFE nanoparticles deposited on porous aluminum alloy, Applied Surface Science, 314 (2014)564-569.
[8] K. Ozeki, K.K. Hirakuri. The effect of nitrogen and oxygen plasma on the wear properties and adhesion strength of the diamond-like carbon film coated on PTFE, Applied Surface Science, 254 (2008) 1614-1621.
[9] Cheng-Lee Lai, Rey-May Liou, Shih-Hsiung Chen, Guan-Wei Huang, Kueir-Rarn Lee.
Preparation and characterization of plasma-modified PTFE membrane and its application in direct contact membrane distillation, Desalination, 267 (2011) 184-192.

[10] A Sarani, N De Geyter, Nikiforov, R. Morent, C. Leys, J. Hubert, F. Reniers. Surface modification of PTFE using an atmospheric pressure plasma jet in argon and argon+CO2, Surface Coating Technology, 206 (2012) 2226-2232.