Anti-Pollution Modification of Polyethersulfone Hollow Fiber Ultrafiltration Membranes

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Abstract: In this work, the MWCNTs -OH/ polyether sulfone (PES) flat membranes were prepared by nonsolvent-induced phase separation (NIPS),.The effect of the contents of MWCNTs -OH was studied. Additionally, the novel membranes were characterized by XRD, FTIR and other methods. The antifouling ability of the membranes were tested in our work, exhibited high flux and rejection when the contents of the MWCNTs -OH were 0.04wt%, the water flux was enhanced to 88.42%, the rejection of BSA was increased to 95.77%, the water contact angle was decreased to 62.21°, The good properties of the MWCNTs -OH /PVDF composite membranes make it possible to be a good potential candidate for water treatment.

1. Introduction

When membranes were used in wastewater treatment, it can be easily polluted, so that the membrane performance degradation leading to the increase of the cost, which matters in the market, therefore membrane fouling is the main reason for the development of ultrafiltration membranes, mainly refers to the pollutants in the aqueous solution of easy adsorption or deposited on the membrane surface, which may lead to membrane pore blockage, [1] specificly displays in: The water flux of the membrane will decrease with the increase of time. Concentration polarization and other membrane hole blockage problems will result in the increase of pressure difference on both sides of the membrane.[2] In this chapter, carbon nanotubes were hydroxylated in the casting solution to explore whether the anti-pollution performance of polyethersulfone hollow fiber ultrafiltration membrane was improved.

2. Preparation of Mwcnts-Oh /Pes Blend Membrane

Carbon nanotubes (CNTS) are nanomaterials with light weight and special structures. They have been widely studied and used in various fields due to their special electrical, mechanical, optical and catalytic properties. In this work, the hydrophilic modification of PES hollow fiber membrane was carried out by mixing PES with MWCNTs-OH to explore whether it can improve the hydrophilicity of the membrane and further improve the anti-pollution performance of the membrane. [3]According to the literatures, hydrophilicity of MWCNTs-OH was significantly improved, so we speculated that the addition of MWCNTs-OH into PES casting solution might make help in some extent. Fig.1 Shows the Possible Mechanism of Ho· Interaction with Mwcnts:

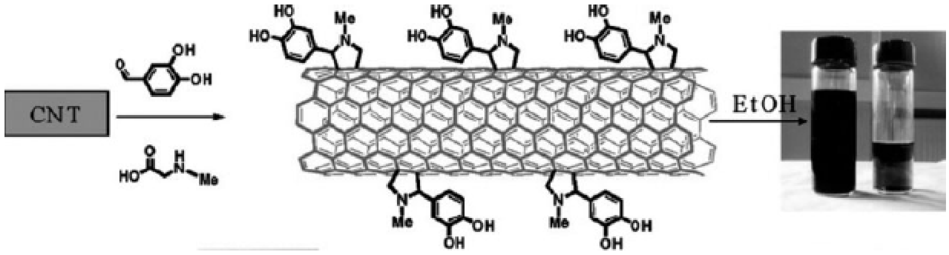

Fig.1 Mechanism of Ho· Interaction with Mwcnts:

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All chemicals and solvents were purchased from commercial suppliers and used without further purification. Adding MWCNTs-OH to DMAC in ultrasonic dispersing until MWCNTs - OH distributed evenly in the solution, and then in the electronic scales weighing PES resin and other hole agents into three flask, then placed three flask in a heating in 80 ℃ for 8 h, until the casting solution was uniform and stable, then pour casting solution spinning machine material tank let stand for 12 h to remove air bubbles, finally the MWCNTs-OH/PES hollow fiber membranes were spinned.[4]

3. X-Ray Diffraction Analysis

Figure 2 is the X ray diffraction analysis additions of different concentration of MWCNTs - OH of the blend membrane, which shows that with the increase of the contents of MWCNTs-OH, the intensity of the diffraction peak height increases, when the content was 0.04 wt %, the peak intensity is maximum, it may be that the MWCNTs-OH in the casting solution acts as the nucleating agent, the crystallization process of PES provides a large number of crystal nucleus. However, when the content of MWCNTs-OH is further increased, the agglomeration phenomenon of MWCNTs-OH nanoparticles maight lead to the decrease of crystal contents, and the increase of grain size due to the enhancement of electrostatic action and spatial hindrance. [5]

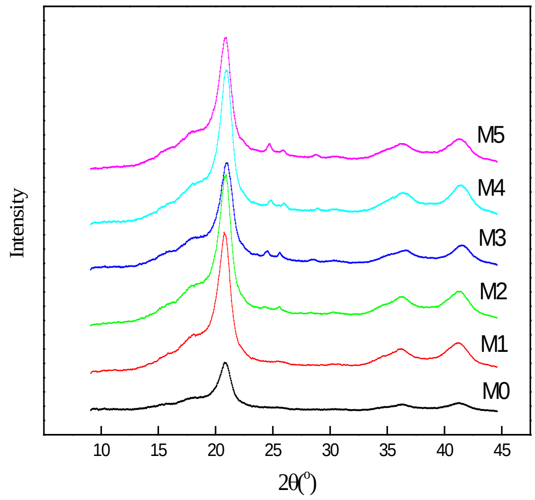

Fig.2 X-Ray Diffraction of the Blend Membranes and the Pure Membranes

4. Membrane Structure Characterization

Figure 3 shows the SEM of the membranes, with different contents of MWCNTs-OH, the blend membranes existed in the finger big pore structures, and spongy, with means that a lower content of MWCNTs-OH can promote the formation of finger holes, with higher levels of MWCNTs-OH, narrow finger holes will become smaller, it may be because of the low contents of MWCNTs - OH dispersed evenly in the solvent, in the subsequent process of phase separation, [6] The rapid exchange between solvent and non-solvent in the casting solution can produce a pull effect on MWCNTs-OH, accelerate the instantaneous phase. However, when the contents of MWCNTs-OH in the casting solution was high, the dispersion of them in the solvent was not uniform, and most of it presented different agglomeration states, which slowed down the exchange rate between solvent and non-solvent to a certain extent, and the delay phase division was the majority, thus inhibiting the formation of macropores.

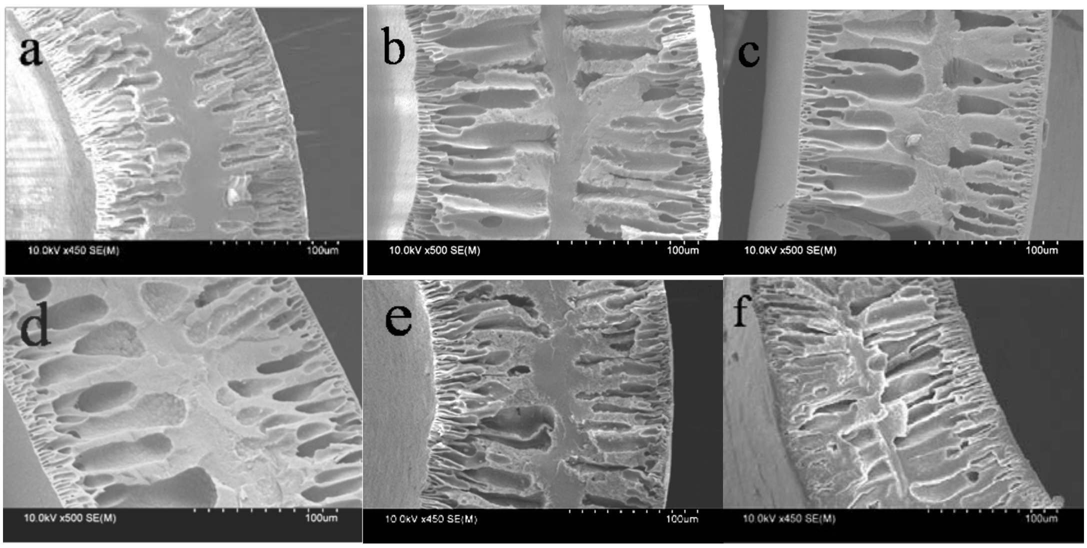

Fig.3 The Sem of Different Additions of the Mwcnts-Oh

5. Influence of Mwcnts-Oh Additions on the Viscosity of the Casting Solution

FIG. 4 shows the relationship between the contents of MWCNTs-OH and the viscosity of the casting solution. It can be seen from the figure that the viscosity of the corresponding casting solution increases with the increase of the amounts of MWCNTs-OH.[7] The main reason may be that with the increase of MWCNTs-OH contents in the casting solution, the electrostatic action and spatial hindrance between carbon nanotubes and other forces wered increased, which might lead to the increase of the friction force of the molecules.

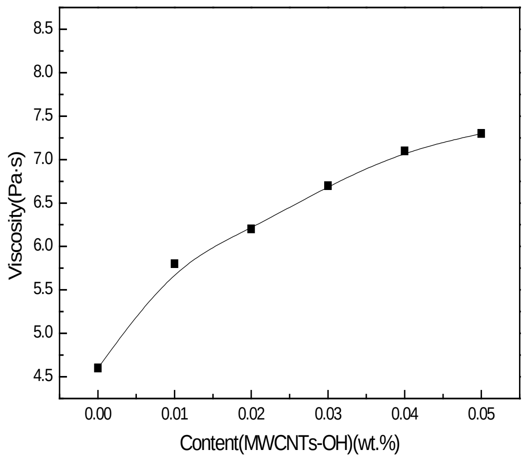

Fig.4 The Influence of the Different Additions of the Mwcnts-Oh

6. Influence of Mwcnts-Oh Addition on Membrane Separation Performance

Figure 5 is the influences of the flux and rejection of the amounts of the MWCNTs-OH of the blend membranes,analysis diagram shows that when the MWCNTs-OH in the casting solution content is 0.04 wt %, the water flux is at its maximum, up to 508.94 L/(h· m^2), the reason may be mentioned in the SEM, which can also see that when the MWCNTs-OH in the casting solution content is low, Macroscopically, the water flux and porosity of the membrane increased. In addition, the presence of a large number of hydroxyl groups can accelerate the dynamic phase of the solution, so that the exchange rate between solvent and non-solvent increases, forming a macroporous structure.[8] However, when the contents of MWCNTs-OH exceeds 0.04wt%, the macroscopic expression is the increase of the viscosity of the casting solution, the majority of the delay phase division is more conducive to the formation of dense pore structure, and the expression is the decrease of porosity and water flux.

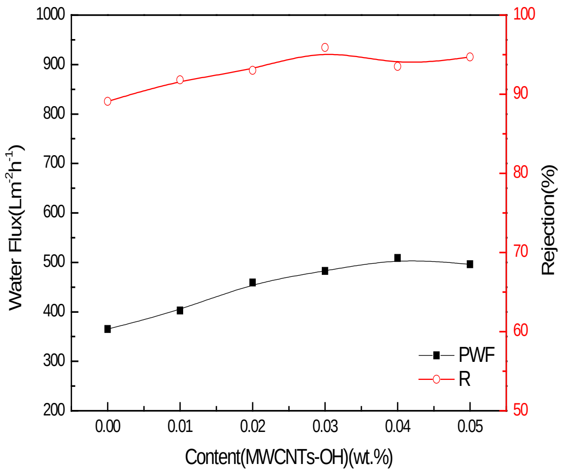

Fig.5 -1 the Flux and Rejection of the Blend Membranes

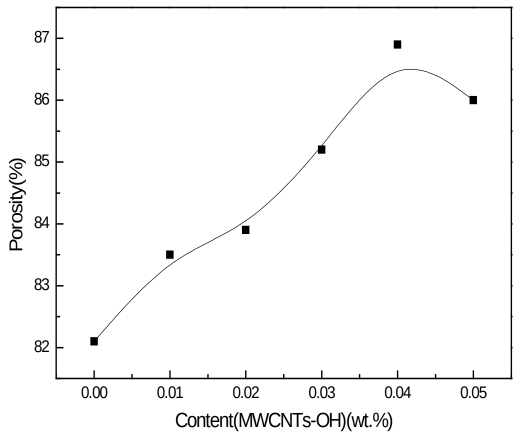

Fig.5 -2 the Porosity of the Blend Membranes

7. Influence of Mwcnts-Oh Addition on Membrane Mechanical Properties

figure 6 shows that the mechanical strength of blend membrane were increased with the increase of MWCNTs-OH up to maximum when it is 0.04 wt % when maximum, it may be because of the MWCNTs-OH in molecular hydrogen bonds formed in the casting solution makes the intermolecular forces stronger. however, with further increase of the MWCNTs-OH, [9]it may be dispersed not completely, MWCNTs-OH itself and other solvent molecules intermingle with each other and even agglomerate, resulting in incomplete phase separation, which is further manifested as a slight decrease in the mechanical strength of the membranes.

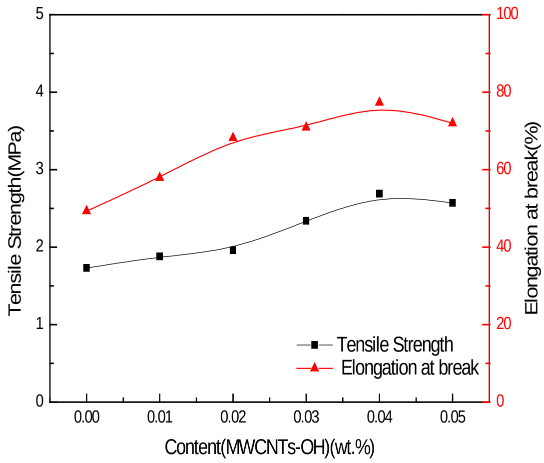

Fig.6 The Mechanism Strength of the Blend Membranes

8. Influence of Mwcnts-Oh Addition on Membrane Water Contact Angle

Figure 7 is a the influence of the MWCNTs-OH content of the membranes, which shows that with the increase of MWCNTs-OH, the water contact Angle showed a trend of decrease , the reason may be that when the the contents of MWCNTs-OH is low, it can be dispersed evenly in the solvent, the existence of hydroxyl also makes the hydrophilic enhancement so that contact Angle decreased, but when the content is higher, MWCNTs-OH tangles or reunion phenomenon happens, hydrophilic group seems to reduce, the contact Angle is increased. [10-13]

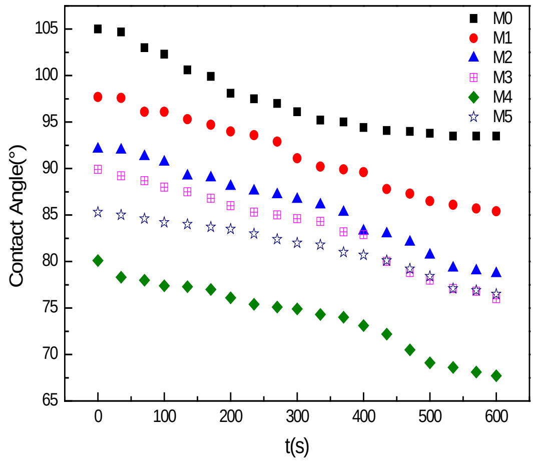

Fig.7 The Water Contact of the Blend Membranes

9. Influence of Mwcnts-Oh on Anti-Fouling and Self-Cleaning Properties of the Membrane

FIG. 8-1and 8-2 show the anti-fouling and self-cleaning properties of the blend membranes. We can see that the flux recovery rate of the membranes are improved compared with the pure membrane, the most prominent is at the amount of 0.04 wt % of the MWCNTs-OH, [14] the flux recovery rate in the three period were all higher than 82%, the reason may be due to he hydrophilicity of the membrane can be improved by the sulfonic acid groups of the MWCNTs-OH, while if the MWCNTs-OH content is higher, it might be not completely dispersed in the casting solution, macro performance for membrane hydrophilic group can be decreased, as well as the hydrophilic. [15]

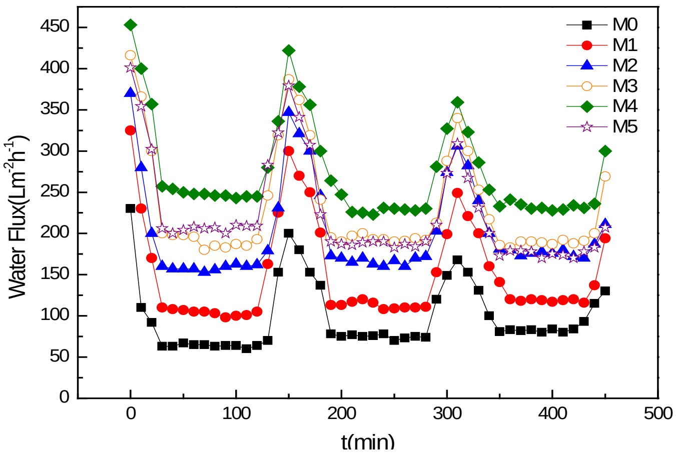

Fig.8 -1 the Flux the Blend Membranes during the Three Pollution

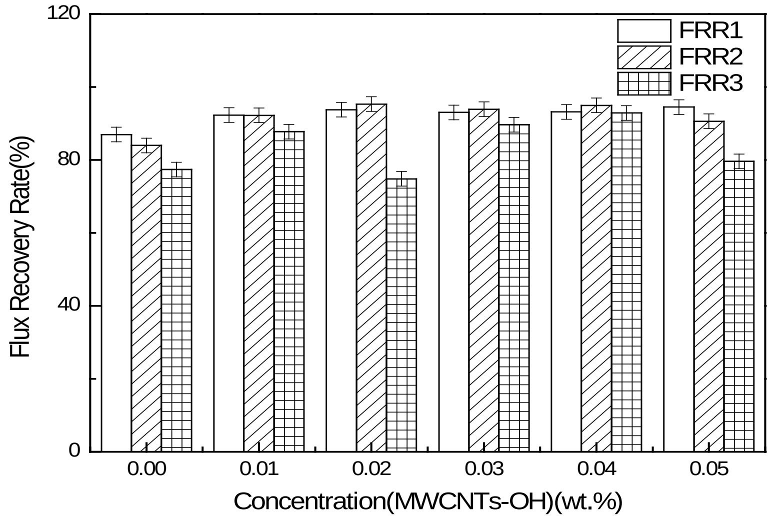

Fig.8 -2 the Frr of the Blend Membranes during the Three Pollution Periods

10. Conclusion

In this work, the MWCNTs-OH/PES blend membranes were preparaed, the MWCNTs-OH content influence on the performance of the membranes were explored through the water contact Angle, porosity, FFR test and others, which shows that the addition of MWCNTs-OH can dramatically improve the hydrophilicty of the membrane, the pollution resistance of the membranes also be improved greatly, in addition, the porosity and mechanical strength of membrane has a certain degree of increase.[16] Through three pollution period tests, the flux recovery rate of MWCNTs-OH was all higher than 82% with the addition amount of MWCNTs-OH was 0.04%, while the flux attenuation rate of the pure PES membrane was 67.3% and the recovery rate was only 33.1%. The anti-pollution property of the membrane was obviously improved.

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