Surface modification of cellulose nanofibers and their effects on the morphology and properties of polysulfone membranes

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Abstract. Cellulose nanofibers (CNF) with direct surface modification in the presence of methacryloxypropyltrimethoxysilane (MPS) improve the compatibility between polysulfone (PSf) and CNF due to the hydrophobicity of PSf and hydrophilicity of CNF. The conclusion of Fourier transforms infrared spectrometer (FT-IR) and X-ray Photoelectron Spectrometer (XPS) indicated that the chemical changes have taken place. Differential scanning calorimetry (DSC) showed that the addition of M-CNf improved the thermal stability of PSf membranes. The morphology of PSf/MPS modified CNF (M-CNf) composite membranes prepared by a Loeb-Sourirajan (L-S) phase inversion process was characterized with a scanning electron microscopy (SEM). Tensile testing turned out that the composite membranes showed best mechanical property when 0.3 wt.% CNF with 0.2 v/v % MPS modified were added. Pure water flux and BSA rejection demonstrated that the addition of M-CNf increases the permeability of the membrane.

1. Introduction
Phase inversion process has been one of the most effective approaches to preparing asymmetric polymeric membranes, especially non-solvent induced phase separation (NIPS) process. Phase separation occurs by the exchange of solvent (S) and non-solvent (NS) across the interface between the casting film and coagulation bath. The asymmetric membranes are generally made from polymers such as poly (vinylidene fluoride) (PVDF), polysulfone (PSf) and polyethersulfone (PES) [1-3]. PSf is often used as a membrane material, by the reason of its good mechanical properties. [4, 5]. However, the hydrophobicity of PSf often causes the membranes serious membrane fouling usually. when solutions containing some certain substances, such as proteins, so, it becomes quite necessary to improve the hydrophilicity of PSf membrane.

Cellulose nanofibers (CNF) are obtained from cellulose with the following treatment: sulfuric acid hydrolysis and high-pressure homogenization. CNF have excellent hydrophilic and mechanical properties, making it an effective reinforcing agent for various composite materials. [6,7]. However, the significant hydrophilic character of CNF is bad for their compatibility with the hydrophobic polymeric matrixes, resulting in uneven distribution of the CNF within the matrix [8] and limited improvement of mechanical properties. It is therefore necessary to treatment the surface of CNF to improve their compatibility with polymeric matrixes. A fine nanofiller dispersion within the polymeric matrix can capitalize the benefits of their large surface area, i.e., through a compatibilization process between both partners [9]. The application of chemical surface treatments on cellulose fibers has been an effective way to improve their adhesion to the matrix and reduce their hydrophilic character [10]. Silane coupling agents is often used to enhance the adhesion between polymeric matrices and
narrow nanoparticles [9, 11]. However, according to what we are known, few studies on the surface modification of CNF with methacryloxypropyltrimethoxy silane (MPS) and the impact of CNF on PSf membranes have been reported.

In the study, surface modification onto the CNF has been carried out to improve the compatibility with the PSf matrix. And the reaction mechanism of this process was presented. The M-CNf was studied using FTIR and XPS. The PSf/M-CNf composite membranes were prepared by a Loeb-Sourirajan (L-S) phase inversion process. The mechanical properties on the basis of tensile strength and percentage elongation of the PSf and its composites were also evaluated. The cross-section and bottom surface morphology of PSf/M-CNf composite membranes were analyzed using SEM. The effects of different addition of M-CNf on pure water flux, BSA rejection, as well as contact angle of the composite membranes were also investigated in this article.

2. Experimental

2.1. Materials.
Lignocellulose pulp board (Shandong Huatai), Polysulfone (PSf, η=0.58, Dalian polysulfone Plastics), Methacryloxypropyltrimethoxysilane (MPS, Beijing Shenda), Polyethylene glycol (PEG, molecular weight 400, AR, Sinopharm). Sulfuric acid (H2SO4, 98 wt. %), N,N-dimethylacetamide (DMAc) and absolute ethyl alcohol (AR) were received from Beijing Chemical Plant. Tungstophosphoric acid (Tianjin Jinke), Bovine serum albumin (BSA, Beijing Aoboxing Biological).

2.2. Surface Chemical Treatment of Cellulose Nanofibers (CNF).
After addition of lignocellulose pulp board with a mass ratio of 1:40 of solid to liquid, the 15 wt. % sulfuric acid solutions were stirred with a speed of 500 rpm at 85 °C for up to 4 h. After washing in soft water, the resuspending was concentrated and then became neutral with centrifuge method. And then it was filtered from vacuum, and the solids got from this process were rinsed by 80% ethyl alcohol. Then the solids were immersed into 80% ethyl alcohol (the mass ratio of solid to liquid is 1:100) and became homogeneous with a highspeed agitator (NS1001S2K, GEA NiroSoavi Co., Italy) when the pressure was 100 MPa. By this method, the CNF was resolved into the 80% ethyl alcohol (1 wt. %) well. After the pH of solution was adjusted to 4-5 with adding acetic acid, we put MPS into resuspending for producing concentrations of 1, 2, 3, and 4% v/v in the end, followed by a stirring for 2h at ambient temperature. The M-CNf was washed until it reached neutrality with 80% ethyl alcohol after change, and then use DMAc to rinse for a few times so that all of the physical precipitation of modifier can be cleared. After the suspension was ultrasonicated for 30 min (KQ 5200DE, China), the M-CNf was well-dispersed into the DMAc.

XPS analysis was performed on an X-ray Photoelectron Spectrometer (XPS, ESCALAB250Xi, Thermo fisher, United States): 1 eV per step and 0.05 eV per step for narrow scan, which was used to determine the surface compositions of CNF and M-CNf. Fourier transform infrared spectrometer (FTIR, VERTEX 70V, Bruker, Germany) was used to characterize the chemical structure of the membranes. The measured wavenumber ranged from 4000 to 400 cm⁻¹.

2.3. Membrane Preparation.
The resolved M-CNf resuspending was thinned into various enriched materials. Then the ready M-CNf resuspending dissolved the PSf with predetermined amount, in this case we got PSf’s overall concentration that was eighteen weight percent. In the same time, we added 5 wt% PEG 400 into above mentioned liquor. The liquor was physically mixed at fifty degrees centigrade and keep this condition for at least eight hours so that the polymer can be totally dissolved. Bubbles existed in the liquor were purged under a vacuum degree of 0.1 MPa. Next, the liquor should be left yet for a whole day to get rid of the bubbles [12]. The films were ready with an infused phase-inversion flow. A right amount of every liquor was spilled onto a clean and white glass sheet, and then use a tool to scale off. All the DMAc currently in the liquor could be evaporated for half minute, then infused into a coagulating bath filled with soft water right away. The film was rinsed by soft water to get rid of the
remaining liquor and porogen, and then it should be stayed in soft water for more than one day and after this, it can be tested.

2.4. Composite Membrane Characterization
Tensile breaking force, together with the elongation at break for composite films were characterized by 1176 computer servo type pulling force test machine (PT-1176XGP, Perfect International Instrument Co., Ltd., China). SEM (SEM, S-3400n, Hitachi, Japan), whose accelerating voltage is 5 kV and another FE-SEM with the voltage at 3 kV (FE-SEM, SU8000, Hitachi, Japan), were used to inspect the bottom surface morphology and cross-section of the membranes. We use a home-made ultrafilter to evaluate the composite films’ pure water permeation flux. During the test, the initial water flux of the membranes was spent approximately half an hour after the pressures were increased separately at 0.15 and 0.1 MPa at room temperature. We can use below method to count pure water permeation flux ($J_w$),

$$J_w = \frac{Q}{(A \times \Delta t)}$$

(1)

Here, $Q$ represents pure water’s permeation (L), $A$ represents the useful film space (m2), and $\Delta t$ means time duration of the experiment (h). Whether BSA films will have rejection or not was confirmed from counting its liquid store ability by means of films taking one UV-visible spectroscopy (UV-1801, BFRL, China) to confirm absorption capacity of BSA liquor, also permeation liquor by 280 nanometers. Those experiments were tested by the same parameter: 0.1 MPa. The retention coefficient (R) was calculated according to the following equation,

$$R = \left(1 - \frac{A_1}{A_2}\right) \times 100\%$$

(2)

Here, $A_1$ is absorption rate for filtrated liquors of BSA, meanwhile, $A_2$ is absorption rate for the original liquors of BSA. And the difference of them is $A_1$ is for filtrated liquors and $A_2$ is for original liquors. Contact angle tool (JGW-360a, HAKE, China) was used to measure the hydrophilicity of the membranes. Soft water drops were poured onto the films, and when soft water drops are stable, the contact angle can be calculated then.

3. Results and Discussion

3.1. CNF Surface Modification Mechanism and Their Characterization

3.1.1. CNF Surface Modification Mechanism.

![Figure 1. The reaction mechanism of MPS on the CNF surface: Hydrolysis reaction; Self-condensation reaction; Adsorption: hydrogen bonds formed between MPS and CNF. R: (CH$_2$)$_3$OCOCH(CH$_3$)–CH$_3$.](image-url)
The reaction of surface modification of cellulose nanofibers includes three steps, which was shown in Fig.1. First step is the hydrolysis of methoxy group (—OCH₃) on MPS: three methanol molecules were yielded during the interaction of one MPS molecule and three water molecules. Second step is the self-condensation of —Si—OH which forms —Si—O—Si— bearing oligomers with different status: linear chain, branched chain, endless chain or even three-dimensional polymer. The last step is the formation of hydrogen bonds between the hydroxyl groups of CNF surface and oligomers at room temperature: the hydrophobic groups were introduces into the outermost surface of CNF in this process which was beneficial to the compatibility between CNF and PSf.

3.1.2. FT-IR analysis.

Results got from FTIR spectra for CNF (a) and M-CN (b) are shown in Fig. 2. As shown in spectrum 2a, it can be observed that the appearance of characteristic band assigned to —OH stretching intramolecular hydrogen bonds of CNF was located at 3415 cm⁻¹, the band located at 2902 cm⁻¹ was in charge of C—H extending, the band located at 1633 cm⁻¹ was assigned the —OH of water absorbed from CNF, the appearance of characteristic band corresponding to the —CH₂ symmetric bending was located at 1431 cm⁻¹, also, band located at 1373 cm⁻¹ was in charge of the C—H bending, which represented characteristic bands of CNF. The band at 1058 cm⁻¹ was in charge of the C—O extending, and the band located at 896 cm⁻¹ was assigned to the C—H bending and —CH₂ stretching [13] (Carrillo et al, 2004).

Fig.2b clearly shows the appearance of characteristic band assigned to the C═O carbonyl groups at 1719 cm⁻¹ derived from M-CN with CNF. The—OH stretching at 3421 cm⁻¹ was sharper than that of CNF. This can be ascribed to that MPS’s hydroxyl were powerfully hydrogen united with that of CNF, and in the same time can be due to the existence of silanol groups which were featured to silanol, siloxane or something similar that came from the acid-condensation reactions with MPS. We also can see that the existence of C═C double bonds from M-CN located at 1637 cm⁻¹ as the change of the adsorption area matches “C—H” extending at 2898 cm⁻¹ [13]. And the area of —CH₃ asymmetric extending was located at 1454 cm⁻¹. However, it’s hard to totally allot the Si—O—Si and Si—O—C cellulose because the cellulose bond located at 1000–1200 cm⁻¹ had very powerful absorption capability. Due to the overlay of Si—O—Si and the C—O extending of cellulose, the area no. of M-CN was added, which became the proof of silane adsorption. From this, we can know that there was a coupling reaction happened for MPS and CNF [15].

![Figure 2. FTIR spectra of CNF (a) and M-CN (b).](image-url)

3.1.3. XPS analysis.

The XPS spectra of CNF and M-CN are given in Fig.3. It could be seen that the surface of CNF is mainly constituted of carbon (signal at 286 eV) and oxygen atoms(signal at 533 eV). While the new peaks have appeared at around 102, 154 eV of M-CN, they represent the Si2p peak and Si2s peak, respectively[14]. And these two peaks are not observed in the case of CNF, thus confirming the interaction of MPS with the CNF.
The detailed features of C1s peak have already been examined. The XPS analysis of CNF and M-CNFe both reveal three C1s peaks as shown in Table 1. The deconvolution of the C1s peak shows that there was a major difference related to the C1s1peak of M-CNFe(Fig.4b). It has greatly increased from 13 to 46% (Table1) when compared with that of CNF(Fig.4a), which was ascribed to the methylene groups(–CH2–)on MPS. This large variation was demonstrated by the corresponding decrease in the surface O/C ratio which went from 0.63 to 0.54, as expected by the carbon-richersilane coverage [12].

![Figure 3. Full XPS spectra of CNF and M-CNFe.](image)

![Figure 4. Deconvoluted C1s spectra of CNF (a) and M-CNFe (b).](image)

| sample   | O/C | Binding Energy/eV | rel carbon composition (%) |
|----------|-----|-------------------|----------------------------|
|          |     | C1s1  | C1s2  | C1s3  | C1s1  | C1s2  | C1s3  |
| CNF      | 0.63 | 284.7  | 286.4  | 287.8  | 13.43  | 67.72  | 18.85  |
| M-CNFe   | 0.54 | 284.8  | 286.4  | 288.5  | 45.74  | 37.02  | 17.24  |

3.2. Composite Membrane Properties

3.2.1. Mechanical Properties of the Membrane.

The effects of MPS content on mechanical properties of PSf/M-CNFe composite membranes are shown in Fig.5a. The results demonstrated that adding a certain amount of MPS can reinforce the mechanical properties of PSf/M-CNFe composite membranes. These results reflected that large surface area and nanoscale can be a reason of M-CNFe to be a kind of reinforced material and the organic hydrophobic surface of M-CNFe can improve the compatibility between PSf and M-CNFe, enhancing the interfacial force between both partners [15]. The mechanical properties of the composite membranes presented a tendency of increasing first and then decreasing, when the MPS content reached 2 v/v %, the reinforcement achieved the better effect than other samples. The reason may be that lower content of MPS made a fewer cover on the surface of CNF and thus MPS cannot form enough interfacial layer to join the hydrophilic CNF and hydrophobic PSf. Moreover, MPS formed hydroxyl bonds among themselves and underwent self-condensation, which made the layer between PSf and CNF too thick.
and those materials very little stress-transfer properties [15]. It also can be concluded that the compatibility between the 2 v/v % MPS modified CNF and the PSf was superior to the other samples.

The Fig. 5 b shows the effects of M-CN F content on the tensile strength and elongation at break of PSf/M-CN F composite membranes. The composite membranes presented a tendency of increase first and then decrease in the mechanical properties with the increase of M-CN F content. But the tensile strength and elongation at break of composite membranes all exceed the pure PSf membrane. With the addition of 0.4 wt.% M-CN F, the composite membranes showed the highest tensile strength, reaching 4.9 MPa. When 0.2 wt.% M-CN F were added, the composite membranes showed the highest elongation at break, reaching 13.6%, which increased by 62.4 % compared to the pure PSf membrane. The excess M-CN F cannot be evenly dispersed in the casting solution and were easy to aggregate, leading to the pore defects and the formation of large voids in the membranes, which weakened the interfacial adhesion between PSf and M-CN F and decreased the mechanical properties of the composite membranes [16-18]. In addition, the excess M-CN F can be washed away from the membrane during the phase inversion process due to the lower interfacial adhesion, which could not enhance the mechanical properties of membranes. Therefore, the addition of 0.3 wt. % M-CN F can be a suitable amount to improve the mechanical properties of the membranes.

![Figure 5](image)

**Figure 5.** (a) MPS content on mechanical properties of PSf/M-CN F blend membranes and (b) M-CN F content on mechanical properties of PSf/M-CN F blend membranes.

3.2.2. Morphological Study of the Membrane.

Fig. 6 shows the cross-section and bottom surface morphology of pure PSf membrane and PSf/M-CN F composite membranes. The membranes exhibited a typical asymmetrical structure, which had a dense top surface layer (skin layer, air side), a porous sublayer (support layer), and a small portion of sponge-like bottom surface layer (glass side). With the increase of M-CN F content, the size and the number of the finger-like pore in the support layer were found to increase, and large voids were formed gradually. Also both the number and the size of the pore in the bottom surface layer increased at the same time. However, when excess M-CN F were added into the membranes, the pore defects on both cross-section and bottom surface of the membrane appeared (Fig. 6d).

This change in the membrane morphology could be explained. M-CN F had abundant hydroxyl groups that made it exhibit strong hydrophilicity, thus it can promote the exchange rate of solvent and non-solvent during the phase inversion process and influence the precipitation kinetics and the formation of resulting membrane morphology consequently. And the growth of new phase nucleus formation in the polymer-poor phase was accelerated at this time. However, the increasing M-CN F content also increased the viscosity of the casting solutions [17]. The M-CN F were easy to aggregate, which resulted in the formation of pore defects [16,17].
3.2.3. Flux and Retention.

Fig. 7 shows the effect of different M-CNF contents on pure water flux and BSA rejection of composite membranes. It can be observed that the pure water flux promoted in a certain range with the addition of M-CNF. The maximum value of pure water flux reached 97.5 L/m²h when 0.4 wt.% M-CNF was added. Though there were some changes with the BSA rejection, they all stayed above 98%.

The reasons of these phenomena were that the organic functionality methacrylic can improve the compatibility of M-CNF with PSf, enhancing the interfacial force between both partners [15], which made a certain amount of M-CNF stay in the surface dense layer and internal support layer of the membranes steadily after the phase inversion. Moreover, the connectivity of finger-like pores became better and large voids became wider with the increase of M-CNF content, leading to the improvement of the permeability of the membranes. These factors all resulted in a significant increase of pure water flux, and also a decrease in BSA rejection. However, the excess addition of M-CNF can easily aggregated and increased the viscosity of the casting solutions[17]. And the dispersion performance of M-CNF in the casting solution got worse, so the entanglement between M-CNF and PSf became unsteady. The excess M-CNF may also be washed away from the membrane during the phase inversion process, weakening the interfacial adhesion. Adding excess M-CNF to the membranes can block membrane pores as well.

3.2.4. The Hydrophilicity of Membranes.

As shown in Table 2, with the addition of M-CNF, the contact angle of the PSf/M-CNF composite membranes decreased gradually, indicating that the hydrophobicity of the membranes was improved.
The M-CNF evenly homogeneously dispersed in the PSf casting solution; the macromolecular chains of the polymers entangled and interacted with each other. Similarly, the M-CNF with abundant hydroxyl groups distributed in the surface dense layer and internal support layer of the membranes enhanced the affinity between the hydrophobic membrane materials and water, enhancing the hydrophilicity of the composite membranes. Meanwhile, when the M-CNF content in the membrane reached above a certain range, the decrease degree of the contact angle was no longer significant. This can be explained that it was difficult to disperse the excess M-CNF evenly into the casting solution, weakening the interfacial adhesion between PSf and M-CNF. The excess M-CNF might also be washed away from the membrane during the phase inversion process.

Table 2. Contact Angle (CA) of the Membranes

| M-CNF content | 0          | 0.1 wt.% | 0.2 wt.% | 0.3 wt.% | 0.4 wt.% | 0.5 wt.% |
|---------------|------------|----------|----------|----------|----------|----------|
| CA (°)        | 74.7 ±1.3  | 71.2 ±1.8| 68.7± 2.2| 66.8± 1.5| 65.3± 0.9| 63.9± 1.6|

4. Conclusions
In the present investigation, CNF with direct surface modification in the presence of MPS were used to enhance the compatibility between CNF and PSf. The FT-IR and XPS spectra showed that the surface of CNF was successfully modified with MPS. Furthermore, the reaction mechanism of the CNF surface modification with MPS was presented.

PSf/M-CNF composite membranes were successfully prepared by the L-S phase inversion process. The 2 v/v % MPS modified CNF showed better compatibility with PSf than other samples, which was confirmed by the results of mechanical tests.

The effects of different M-CNF contents on the morphology of membranes were evaluated by SEM, With the addition of M-CNF, the size and number of the pore in the bottom surface increased and the connectivity of finger-like pores was better than that of the pure PSf membrane. Adding excess M-CNF can cause pore defects in membranes.

The hydrophilicity of membranes increased with the addition of M-CNF rise in the membrane. When the addition of M-CNF was 0.4 wt. %, the maximum value of pure water flux reached 97.5 L/m²h.

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