



Improving the antifouling property of polyethersulfone ultrafiltration membrane by incorporation of dextran grafted halloysite nanotubes

Haoxia Yu, Yatao Zhang*, Xiaobo Sun, Jindun Liu, Haoqin Zhang*

School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China

HIGHLIGHTS

- Dextran grafted halloysite nanotubes were used as novel hydrophilic filler.
- Hydrophilicity of membranes was significantly improved after adding HNTs-Dextran.
- HNTs-Dextran/PES hybrid membranes showed good antifouling property.

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ABSTRACT

Polyethersulfone (PES) ultrafiltration membrane with improved antifouling property was prepared via traditional phase inversion method by incorporation of dextran grafted halloysite nanotubes (HNTs-Dextran). Fourier transforms infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM) results showed that HNTs were modified by dextran successfully. The hybrid membranes were characterized by contact angle, scanning electron microscopy (SEM), and cross-flow filtration and antifouling measurements. The results indicated that the surface hydrophilicity of membranes was significantly improved after adding HNTs-Dextran. Compared with the pure PES membranes, the hybrid membranes possess higher flux and good antifouling properties. In addition, the content of HNTs-Dextran in the hybrid membranes was an important factor affecting the morphology and separation properties of the membranes.

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1. Introduction

Polyethersulfone (PES) is one of the most important polymeric materials with excellent temperature, pH, chemical stability and predominant mechanical strength, which is widely used in separation fields, such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) [1–3]. However, the main disadvantage of PES membranes is related to its inherent hydrophobic character, which often results in a high fouling tendency when PES membranes were exposed to protein-containing solutions. Membrane fouling is an important problem in membrane filtration, resulting in higher operation cost, shorter lifetime, unpredictable separation performance and smaller application range [4,5]. Therefore, practical usage of PES membranes is still greatly restricted by membrane fouling.

Many studies have concluded that membrane fouling is directly related to hydrophobicity, and increasing the hydrophilicity of a membrane surface could effectively minimize membrane fouling

[6–8]. A number of strategies to improve the hydrophilicity of PES membranes have been performed, such as membrane surface modification and blending. Surface modification of PES membranes could retain the original structures and properties of the membrane, including coating [9], and chemical modification [10,11]. However, surface modification, especially grafting or adsorption of hydrophilic polymers, often leads to decreased flux due to the narrowing and blocking of surface pores [12].

Another method to improve the hydrophilicity of PES membrane is blending. Many works have been done to increase the hydrophilicity of PES membranes by blending with amphiphilic graft copolymers or inorganic materials as additives [13,14]. Recent works have also reported the valuable effects of membranes blending with nanoparticles on the alleviation of membrane fouling, such as SiO₂ [15,16], TiO₂ [17], carbon nanotube [18], and ZnO [19]. Celik et al. [20] reported that the addition of inorganic nanoparticles in the polymer matrix leading to an increase in membrane permeability and a better control of membrane surface properties.

Halloysite nanotubes (HNTs) (Al₂Si₂O₅(OH)₄·2H₂O) is a kind of naturally clay silicate minerals, it has been preliminary studied as a new functional material due to its hollow nanotubular

* Corresponding authors. Tel./fax: +86 371 67781734.

E-mail addresses: zhangyatao@zzu.edu.cn (Y. Zhang), zhanghaoqin@zzu.edu.cn (H. Zhang).

structure in submicrometer range and large specific surface area. HNTs possess good hydrophilic property due to a few hydroxyl groups on the surface. Because of these physical and chemical properties, HNTs have been used as an additive to prepare the membranes [21,22].

Dextran is a kind of natural polysaccharide, which has strong hydrophilicity. In this work, dextrans were grafted onto the HNTs, and then HNTs-Dextran composites were used as an additive to improve the hydrophilicity of PES membrane. The objective of this work is to determine the protein fouling behavior of the blending HNTs-Dextran/PES membranes using bovine serum albumin (BSA) solution. The modified HNTs were characterized by FTIR, TGA and TEM. The separation performance and water contact angle of the membranes were also investigated in detail. Moreover, the microstructure of the membranes was observed by SEM.

2. Materials and methods

2.1. Materials

Polyethersulfone was supplied by BASF Company. N,N-dimethylacetamide (DMAC), Polyvinylpyrrolidone (PVP) and PEG 20000 were purchased from Kewei Chemical Reagent Company (Tianjin, PRC). PVA 30000–70000 was supplied by SIGMA-ALDRICH Company. Dextran was obtained from Aladdin Chemistry Co., Ltd. 1,6-hexamethylene diisocyanate (HDI) and dibutyltin dilaurate were purchased from J&K Scientific. Dimethyl sulfoxide, acetone and other reagents were gained from Shuangshuang Chemical Company (Yantai, PRC). All reagents were analytical grade and used without further purification.

2.2. Modification of HNTs with dextran

In order to get the modified halloysite nanotubes grafted with dextran, a series of reactions took place. Fig. 1 showed the basic principles of the reactions, which mainly involved the following two steps.

2.2.1. HNTs modified with HDI

Before the reaction, HNTs should be dried at 400 °C for 5 h to remove the adsorbed water molecules. Firstly, 1 g of raw HNTs was added into 50 mL of acetone and was ultrasonicated for 1 h. Thereafter, about 2.7 g of diisocyanate was added into the resulting mixture,

then 0.1 g of dibutyltin dilaurate was added into the mixture, and the resulting mixture was refluxed at 70 °C for 3 h. At last, the modified HNTs grafted with HDI (HNTs-HDI) was obtained by centrifugation and washed with acetone for 3–4 times. Finally, the product was dried in a vacuum oven at 60 °C for 48 h.

2.2.2. Dextran grafting on HNTs

Four gram of functional HNTs and 8 g of dextran were added into 100 mL of dimethyl sulfoxide, and then 0.1 g of dibutyltin dilaurate was added into the mixture. The mixture was stirred at 80 °C for 6 h, and the final precipitation was obtained by centrifugation. Finally, the HNTs-Dextran composites were dried in vacuum drying chamber at 60 °C for 48 h.

2.3. Preparation of HNTs-Dextran/PES ultrafiltration membranes

Pure PES membrane and HNTs-Dextran/PES composite flat membrane were prepared by the phase inversion method. To prepare casting solutions, firstly, HNTs-Dextran composites were added into 73.2 g of DMAC at different concentrations (0, 0.01, 0.02 and 0.03 HNTs-Dextran /PES ratios, w/w, respectively) and stirred continuously for half an hour for good dispersion. After dispersing HNTs-Dextran composites in solvent, PES (18 wt.%), PVP (8 wt.%) and acetone (0.8 wt.%) were dissolved in the dope solution by continuous stirring at room temperature until the solution became uniform and homogenous. Then the dope solution was degassed by vacuum deaeration to ensure complete removal of air bubbles before casting. The solution was casted on a glass plate using a casting knife with the thickness of 0.3 mm at room temperature. The nascent membrane was evaporated at 25 °C for 30 s, and then the glass plate was immersed in water at 40 °C. A thin polymeric film separated from the glass within a few minutes, and then the formed membrane was kept in deionized water. Notice that the deionized water should be replaced everyday.

2.4. Characterization of modified HNTs

2.4.1. Fourier transform infrared spectroscopy

FTIR spectra was used to investigate the changes in the chemical composition of the modified HNTs. Results for the pristine, isocyanate and dextran modified HNTs were recorded using Thermo Nicolet IR 200 spectroscope (Thermo Nicolet Corporation, USA) with horizontal. FTIR spectra of all the HNTs were performed at 2 cm⁻¹ resolution using KBr pellets. Typically, 64 scans were signal-averaged to reduce spectral noise.

2.4.2. Thermal analysis

Thermogravimetric analysis (TGA) measurements were carried out using a TG-DTA, DT-40 system (Shimadzu, Japan). The samples were heated from 0 to 800 °C at the speed of 10 °C per min.

2.4.3. Transmission electron microscopy (TEM)

The morphology of the raw HNTs and modified HNTs were analyzed by a FEI Model TECNAI G² transmission electron microscope operating at 120 kV. In brief, the samples for analysis were ground in ethanol and agitated in a glass vial to disperse the particles within the solvent. The suspended particles were transferred and allowed to dry on a copper grid (400 meshes) coated with a strong carbon film.

2.5. Membrane characterization

2.5.1. Scanning electron microscopy (SEM)

A JEOL Model JSM-6700F scanning electron microscope (Tokyo, Japan) was utilized to visualize the cross-sectional morphology of the membrane. The membranes were cut into small pieces and

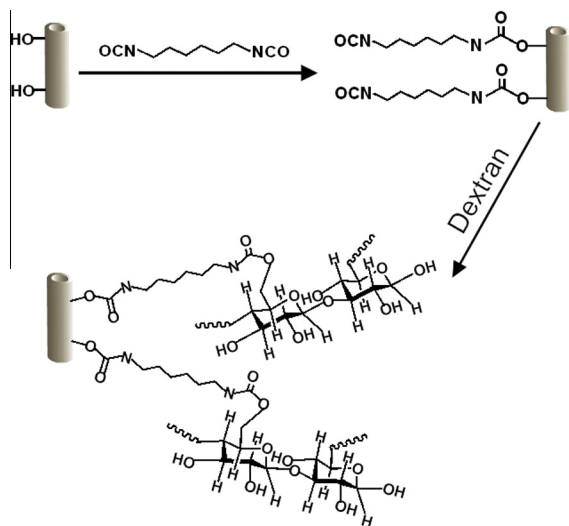


Fig. 1. Basic principles of the reactions which modified HNTs.

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