Super-wetting membrane with internalized PVA-TA gel networks for oil/water separation

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Abstract. In this paper, dimethyl sulfoxide (DMSO) was used as the hydrogen bond inhibitor to realize the co-dissolution of polyvinyl alcohol (PVA) and tannic acid (TA) in the casting solution. When the casting solution was placed in a water coagulation bath, the hydrogen bond cross-linking between PVA and TA is re-established, realizing the in-situ hydrogel network modification of the ultrafiltration membrane. The results show that the as-prepared membranes have underwater super-oleophobic properties and exhibit excellent anti-fouling ability during the separation of oil-in-water emulsions.

1. Introduction
The discharge of oil-bearing wastewater from industrial production has caused grievous detriment to the environment and biological existence. [1] So far, various methods such as adsorption, centrifugation, coagulation and membrane separation are used to treat oily wastewater.[2] Among them, membrane separation technology has better application prospects due to its advantages of high efficiency, low cost, and simple operation.[3] However, the oil pollution accompanying the application of membranes is the biggest test that restricts the large-scale application.

In recent years, hydrophilic additives are usually introduced into polymeric membranes, which combine with water molecules to form a stable hydration layer to resist direct contact between pollutants and membranes.[4] However, the stable residence of hydrophilic additives in membrane substrates remains a challenge. Therefore, the formation of three-dimensional networks (i.e., hydrogels) of hydrophilic polymers by means of cross-linking holds promise for the stable presence of additives in membranes. Moreover, based on the good water absorption and water retention capacity of hydrogels, it is generally considered an ideal candidate to resist oil pollution. Unfortunately, the conventional hydrogel synthesis process involves the polymerization and cross-linking of monomers, which makes it difficult to achieve the in situ generations of hydrogel networks during short-lived non-solvent-induced film formation. In addition, the post-crosslinking preparation method of the existing polymer also involves multiple steps, and the diffusion of the polymer chain is difficult to control.[5]

In this study, a solvent-regulated method for the crosslinking of PVA and TA is proposed to achieve in situ crosslinking of PVA-TA hydrogel networks during a non-solvent-induced phase separation process. Specifically, DMSO in the casting solution obstructs the H-bonding cross-linking between PVA and TA, but their hydrogen bond crosslinks were re-established during water solidification. Benefiting
from the hydrophilicity of the hydrogel network, the prepared composite membrane achieved underwater superoleophobicity, and the flux recovery rate increased from 41% to 84% of the pristine PES membrane.

Scheme 1. Schematic diagram of the preparation of ultrafiltration membranes with embedded PVA-TA hydrogel network.

2. Experimental section

2.1. Membrane preparation

The membranes were prepared by the nonsolvent-induced phase separation method. The detailed composition of the casting solutions is shown in Table 1. Firstly, a certain amount of PES, PVA and TA were dissolved in DMSO, stirred at 60 °C for 6 h, and then allowed to stand for 24 h for defoaming. The casting solution was then applied to the glass plate with a casting knife of 200μm and immediately transferred to deionized water to obtain the finished membrane.

2.2. Characterization of membranes

A scanning electron microscope (SEM, JMS-6490 LV) was used to observe the microstructure of samples. The images of emulsion droplets before and after filtration were observed with an optical microscope (Mshot MC50). The particle size distribution of emulsion before and after separation was measured by dynamic light scattering (DLS-90 plusPALS). The contact angles were measured by the SDC-200S machine. The mechanical properties of the membranes were tested by an electronic universal Instron machine at 5 mm/min. The preparation of oil-in-water emulsions and the experimental protocol of emulsion filtration refer to our previous work. [2]

| Membranes   | Casting solution |
|-------------|------------------|
|             | PES (g) | PVA (g) | TA (g) | DMSO (mL) |
| PES         | 1        | 0       | 0      | 8         |
| PES+PVA     | 1        | 0.05    | 0      | 8         |
| PPT-1       | 1        | 0.05    | 0.05   | 8         |
| PPT-2       | 1        | 0.10    | 0.10   | 8         |
| PPT-3       | 1        | 0.15    | 0.15   | 8         |

3. Results and Discussion

In general, membrane permeability mainly depends on its porosity, and the membrane with high porosity
usually has a higher separation flux.[6] As shown in Figure 1a, the introduction of PVA led to the porosity of the membrane showing a trend of increased first and then decreased. This was mainly attributed to the fact that when the PVA content was low, it acted as a pore-foaming agent to increase the porosity of the membranes, but with the further increase of the PVA content, the viscosity of the casting solution increased resulting in porosity decreased. In addition, the introduction of TA cross-linked PVA, further hindered the solvent-nonsolvent exchange process. The moisture content of the membrane reflected the formation of its internal hydrogel three-dimensional networks to a certain extent, as shown in Figure 1b, the introduction of PVA and TA increased the strength of the membranes, which was mainly attributed to the strong hydrogen bonding between PVA and TA. In addition, the PVA-TA hydrogel networks also increased the tensile strength of the membranes (Figure 1c). However, the tensile strength of PPT-3 did not increase further with the densification of the PVA-TA network, which was due to the fact that PVA and PES were prone to phase separation in the casting solution, destroying the structural integrity of the PES-based composite membrane.

The morphology of membranes was closely related to wettability, and determined its water flux and rejection to some extent. As shown in Figure 2, the surface of the pristine PES membrane showed a uniform porous morphology, and the cross-section was a typical finger-like pore structure. When PVA was introduced, the surface pore size of the PES+PVA membrane decreased compared to PES, and the cross-section showed a spongy pore structure. Interestingly, the introduction of TA resulted in a further reduction in the pore size of the membrane surface and the appearance of spherical structures on the membrane surface, which may be attributed to the self-assembly induced by the surface segregation of hydrophilic PVA and TA during the solvent-nonsolvent exchange process.

Figure 1. The porosity (a), moisture content (b), and stress-strain curves (c) of membranes.

Figure 2. Upper surface SEM images and cross-section images of PES, PES+PVA and PPT-1.
Figure 3. Water contact angle (a) and under-water oil contact angle (b) of membranes; (c) Images show the adhesion behaviour of oil droplets on the surfaces of the pristine PES and PPT-1.

Generally, the wettability of the membrane was related to the chemical groups and rough structures of the membrane surface. Figure 3a showed that the pristine PES membrane had a contact angle of 82.3°, showing the inherent hydrophobicity of PES. After the introduction of PVA, the surface contact angle of the PES+PVA changed little, probably due to the diffusion of a large amount of PVA into the coagulation bath during the membrane formation. In contrast, the contact angle of the membrane cross-linked by TA showed a significant decrease, and with the increase of PVA and TA content, the contact angle slightly increased, which was mainly due to the weakening of capillary action due to the decrease of membrane surface pore size. The underwater contact angle showed the resistance of the membrane to oil droplets (Figure 3b). The pristine PES exhibits typical viscous-oil properties. With the introduction of the PVA-TA hydrogel network, the composite membranes exhibited super-oleophobic. In addition, the oil droplets on the surface of PPT-1 can be easily removed compared to the PES membrane (Figure 3c). These results comprehensively reflect the crucial influence of the PVA-TA network on the antifouling ability of the membrane.

Figure 4. (a) Pure water flux of membranes. (b) Oil-in-water emulsion flux and rejection of membranes. (c) The flux recovery rate of membranes. Microscopy images and particle size distribution of emulsion before (d) and after (e) filtration using the PPT-1 membrane.
The separation flux and antifouling properties of the as-prepared membranes were tested by means of stirred dead-end filtration system. As exhibited in Fig. 4a, with the introduction of PVA, the pure water flux remained balanced. However, when TA was introduced, the flux decreased sharply, which was caused by the swelling of the PVA-TA hydrogel network in the membrane matrix and blocked the pores on the surface of the ultrafiltration membranes. In contrast, ultrafiltration membranes containing PVA-TA showed obvious advantages in the separation of oil-in-water emulsions. Due to the inherent lipophilicity of PES, its contamination flux by oil droplets during the separation of emulsions decreased dramatically. However, membranes containing the PVA-TA network had a much larger flux than pristine PES based on its good underwater antifouling ability. Also, as can be seen from Figure 3c, the flux recovery rate of pristine PES was only 41%, while the flux recovery rate of the membrane containing the PVA-TA hydrogel network was greater than 80%. Figure 3d showed the photographs and optical microscope images of the emulsion before separation. The emulsion is milky, and oil droplets of different sizes can be clearly seen in the optical microscope; after filtration, a transparent filtrate is obtained (Figure 3e). DLS measurements confirmed that the size distribution of oil droplets in the emulsion was between 200 and 800 nm, while the size distribution of oil droplets in the filtrate was narrower, less than 200 nm.

4. Conclusion
In summary, a strategy for DMSO to temporarily hinder the H-bonding crosslinking of PVA and TA was proposed, and ultrafiltration membranes containing PVA-TA hydrogel networks were fabricated in situ in a water coagulation bath. The as-prepared membrane exhibits underwater super-oleophobic properties, and shows excellent separation efficiency (flux $> 1100$ L/m²·h, rejection $> 99\%$) and antifouling performance during the separation of oil-in-water emulsions. The current work has broad application prospects in the field of industrial oil-containing wastewater purification and provides ideas for the preparation of ultrafiltration membranes containing hydrogel-embedded network ultrafiltration membranes.

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