Fabrication of cellulose-based composite membranes for organic solvent nanofiltration

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Abstract. In this paper, the methods for obtaining delamination-resistant composite cellulose membranes were considered. Different approaches to improve the adhesion of the cellulose layer to the polyester non-woven support were analyzed. The first approach, consisting in etching the PET support with solutions of trichloroisocyanuric acid in acetone, had a negative effect on the formed membranes. The negative effect was to increase the hydrophobicity of the support, resulting in peeling off of the cellulose layer. Suppression of delamination was achieved by reduction of cellulose shrinkage: by its plasticization with glycerol or sequential treatment by liquids with gradually decrease of their affinity to cellulose. Nevertheless, treatment of the membrane with an aqueous solution of glycerol resulted in a decrease of the dye rejection. The optimal technique is sequential post-processing of composite membranes with ethanol and hexane, which makes it possible to obtain strong composite cellulose membranes with high values of the rejection of the nanosized anionic dye.

1. Introduction

Aprotic polar solvents (such as tetrahydrofuran (THF), dimethylformamide (DMF), N-methylpyrrolidone (NMP), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO)) are widely applied in various fields of the chemical industry. For example, THF, NMP, and DMSO are actively used as a medium in interfacial catalysis [1]. DMF and NMP are used as extractants to remove oxidized products in the process of desulfurization of fuels [2], and also for the isolation of benzene-toluene-xylene fraction from the mixture with naphthenes, paraffins, and olefins. Due to anti-inflammatory, antiseptic, analgesic, and fibrinolytic action, DMSO is used in pharmaceutics [3, 4]. In this regard, aprotic solvents must be thoroughly cleaned and regenerated for reuse; also, a separate task is to isolate the target components from them. Traditional methods for purification of these organic solvents are energy-intensive and carry a heavy load on the environment due to the use of high temperatures and solvent evaporation. An alternative to these methods can be the process of organic solvent nanofiltration (OSN) – it is a baromembrane process of separation of liquids [5]. The main requirements for membranes used in OSN are mechanical and chemical stability in used media, high selectivity of separation, and the filtration of the target components.

Due to the sharp reduction in crude oil reserves and environmental degradation in the world, in recent years there is a trend to use biodegradable, renewable polymers, including for the production of membranes. Cellulose is the most common organic substance in nature. The content of cellulose in plants is in a wide range from 15 to 99 wt % [6, 7]. Cellulose is a linear syndiotactic homopolymer with a molecular formula \((\text{C}_\text{H}_\text{O})_{n}\), composed of D-anhydroglucopyranose units, commonly referred to as...
glucose units [8]. Due to the presence of hydrogen bonds, whose energy is 17 - 34 kJ/mol, cellulose has a high chemical resistance to most organic solvents, which makes it promising as a membrane material for OSN. But at the same time, this chemical stability of the biopolymer makes it difficult to create membranes. For OSN it is possible to use cellophane [9, 10], but the traditional viscose method used to produce cellophane films is very laborious and involves a large number of reagents that are hazardous to both humans and the environment.

One of the promising and environmentally friendly solvents for cellulose is N-methylmorpholine N-oxide (MMO) [11, 12]. It is already widely employed for the production of fibers and yarns [13], as well as for the production of cellulose membranes for gas separation, pervaporation, ultrafiltration, and organic solvent nanofiltration [14-18]. The main disadvantage of the MMO, which is in the crystalline state at room temperature, is the high melting point and, correspondingly, the high temperature of the dissolution of cellulose (>100°C). Other promising solvents for cellulose can be eco-friendly ionic liquids (ILs) [19, 20]. There are works where ILs are used to make nanofiltration membranes; to reduce the viscosity of the molding solution and to reduce the cost of the process, a co-solvent (e.g., acetone [21] and DMSO [22, 23]) is added to the basic ionic solvent. In order to eliminate the deformation of the cellulose membranes due to the strong shrinkage of the natural polymer under drying, the cellulose layer is applied to a non-woven polyester support. The main problem of composite membranes is the peeling of the cellulose layer due to the poor adhesion between the support material and the cellulose layer, and also due to the strong shrinkage. Therefore, the aim of this research is to develop a technique for manufacturing delamination-stable composite cellulose membranes.

2. Experimental

Cellulose (the degree of polymerization is 600; the moisture content in cellulose is no more than 8%; alpha-cellulose content is 92%) produced at Baikal Pulp and Paper Mill (Russia) was used. 1-Ethyl-3-methylimidazolium acetate ([Emim]OAc) with a density of 1.27 g/sm³ (Sigma-Aldrich) was used to dissolve cellulose. DMSO and DMF of reagent grade were purchased from Khimmmed (Russia). Cellulose was applied on a polyethylene terephthalate (PETF) nonwoven fabric (Crane Technical Materials, United States). The nonwoven fabric had a density of 87 g/m², a thickness of 90–99 μm, and an air permeation of 16.0–29.6 sm³/(sm²-s·Pa).

All composite membranes were made from 14% cellulose solution in the mixture of [Emim]OAc with DMSO (ratio 1:1), the dissolution temperature of the cellulose was 80°C [22]. The method for preparing molding solutions, consisting in their degassing was developed, to obtain defect-free membrane samples. After completely dissolving of the cellulose in the mixture of [Emim]OAc with DMSO and obtaining of homogeneous solutions, they were transferred in the oven at the temperature 80°C for 2 hours to remove air bubbles dispersed in the solution. Further, the solutions were degassed using the vacuum pump for an hour. After complete degassing, the solutions were placed in the desiccator at 80°C. Then the hot solution of cellulose in the mixture of [Emim]OAc with DMSO was applied to the non-woven polyester support and then the membrane was formed using the laminator HLCL-1000 (ChemInstruments, USA) at the temperature 80°C. The laminated membrane was precipitated in water immediately.

The commercially available chlorinating agent Satreat® was used for etching of the support. It is the solution of trichloroisocyanuric acid (Fig. 1) in acetone. The polyester supports were held in this agent until completely wetted, and then they were dried.
Figure 1. Structural formula of trichloroisocyanuric acid.

The efficiency of the chemical treatment of the support was evaluated from the change in the contact angle. The contact angle values were measured by via the conventional sessile drop technique using the LK-1 goniometer (Open Science, Russia). Measurement error was ± 2°.

The second method was made in two ways. The first method consisted in sequentially treating of the precipitated membranes using ethanol and then hexane; and the second is the treatment of the precipitated composite membranes with 20% aqueous solution of glycerol.

The filtration experiments were carried out in the set-up with dead-end filtration cells described elsewhere [24]. Helium was used to pressurize the liquid above the membrane due to insignificant difference in solubility of the gas in ethanol. The chamber above the membrane was filled with liquid (solvent or its dye solution). The permeate collector was arranged so as to minimize solvent evaporation; the volume of each collected liquid sample was 2.5±0.5 ml. The permeation of membranes was analyzed with respect to the aprotic solvent – DMF. To determine the separation properties of the resulting membranes, anionic dye – Remazol Brilliant Blue (Sigma-Aldrich) – were used.

3. Results and discussion

The main problem of the obtained membranes was the detachment of the deposited layer due to weak adhesion between the material of the support and the cellulose layer, and also due to high cellulose shrinkage under drying, which in summation led to the adhesive separation of the cellulose – polyester support system after dimethylformamide filtration (Fig. 2).

Figure 2. The composite cellulose membrane sample: a) freshly prepared; b) after DMF filtration.

To prevent cellulose layer detachment from the support, two approaches were analyzed:
- the preliminary etching of the polyester support before cellulose deposition;
- the decrease of cellulose shrinkage by post-treatment of membrane.

The images of the water and [Emim]OAc/DMSO mixture drops on initial and etched PET films (Fig. 3) as well as contact angles are given below.
Figure 3. The images of the water and [Emim]OAc/DMSO mixture drops on initial and etched PET films.

It can be noticed that both water drop and drop of [Emim]OAc solution in DMSO spreads worse on the etched PET film, which indicates surface wettability decrease. The contact angle between the liquid and the support also enhances, so it can be concluded that PET support etching leads to hydrophobicity increase. This means that the approach including non-woven support etching can degrade adhesion between PET and cellulose layer of the membrane instead of elevating it.

The composite membrane post-treatment was carried out by two methods. The first method involved successive shrinkage of membrane, which was immersed successively into the liquids with different affinity to cellulose; whereas the second method included cellulose plasticization in order to decrease the level of internal stresses of the polymer. The results of the testing of composite cellulose membranes treated for preventing of the detachment of the deposited layer from the support are shown in Table 1.

Table 1. The comparison of the effectiveness of approaches to the suppress of the delamination

| Etched PET | Coagulation | Post processing | $P^*$, kg/m$^2$ h bar | $R^*$*, % | Adhesion failure |
|------------|-------------|-----------------|----------------------|------------|-----------------|
| No         | Water       | Water           | 0.40                 | 76         | Yes             |
| Yes        | Water       | Water           | 0.26                 | 75         | Yes             |
| No         | Water       | Ethanol          | 0.27                 | 51         | No              |
| No         | Water       | 20% aqueous solution of glycerol | 2.40 | 8 | No |
*Permeation of DMF

**Rejection of Remazol Brilliant Blue R

These data indicate that DMF permeation of composite cellulose membranes obtained by using etched support is the same as in case of ethanol and hexane pretreatment. Although the dye rejection coefficient for the etched membrane reached the highest values in comparison with other samples (75%), however, the cellulose layer exfoliated from non-woven polyester support. The post-treatment with 20% glycerol solution led to cellulose shrinkage decrease in the same way as for successive treatment with ethanol and hexane that also prevented the detachment of the deposited layer. On the other hand, the treatment with aqueous glycerol solution suppressed cellulose layer pores contraction during the drying, as evidenced by high value of DMF permeation through the obtained membranes. Permeation was approximately in 10-times higher than it was in case of membranes treated with ethanol and hexane. However, the rejection coefficient in case of membrane soaked in glycerol solution fails to meet the requirements of nanofiltration process.

4. Conclusion

Techniques were developed for the preparation of delamination-resistant cellulosic membranes. Two approaches have been analyzed to eliminate the adhesive peeling of the upper cellulose layer from the polyester nonwoven support during the filtration of the aprotic DMF solvent. The first approach, consisting of etching the PET support with solutions of trichloroisocyanuric acid in acetone, had a negative effect on the formed membranes: the cellulose layer left the support after the filtration experiments. The negative effect was also confirmed by an increase in the contact angles of water or the mixture of [Emim]OAc and DMSO for the initial and etched PET, indicating an increase in the hydrophobicity of the surface of the support film. The contact angle of the water for the initial PET film is 71°, and for the etched is 94°. The use of the second approach, which consisted in the post-processing of molded membranes, eliminated peeling. Treatment of the membranes with aqueous solutions of glycerol led to an increase in the permeation of DMF in 10 times, but the dye rejection dropped sharply to 8%. Therefore, as an optimal technique, sequential post-processing with ethanol and hexane was chosen, which makes it possible to obtain composite cellulose membranes with a high value of the rejection coefficient of the anionic dye.

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