Novel mixed-matrix membranes based on polyvinyl alcohol modified by carboxyfullerene for pervaporation dehydration

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A B S T R A C T

Novel mixed-matrix membranes based on polyvinyl alcohol and its composites with carboxyfullerene were developed. Carboxyfullerene was simultaneously used as a modifier and a cross-linker for polyvinyl alcohol. The structural properties of the developed composites were studied by nuclear magnetic resonance, X-ray diffraction analysis, scanning electron microscopy, and sorption experiments. Thermal properties and stability were investigated by thermogravimetric analysis and differential scanning calorimetry. Surface features were studied by measuring the contact angles by water. The transport properties of the developed membranes were studied in ethanol-water mixtures separation by pervaporation (4.4–90 wt.% water in the feed) at different temperatures (22, 35, 50 °C). All membranes were selective with respect to water. The optimal transport properties were obtained for the PVA-carboxyfullerene (3.5 wt.%) membranes containing catalyst p-toluenesulfonic acid.

1. Introduction

Nowadays the field of membrane technology for dehydration and water purification is rapidly developing [1–7] and the search for new and effective membrane materials is very relevant and necessary [8–12]. Water soluble polymers possess high selectivity with respect to water but these polymers, as a rule, should be previously cross-linked to prevent the solubility of the polymers in water containing feed mixtures [13–16]. Varying the conditions of cross-linking makes it possible to obtain a material with predetermined properties, depending on the separation task (dilute or concentrated aqueous solutions) [12,14,16–18]. Among water soluble polymers one of the most used polymers for membrane dehydration is polyvinyl alcohol (PVA) because of its good chemical and thermal resistance, as well as film forming properties [7,16,19–23]. Up to now there have been more than 350 publications related to this field. And even some industrial companies provide commercially available membranes based on polyvinyl alcohol for dehydration (Pervap™ membranes of Sulzer Chemtech GmbH company [24] and etc.). PVA is highly selective to water but like most polymers, it has low permeability and should be cross-linked.

However, the use of different organic cross-linking agents (chemical cross-linking) or thermal treatment (physical cross-linking) as a rule leads to the deterioration of selectivity or permeability of a membrane [16,25–27]. Both physically (heat treated) and chemically cross-linked membranes, treated by different agents such as hydrochloric or fluoric acid [26,27], tetraethoxysilane (TEOS) [18], amic acid (with imidization at 150 °C) [28], poly(acrylic acid) (with heat treatment at 150 °C) [29], maleic acid or citric acid [30], exhibited less swelling that leads to the higher separation factor and lower water permeability in dehydration process by pervaporation as compared to non-treated PVA membrane. In case of such cross-linkers as fumaric acid [31] and glutaraldehyde [32–34] the opposite effect on transport properties was observed: cross-linked membranes possess increased flux and decreased separation factor.

A recent review on the dehydration of aqueous ethanol by pervaporation was published by Brian Bolto et al. [16]. In this review, cross-linked and hybrid PVA membranes were considered for the pervaporation of ethanol-water mixtures. Overall, the comparison of hybrid membranes with the results for organically cross-linked PVA membranes showed that there was still no advantage in introducing

inorganic particulates into polymer matrices. It was shown that the highest fluxes were obtained when the cross-linking agents were different carboxylic acids. Among them the PVA membrane cross-linked by poly(acrylic acid) had the highest flux ((J) = 2.8 kg/(m^2 h)) during the separation of 50 wt.% water-ethanol mixture at 75 °C, but at the same time very low separation factor equals to 60. As regards hybrid membranes described in this review, the most selective membrane was PVA cross-linked with 25 wt.% of TEOS (tetraethyl orthosilicate) when the annealing temperature was 130 °C (separation factor = 893, flux = 0.04 kg/(m^2 h)) for pervaporation of ethanol - water (15 wt.%) mixture at 40 °C. Hybrid membrane based on PVA/sulfated zirconia was the most permeable (separation factor = 61, flux = 1 kg/(m^2 h)) during the dehydration of 30 wt.% aqueous ethanol solution at 50 °C.

One of the promising ways to improve PVA transport properties is the creation of mixed-matrix membranes by means of PVA modification with inorganic and organic particles following simultaneous cross-linking of the PVA chains with different cross-linking agents (for example, with carbon nanotubes [35], zeolites [36], metal–organic frameworks [37], chitosan [38] with simultaneous cross-linking of the PVA by glutaraldehyde). The application of the mixed-matrix membranes without cross-linking agents is possible for the separation of feed mixtures containing small water content (up to 20 wt.%). However, these membranes, as a rule, will swell irreversibly in water and the transport characteristics of these membranes will change over time. One of the ways to modify and cross-link the PVA at the same time is by using for PVA modification functionalized particles that are able to interact with PVA through different type of bond formation. In our previous works [25,39–41] polyhydroxylated fullerene (fullerenol) was used for PVA as a modifier and a cross-linker. Due to OH-groups the fullerenol was able to create H-bonds with PVA in the aqueous solution and in solid state (in membrane) [25,39]. These H-bonds were transformed to ether bonds during heat treatment and the PVA membrane was properly cross-linked. Depending on cross-linking treatment (chemical treatment by addition of maleic acid or physical treatment by heat application) the membranes possess different transport characteristics. Physical treatment of PVA-fullerenol membranes led to decrease of flux and increase of selectivity while chemical treatment of PVA-fullerenol by maleic acid led to the improvement of membrane flux and an insignificant drop in selectivity [39,40].

Successful modification of PVA by fullerenol led us to the idea of using another fullerene derivative - namely, carboxyfullerene - as a modifier and a cross-linking agent. This fullerene derivative can promote an esterification reaction with polyvinyl alcohol, which leads to a new chemical structure of PVA (cross-linking of polymer chains) and to an increase of membrane stability in the processes of dehydration and water purification. It should be noted that fullerene derivatives have high stability in a wide range of organic solvents including aggressive compounds [42,43] and can be used as perspective polymer modifiers [44,45].

The aim of this study was to obtain (develop) novel and effective dense pervaporation membranes based on PVA modified by carboxyfullerene and to study the influence of the modification on physicochemical and transport characteristics. To study structural and physicochemical characteristics the obtained samples were investigated by various methods of analysis (TGA, DSC, NMR, XRD, SEM, contact angles, sorption experiments). To evaluate the membrane materials for industrial scale applications, it is also necessary to take into account the possibility of membranes to dehydrate mixtures in a wide concentration range at different elevated temperatures. Transport properties of the membranes were investigated in separation of the ethanol-water mixtures (4.4–90 wt.% water in the feed) by pervaporation at different temperatures (22, 35, 50 °C). It should be noted that the study of dense membranes allows to accurately characterize the properties of the developed PVA and PVA-carboxyfullerene membranes for further formation of supported membranes with a thin selective layer on a porous support to increase permeability, which is required for higher

productivity in industrial application [41,46–48].

2. Material and methods

2.1. Materials

Polyvinyl alcohol (PVA) (141,000 g/mol, a degree of hydrolysis 99.3%) was used for the preparation of membranes. Ethanol, p-toluenesulfonic acid (TSA) as well as PVA were obtained from ZAO "LenReaktiv" with analytical grade. Carboxyfullerene (CF) $C_{60}(C(COOH)_2)_3$ (Fullerene technology company, 99.5 wt.%) was used as acquired for PVA modification. The data on the identification of CF carried out using a complex of physicochemical investigation methods are presented in "Supplementary Material."

2.2. Membrane preparation

Hybrid membranes based on composites of PVA and carboxyfullerene (CF) were prepared by a solution casting method and dried by solvent evaporation. PVA-0 is the membrane based on pure PVA without any treatment. Physical and chemical cross-linking of PVA membrane were achieved by two procedures. The physically cross-linked membranes were obtained by heating pure PVA membrane (PVA-1) and PVA/carboxyfullerene (3.5 wt.%) membrane (PVA-2) at 140 °C for 60 min. Chemically cross-linked PVA membranes with carboxyfullerene (3.5 wt.%) were prepared with catalyst p-toluenesulfonic acid (TSA) and heated at 140 °C for 60 min (PVA-3).

The procedure for PVA-CF composite preparation was as follows:

The desired quantity of CF (0–10% w/w with respect to the polymer weight) was dispersed in 2 wt.% PVA solution in water by ultrasonic treatment with a frequency of 35 kHz for 40 min to prepare the PVA-CF composite. The solution was further casted into films on a Petri dish and dried at 40 °C for 24 h to get dense polymer film (membrane). Membranes were further subjected to physical (thermal) treatment at 140 °C for 60 min to improve the degree of cross-linking of polymer chains.

TSA was added as a catalyst to carry out chemical membrane cross-linking (esterification reaction) to prepare the PVA-CF-TSA membranes (PVA-3). The procedure for composite preparation was similar to PVA-CF composite, but during the process of ultrasonic treatment, TSA was added into PVA-CF nanocomposite solution. Then the PVA-CF-TSA films were subjected to heat-treatment at 140 °C for 60 min (PVA-3).

The optimal conditions for the cross-linking were achieved by heating the membranes at 140 °C for 60 min. These conditions are optimal because over 140 °C the CF molecule can be destroyed because of the loss of −COOH groups. There were no polymer swelling changes after heat treatment for 60 min, which indicated that the maximum degree of cross-linking had been achieved. The thickness of the prepared films was ∼45 ± 2 μm.

Carboxyfullerene concentrations exceeding 10 wt.% resulted in a poor dispersion in PVA solution. Moreover, the optimal content of carboxyfullerene was found to be 3.5 wt.% for physically and chemically cross-linked membranes because the inclusion of higher CF concentrations to the PVA membrane led to the removal of CF from the PVA matrix when the membrane was immersed in water. It was tested by the membrane immersion in water for 1 month and the monitoring of CF concentration in water by spectrophotometry.

The preparation conditions and names of the fabricated membranes are listed in Table 1.

2.3. Methods

2.3.1. Nuclear magnetic resonance

^{13}C NMR experiments were configured at room temperature by a Bruker Avance III HD 400WB NMR spectrometer (magnetic field of 9.4 T) using a double resonance probe with CP/MAS detection system.