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Full Length Article

Investigation of new modification strategies for PVA membranes to improve their dehydration properties by pervaporation

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ABSTRACT

Novel supported membranes based on polyvinyl alcohol (PVA) were developed using two strategies: first, by the modification of the PVA network, via so-called bulk modification, with the formation of the selective layer accomplished through the introduction of fullerenol and/or poly(allylamine hydrochloride), and second, by the functionalization of the surface with successive depositions of multilayered films of polyelectrolytes, such as poly(allylamine hydrochloride) and poly(sodium 4-styrenesulfonate) on the PVA surface. The membrane surface modification was characterized by scanning electron microscopy and contact angle measurements. The modified PVA membranes were examined for their dehydration transport properties by the pervaporation of isopropyl alcohol-water (80/20% w/w), which was chosen as a model mixture. Compared with the pristine PVA membrane, the main improvement was a marked increase in permeability. It was found that the surface modification mainly gave rise to a higher permeation flux but with a strong reduction in selectivity. Only the combination of both bulk and surface modifications with PEL could significantly increase the flux with a high water content in the permeate (over 98%). Lastly, it should be noted that this study developed a green procedure to prepare innovative membrane layers for dehydration, making use of only water as a working medium.

1. Introduction

PVA is a reference hydrophilic polymer known for its economic advantages, high selectivity to water and dehydration properties by pervaporation because of its good film-forming properties [1,2]. These reasons account for why PVA has already been used to prepare several series of commercial membranes [3]. Improving the properties of PVA membranes nevertheless remains a challenging task [4–7]. In this work, two distinct strategies to this end were investigated, i.e., bulk and surface modifications. Indeed, surface and bulk functionalizations can allow for the tailoring of the properties of polymer materials [8–10]. These modification methods have already been applied in the field of membrane technology, since they help in developing membranes with improved parameters, such as anti-fouling properties and/or improved transport characteristics (flux, selectivity, permeance, barrier and mechanical properties) [11–14]. In particular, nonporous membranes are very sensitive to these modification procedures, which can affect the solution-diffusion mechanism behind gas separation and pervaporation.

The most suitable and prospective way to study and evaluate the effects of internal and surface modifications of a pervaporation membrane is to quantify the membrane mass-transfer. According to the solution-diffusion mechanism, there are three steps in membrane mass transfer:

(1) The upstream-side sorption, preferably favoring one of the components of the mixture in the membrane network. In this step, the membrane coating or surface functionalization can play a significant role.
(2) The diffusion of the components through the membrane. In this step, the available free volume linked to the bulk membrane modification can play a major role.

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(3) The desorption of the components from the downstream side at low pressure. Usually, this step is assumed to be very fast; hence, it has a minor effect on the mass transfer.

Pervaporation is a well-known alternative method to classical distillation for the dehydration of alcohols when azeotropes are formed or when close-boiling component mixtures are considered. In such cases, pervaporation can provide substantially higher selectivity and thus a significant reduction in energy consumption [1,2]. The mixture of isopropyl alcohol (i-PrOH)-water is often studied as a model separation system for dehydration by pervaporation, since i-PrOH is an industrial solvent that can be used as a substitute for ethanol. i-PrOH is widely applied in such fields as perfumery, cosmetics, and medicine [15,16]. A 12 wt.% water – 88 wt.% isopropanol mixture forms an azeotropic mixture [17], which makes it difficult to dehydrate the alcohol by traditional separation methods (distillation and rectification). Using traditional separation methods, it is necessary to add harmful organic solvents that form stronger azeotropic mixtures with water, which prohibits the production of a high-purity alcohol. In addition, these separation methods are energetically expensive. Therefore, a promising way of dehydrating isopropanol-water mixtures is pervaporation, which can extract water through a membrane without any additional chemical reagents for dehydration. Various PVA membranes have already been widely used for the dehydration of isopropanol by pervaporation. However, to prevent strong swelling of the PVA in the aqueous solution and improve its stability, various methods for the modification or cross-linking of PVA have been attempted, for example, the creation of mixed-matrix blend membranes based on copolymers PVA/poly(N-isopropylacrylamide) (PNIPAAm) [18], PVA/sodium carboxymethylcellulose (NaCMC)/poly [19,20], and PVA/chitosan [21]; cross-linking with polyacrylic acid (PAA) [22], glutaraldehyde (GA) with concentrated HCl [19,20], oxalic acid (OA), dimethylol urea (DMU) and tetraethyl orthosilicate (TEOS) [23]; and the introduction of a zeolite or hydrophilic aluminosilicate filler into the PVA matrix [19,23]. However, PVA membrane performance still needs improvement for industrial separation processes.

A promising approach to improve the performance of membrane materials is the functionalization of membranes by the deposition of nanoscale layers on the surface of a selective polymer layer of the supported membrane [24,25]. The creation of an ultrathin film on the surface can be realized by such classical methods as the Langmuir–Blodgett technique and the synthesis of self-organizing layers [26]. However, these approaches have significant drawbacks: first, the Langmuir–Blodgett technique requires expensive equipment to create layers, and this method is not applied to all polymers. Second, the self-assembled layer method is not suitable or useful for multi-layer fabrication [26]. To create a multilayer film on the membrane surface, a relatively modern approach is applied, which is layer-by-layer (LbL) deposition [27–30]. This method is simple, inexpensive and suitable for many polymer materials; it is also easily automated. With this approach, various substances can be applied to the membrane material: polyelectrolytes [31], metallic nanoparticles [32], silicon nanoparticles [33] and many others. One of the promising directions to improve the performance of membranes is the deposition of polyelectrolytes onto the polymer film because of the unique properties of the deposited layers. Such a layered deposition leads to a charged film surface with a highly hydrophilic property, and consequently, a stronger affinity for water molecules. A dense electrostatic layer should only cause a moderate swelling of these membranes while in contact with water, which makes polyelectrolytes attractive for the functionalization and coating of pervaporation membranes [31].

The efficiency of pervaporation membranes can be significantly improved by varying the type of polyelectrolyte pairs and the application conditions (the deposited bilayer numbers, ionic strength and pH [34–36]). For example, alcohol/water pervaporation separation by polyelectrolyte multilayer membranes prepared via electrostatic layer-by-layer (LbL) adsorption of cationic (polyvinylamine (PVA)) and anionic (polyvinylsulfonate (PVS), polyvinylsulfate (PVS) and polyacrylate (PAA)) polyelectrolytes has been described [37]. It was shown that the hydrophilic PVA/PVS membrane had optimal transport properties for the separation of a feed with low water content (<20 wt.%), while the less hydrophilic PVA/PAA membrane was suitable for the separation of mixtures with higher water concentrations.

For better adhesion between the dense membrane and polyelectrolytes, an effective method that can be applied is the plasma treatment (e.g., O_2 and Ar) of the pristine membrane surface to create negative charges. Films based on plasma-treated polydimethylsiloxane (PDMS) have been further functionalized by the LbL deposition of more than 5 bilayers of poly (diallyldimethyl ammonium chloride) (PDADMAC) and poly(styrene sulfonate) (PSS) [38]. The optimal plasma treatment conditions for the films were chosen to obtain a full surface coating, resulting in defect-free and hydrophilic PDMS surfaces, as confirmed by SEM images and contact angle measurements.

This work aimed at improving the transport properties of PVA membranes for the dehydration of isopropanol by using two complementary strategies: bulk and surface modifications.

Several types of additives were considered for bulk modification, namely, fullerenol and poly(allylamine hydrochloride). Based on previous studies [39–43], fullerenol was chosen as one of the modifiers and cross-linking agents. During the chemical cross-linking of a membrane based on a PVA-fullerenol composite with maleic acid, the permeability of a membrane increased significantly with a slight decrease in selectivity during the separation of ethanol-water mixtures [42] because of the changes in the degree of crystallinity, surface polarity and free volume [42,41]. Poly(allylamine hydrochloride) has been used to improve the dispersion of carbon nanoparticles as well as to increase the adhesion of nanolayers of polyelectrolytes deposited on a membrane surface by LbL assembly.

The surface modification of mixed-matrix PVA membranes was accomplished by LbL deposition coating with 10 or 20 bilayers of polyelectrolytes: poly(allylamine hydrochloride) as the polycation and poly(sodium 4-styrenesulfonate) as the polyanion. This modification method is very promising for the functionalization of membrane surfaces with thin functionalized layers (10–100 nm) and can lead to significant changes of surface properties, such as an increased hydrophilicity, which can greatly modify the performance and transport characteristics of the membrane.

The transport properties of the membranes were studied with isopropyl alcohol (80 wt.%) – water (20 wt.%) feed mixtures in pervaporation. Scanning electron microscopy and contact angle measurements were used to characterize the membrane surface before and after pervaporation experiments to evaluate the stability of the thin active layers. The transport properties of the developed membrane were compared with a commercially available analogous PVA membrane, i.e., PERVAP™ 1201, for isopropanol dehydration.

2. Materials and methods

2.1. Materials

The membrane material used was PVA with a molecular weight of 141 kDa from ZAO LenReaktiv (certificate of analysis № 553041-3013, date of manufacture 09.2011). The polyhydroxylated