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Investigating the sorption influence of poly(vinyl alcohol) (PVA) at different crosslinking content

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ABSTRACT

Polymer crosslinking has significant importance in the relevant retrofitting of the microstructure of polymer network in terms of polymer swelling, membrane performance and its stability. This research was focused on investigating the sorption influence on membrane selectivity in terms of measuring swelling of poly (vinyl alcohol) (PVA) at varying polymer crosslinking in alcohol/water solutions. ATR–FTIR spectra for different crosslinked PVA were obtained using Nicolet FTIR spectrometer, and solvent concentration was determined by refractometer. The experimental results showed that swelling degree decreased with increasing crosslinking content, which led to a more rigid polymer network structure resulting in less free volume as well as reduced absorbed liquid in the polymer. The addition of crosslinker resulted in the reduction of PVA hydrophilicity influencing the sorption of alcohol into the polymer. It was found that PVA at all crosslinking contents was selective towards ethanol in ethanol/water mixture and becomes more water selective in an isopropanol/water mixture.

Introduction

Nanofiltration has many potential applications as a separation technology for processes that use mixtures of aqueous and organic solvents, for example alcohol/water mixtures. For separation of these organics as an end-of-pipe treatment, membranes are more likely where process volumes are less than 50,000 gal (190 m^3) per day [1]. Membrane separation is a proven technology that is used with a high efficiency in aqueous media, whereas it is characterized by its slower rate of uptake in aqueous/organic mixtures. This slow behaviour could be attributed to the interaction between membrane and solvent(s) that limits both the permeability and selectivity of the membrane [2]. The determination of waste/membrane interactions, permeability, selectivity, and swelling characteristics of the membrane is necessary. Membrane swelling plays a key role in the transport of molecules through membranes, as swelling changes the physical and chemical structure of the polymer. Previous studies have shown the importance of membrane swelling in transport processes through NF membranes [3,4]. Swelling is a thermodynamic phenomenon in which a solvent transfers from a liquid phase to a polymer phase, and deformation of the polymer network occurs as a result. The swollen material can be considered to be a mixture of solvent and polymer, and the thermodynamics of liquid mixtures can be extended to swollen polymers [5]. Swelling of dense polymers leads to an increase in the free volume. The membrane becomes more open and allows more liquid to move through, which influences both permeability and selectivity. However swelling of porous membranes leads to contraction of the pores walls and pores becoming more narrow, which enhances selectivity but decreases permeability [6]. Researchers examined the swelling of many different NF membranes with several species, in both aqueous and non-aqueous systems. Yeom et al. [7] used the degree of PVA swelling to assess the membrane selectivity in ethanol/water mixture. In the case of a highly swollen membrane, the membrane pores influenced and hence transport through the membranes. Praptowidodo et al. [8] prepared polyvinyl alcohol (PVA) of different crosslinking content to separate ethanol/water using pervaporation. They suggested that swelling of PVA lead to an increase in free volume which allowed more liquid to penetrate. They concluded that water flux increased and selectivity decreased, as a result of PVA swelling degree increased. Yu et al. [9], who found that increasing PVA crosslinking density reduced

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permeate flux and increased selectivity. They concluded that isopropanol is difficult to permeate through a PVA structure due to its relatively large molecular size. Z. Abdeen [10] prepared crosslinked PVA using glutaraldehyde as crosslinked agent, and found that the swelling and reswelling properties of PVA can be improved by blending PVA with certain ratio of crosslinking polymer. Previous works concluded that improvements of polymer swelling can be accomplished by modifying the conditions of its preparation, including crosslinking content [11].

Membrane swelling characteristics have an impact on membrane rejection. Rejection is not governed by a single mechanism but it is a contribution of different mechanisms, which occurs through several mechanisms [13]:

- Size exclusion: molecules are too large to enter the transport region within the membrane.
- Surface repulsion: molecules can be repelled due to hydrophobic/hydrophilic interactions with membrane materials or electrostatic forces.
- Sorption: the membrane surface absorbs one or more molecules selectively.

Crosslinking changes the physical and chemical structure of the polymer, as the addition of more cross-linker to the polymer main chain changes the microstructure of the polymer network, therefore affects membrane performance and stability. In this work, PVA swelling in solvent mixture is used to assess the solvent–polymer interaction at different polymer crosslinking, and investigates the influence of sorption alone on selectivity and it is part of characterization of PVA polymer in order to perform filtration. For this purpose an experimental system was designed to measure swelling of PVA at different polymer crosslinking in ethanol/water and isopropanol/water solvents.

Experimental

PVA has a poor stability in aqueous solutions, so crosslinking was used to create a stable PVA polymer.

Materials

The polymer was manufactured using poly(vinyl alcohol) powder, PVA with an average molecular weight of 89,000–98,000. Glutaraldehyde (GA) is a solution of 25 wt% concentration in water, and hydrochloric acid were both supplied by Sigma–Aldrich.

Preparation of PVA samples

The crosslinking content was calculated as the weight of GA in the reaction solution as a proportion of the combined weight of PVA and GA. Crosslinked PVA was prepared by dissolving 19 g of PVA powder in 50 ml deionized water. The solution was heated and stirred at 60 °C until complete dissolution was achieved. A glass cylinder of 20 mm diameter and 80 mm length was used as a mould.GA was diluted to 2.5 wt% before use as crosslinker [12,26]. When the GA solution content was less than 2.5 wt% in the reaction solution, insufficient crosslinking occurred due to a lack of crosslinking agent; hence, the resulting polymer dissolved partially or completely in water. Stable polymers could be prepared with GA solution content at or above 2.5 wt%. The crosslinker solution was prepared by mixing 1 g of GA 2.5 wt% and 1 g of 36 wt% hydrochloric acid. The crosslinker solution was added to the PVA solution, and the mixture left to crosslink for 4 h at 40 °C.

PVA polymers were previously prepared in a form of a thin membrane film [14–21]. To the knowledge of the author the investigation of swelling of a block of dense PVA has never been performed before. For the purpose of studying the effect of crosslinker loading on crosslinked PVA swelling degree, This procedure was repeated to prepare different samples with different crosslinking degrees of 5, 10, 15, 20, and 25 wt%. The degree of crosslinking was calculated using the following equation:

$$\text{crosslinking content} \frac{\text{weight of GA}}{(\text{weight of GA} + \text{weight of PVA})}\% \quad (1)$$

Characterization

Attenuated Total Reflectance–Fourier Transform Infrared spectroscopy (ATR–FTIR) analysis was used to characterize the reactants and product of the crosslinking process. The analysis was conducted using A Nicolet 6700 ATR–FTIR spectrometer with ZnSe crystal, where samples were kept in direct contact with the ATR crystal. by using a pressure arm that was positioned over the sample area and the applied force pushed the sample into the diamond surface [29].

Swelling measurements

The polymer was pre-weighed and immersed in a bottle containing 30% alcohol/water at liquid to solid ratio of 5. The samples were weighed, and the experiments were carried out at ambient temperature. After being taken out of the sealed bottle the polymer sample was weighed, and then replaced in the bottle until the swollen weight reached equilibrium. The swelling degree at equilibrium (SD%) is expressed as a percentage according to Eq. (2).

$$\text{SD}\% = \left(\frac{m_{\text{fp}} - m_{\text{ip}}}{m_{\text{ip}}}\right) \times 100 \quad (2)$$

where m_{fp} and m_{ip} are final and initial mass of the polymer, respectively.

Sorption experiments

Sorption was based on batch experiments, where the solvent concentration was determined using the refractive index (RI) measurement technique, which is based on the change in RI of a binary solvent mixture as a function of solvent concentration. Experiments were performed using a refractometer (Mettler Toledo Refractometer 30 PX) at a temperature of 20 °C. Calibration curves were prepared, and used for mass balance calculations. Solvent concentration in the remaining liquid was calculated from a calibration curve, and the corresponding solvent concentration in the swollen polymer was calculated using a mass balance. The mass balance was based on equilibrium between polymer and solvent mixtures.

Results and discussion

ATR-FTIR characterizations

ATR–FTIR spectra for the different polymers are shown in Fig. 1.

The IR spectra shows the corresponding groups such as ether/acetal (—COC), aldehyde (CHO—), methylene (—CH_2—), and hydroxyl (–OH) groups. The appearance of the ether/acetal peak indicates that the acetylation reaction occurs between aldehyde and hydroxyl in the polymer [29]. The IR spectra show the following three significant changes with increasing crosslinking content.

1 A decrease in hydroxyl groups from 5 to 25% crosslinked PVA. The spectral change results from the disappearance of the hydroxyl groups upon reaction with more aldehyde.