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Polyacrylonitrile-graft-poly(ethylene oxide)

2. Membranes of polyacrylonitrile and polyacrylonitrile-graft-poly(ethylene oxide) blends for separation of water/ethanol mixtures by pervaporation

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Summary

Membranes of polyacrylonitrile (PAN) and polyacrylonitrile-graft-poly(ethylene oxide) (PAN-graft-PEO) blends were prepared by casting from N,N-dimethyl formamide solution. The membrane performance with different PEO branch content in the PAN-graft-PEO was evaluated for separation of water/ethanol mixtures by pervaporation.

Introduction

Pervaporation is a membrane separation process in which the liquid feed mixture is in contact with the membrane in the upstream and the permeate is removed from the downstream as a vapor. Pervaporation is based on a solution-diffusion mechanism, that is, the permeation rate is a function of solubility and diffusivity. Both properties affect permeate flux and selectivity of membranes.

In recent years pervaporation has been used for the separation of many organic liquid mixtures. The development of more effective membranes for the separation of water/ethanol mixtures has been obtained by incorporating a functional group into membranes. For the case where water must be separated from water/ethanol mixtures, copolymer membranes were synthesized containing functional groups that strongly interact with water by hydrogen bonding (1,2).

Polymer blends can also be use to prepare permselective membranes for pervaporation, due to control of the hydrophilic-hydrophobic balance in the membrane. However, for the separation of water/ethanol mixtures only a few workers have reported some results using polymer blends (3-5).

Poly(acrylonitrile-co-acrylic acid) was blended with PEO and used as membranes for the separation of water/ethanol mixtures. In this case, the PEO was thought to act as a plasticizer as well as a preferential water absorbing and diffusing component (6).

In this study, membranes of commercial PAN and PAN-graft-PEO synthesized in our laboratory were blended and used for the separation of water/ethanol mixtures. Pervaporation performance was analyzed in terms of copolymer composition.

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Experimental

Materials

Reagent grade ethanol (Rio Lab) and N,N-dimethyl formamide (DMF, Rio Lab) were used without further purification. PAN (Bayer, 99.2 AN wt%) was used without further purification. PAN-graft-PEO were synthesized by radical copolymerization of methacrylate-headed PEO macromonomer and AN in DMF solutions. The copolymers were purified by dissolutions and precipitations in DMF and distilled water, respectively. After filtered, washed with ethanol, and dried in an oven at 65°C to constant weight, the products were characterized by the Kjeldhal method. The PEO branch content of grafts synthesized were: 32%, 40%, 50% and 62% (7).

Preparation of membranes of PAN and PAN-graft-PEO blends

Casting solutions were prepared by dissolving commercial PAN and PAN-graft--PEO in DMF at a total concentration of 10 wt%. The PAN-graft-PEO was used at 10 wt% over PAN. Clear and homogeneous solutions were obtained after stirring the solutions at room temperature for 6 h. No visible phase separation was observed. The blend membrane was obtained by casting the solution over glass plates, with the aid of a stainless knife to appropriate thickness, and dried at 60°C in an oven for three hours. The membrane was peeled off from the glass plate by using a distilled water bath and dried until constant weight. Before the pervaporation experiment, the membrane was immersed in the water/ethanol mixture overnight.

Measurement of degree of swelling and sorption selectivity

Equilibrium sorption experiments were performed at 50°C using thick strips of membranes. Strips were dried at 60°C in an oven until no significant weight change was observed. The strips were immersed in water/ethanol mixture (50:50 wt%) at 50°C. After equilibrium was reached (about 48 h), the membranes were blotted between tissue paper and transferred to the desorption system. The sorbed mixture was collected in a cold glass trap maintained at reduced pressure by a vacuum pump and analyzed by gas chromatography. From the difference of wet weight (after equilibrium sorption) and dry weight of the membranes, the degree of swelling (%) was calculated. All experiments were performed in duplicates and the results were averaged. The sorption selectivity α_S are defined by:

$$\alpha_S = \frac{Y_{1S}/Y_{2S}}{X_{1S}/X_{2S}} \qquad (1)$$

where Y_{iS} is the weight fraction of sorbed mixtures (polymer free) and X_{iS} is that of the feed. The subscripts 1 and 2 denote water and ethanol, respectively.

Pervaporation experiment

The membrane was deposited in a stainless steel permeation cell. The thermostatically-controlled feed mixture (water/ethanol 50:50 wt%) at 50°C was continuously supplied into the pervaporation cell by a peristaltic pump. The effective membrane area in contact with liquid was about 64 cm^2. The permeation side of the membrane was evacuated by a vacuum pump and the downstream pressure was lower than 5 mmHg. The permeate was collected in the glass trap cooled in a liquid nitrogen filled Dewar. The composition of the permeate was analyzed by gas chromatography (Perkin-Elmer G.C. 3920), equipped with a 3-m long column packed with Porapak Q and with a thermal conductivity detector. The separation factor (α) and permeate flux (J) are defined, respectively, as follows:

$$\alpha_{1,2} = \frac{Y_1 / Y_2}{X_1 / X_2} \qquad (2)$$

$$J = \frac{Q}{A.t} \qquad (3)$$

where Y_i is the weight fraction of permeates and X_i is that of the feed. The subscripts 1 and 2 denote water and ethanol, respectively. Q, A, and *t* represent the weight of permeate (g), effective membrane area (m^2), and time (h). The permeate flux was normalized for a hypothetical thickness of 10 μm, assuming linearity of permeate flux with thickness.

Results and discussion

Membranes of commercial PAN and PAN-graft-PEO blends were characterized by sorption and pervaporation experiments. This copolymer synthesized in our laboratory and containing distinct PEO branch content was selected due to the similarity with PAN.

In Figure 1 the results of degree of swelling and sorption selectivity for the blend membranes are plotted against the PEO branch content in the copolymer. It can be observed that the degree of swelling increases with the PEO branch content in the PAN--graft-PEO. This result indicates that the addition of PAN-graft-PEO to PAN increases the affinity of the polymer blend toward the feed solution, and thus the membrane absorbs the feed solution more easily. On the other hand, the decrease of the sorption selectivity with the increasing of PEO branch content, also shown in Figure 1, indicates that the ethanol was sorbed more easily due to the degree of swelling. This behaviour is similar when hydrophilic membranes are submitted at swelling in water/ethanol mixtures at different concentrations. In this case, the degree of swelling increases and the sorption selectivity decreases with the increase of water concentration in the feed.

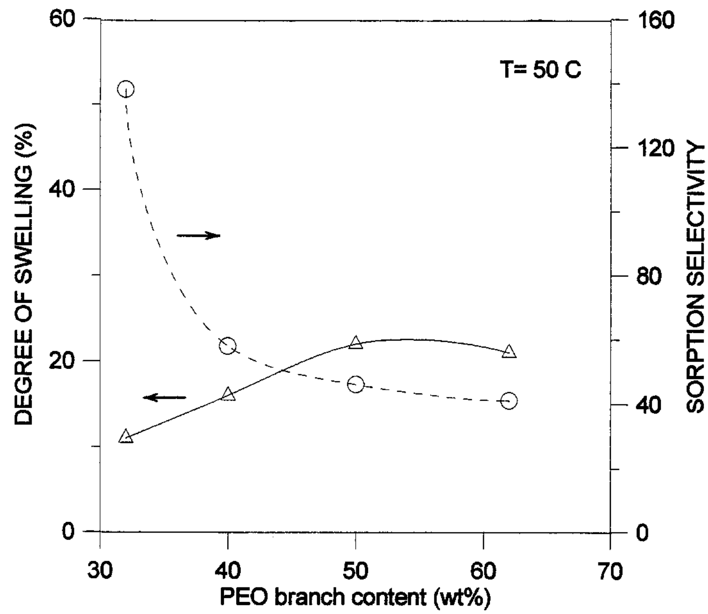

Figure 1 The effect of PEO branch content on the swelling ratio and sorption selectivity in blend membranes. Feed: water/ethanol mixture (50:50 wt%).

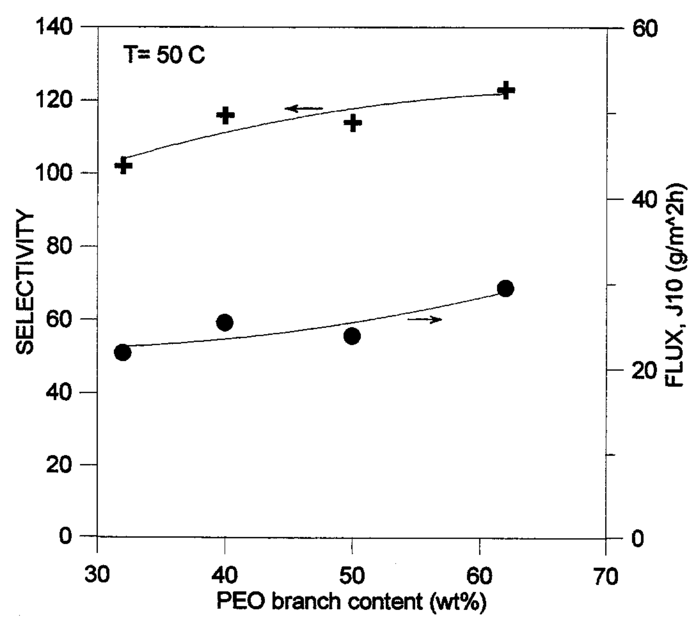

Figure 2 Selectivity (α) and permeate flux (J_{10}) in pervaporation of water/ethanol mixtures in membranes of PAN and PAN-graft-PEO blend. Feed: water/ethanol mixture (50:50 wt%).

In Figure 2 the results of selectivity and permeate flux for commercial PAN and PAN-graft-PEO blend membranes are plotted against the PEO branch content in the copolymer. It can be observed that the higher PEO branch content the higher the selectivity and permeate flux in the pervaporation process. Although the sorption selectivity has decreased due to ethanol concentration in swelling the membrane, the diffusion coefficient of ethanol into the membrane is lower than that of water. The difference between the diffusion coefficients is related to the difference in molecular size of these compounds.

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