

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Synthesis and Characterization of Biopolymeric Blend Membranes Based on Sodium Alginate for the Pervaporation Dehydration of Isopropanol/Water Mixtures

K. S. V. Krishna Rao^a; B. G. Lokesh^b; P. Srinivasa Rao^c; K. Chowdoji Rao^b

^a Department of polymer Science and Engineering, Pusan National University, Pusan, South Korea ^b

Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur, India ^c

Department of Chemistry, National Chung Hsing University, Taichung, Taiwan

To cite this Article Rao, K. S. V. Krishna , Lokesh, B. G. , Rao, P. Srinivasa and Rao, K. Chowdoji(2008) 'Synthesis and Characterization of Biopolymeric Blend Membranes Based on Sodium Alginate for the Pervaporation Dehydration of Isopropanol/Water Mixtures', Separation Science and Technology, 43: 5, 1065 — 1082

To link to this Article: DOI: 10.1080/01496390801888045

URL: <http://dx.doi.org/10.1080/01496390801888045>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Synthesis and Characterization of Biopolymeric Blend Membranes Based on Sodium Alginate for the Pervaporation Dehydration of Isopropanol/Water Mixtures

K. S. V. Krishna Rao,¹ B. G. Lokesh,² P. Srinivasa Rao,³
and K. Chowdoji Rao²

¹Department of polymer Science and Engineering, Pusan National
University, Pusan, South Korea

²Department of Polymer Science and Technology, Sri Krishnadevaraya
University, Anantapur, India

³Department of Chemistry, National Chung Hsing University, Taichung,
Taiwan

Abstract: Synthesized graft copolymers of hydroxyethylcellulose and acrylamide (HEC-g-AAm) were prepared by solution polymerization method. The grafting reaction was confirmed by Fourier transform infrared spectroscopy and differential scanning calorimetry. The graft copolymers were blended in different ratios with sodium alginate (NaAlg), and the membranes were prepared by the solution casting method. The resulted membranes were then crosslinked with glutaraldehyde (GA) in acetone-water medium. Swelling experiments were performed on the blend membranes in water-isopropanol mixtures at 30°C. Pervaporation experiments were performed at 30°C for the feed mixtures ranging from 10–50 wt.% of water in water-isopropanol mixtures. Flux and selectivity of the membranes increased with an increasing amount of HEC-g-AAm copolymers in the blend membrane. The membrane NaAlg/HEC-g-AAm-30 appears to have a good potential for dehydrating 10 wt.% water with a high selectivity of 2036 and a substantial water flux of

Received 14 June 2007, Accepted 14 November 2007

Address correspondence to P. Srinivasa Rao, Department of Chemistry, National Chung Hsing University, 402, Taichung, Taiwan; Tel.: +886-972282524; Fax: +886-4-22853148; E-mail: popurishrinu@gmail.com

1.036 kg/m² · h. Flux increased with increasing amount of water in the feed, but selectivity decreased considerably.

Keywords: Grafting, hydrophilic polymers, pervaporation, sodium alginate, swelling

INTRODUCTION

Pervaporation (PV) is a potential industrial method used for the separation of liquid mixtures and its technology represents one of the most effective and energy-saving means to separate azeotropic mixtures, close boiling point mixtures, or isomers (1). Based on the aims of separation, various pervaporation processes have already been classified. According to it, depending on the target products of water–organic mixtures, one of the important applications of PV in industry is dehydration of isopropanol solutions, which required hydrophilic membranes, such as poly(vinyl alcohol)/sodium alginate (2), poly(vinyl alcohol)-*g*-acryl amide (3) and sodium alginate/gour gum-*g*-acryl amide blend membranes (4).

Sodium alginate (NaAlg), a natural polysaccharide, derived from brown seaweeds, is composed of D-mannuronic acid and D-guluronic acid. This polysaccharide is extensively used in food industry as a gelling agent. Reports in the previous literature show NaAlg was used as a membrane in the dehydration of water-organic mixtures (5–8) and also been widely used as an encapsulent for drug delivery (9–11). Hydroxyethylcellulose is a non-ionic water-soluble cellulose ether, which is compatible with a wide range of other water-soluble polymers has also been used in separation studies (12, 13). It is an important carbohydrate polymer used in paints, paper finishing (12), and in membrane designing (13). However, reports on the usage of hydroxyethylcellulose membrane in pervaporation applications are few (14–16).

Extractive distillations can also be used for the separation of liquid mixtures, but these processes are expensive due to the azeotropic formation of water and isopropanol in dilute aqueous region. Isopropanol forms aqueous azeotrope at 12.5 wt.% of water. Moreover, the process is not environmentally clean. In an effort to tackle this problem and to search for new environmentally friendly materials, we thought of using NaAlg and graft HEC polymers to develop novel membranes for the PV separation of water-isopropanol mixtures.

Grafting of vinyl monomers on various surfaces is a convenient method for preparing hydrophilic membranes of various substrates and during recent years radical polymerization was extensively used as a method in network formation and inducing surface grafting. The experimental conditions for the grafting have tremendous influence on different structural aspects of polymer network. Thus a desired polymer can be obtained by tailor-made combination of properties of the constituents. In the present study sodium

alginate and hydroxyethylcellulose were used as model polymer matrix with acryl amide to obtain hydrophilic interpenetrating network membranes. During the graft copolymerization of vinyl monomers on cellulose, radical sites are generated on the cellulose backbone either by various chemical initiators or by radiation. After Mino and Kaizerman (17) grafted various monomers such as acryl amide, acrylonitrile, and methyl methacrylate on polyvinyl alcohol by using Ce^{+4} initiator, different vinyl monomers were grafted on cellulose by direct oxidation with this initiator (18–20).

In the present study, we prepared the blend membranes of NaAlg and acrylamide-grafted-hydroxyethylcellulose (HEC-*g*-AAM) with varying amounts of HEC-*g*-AAM and were used in the PV separation of water-isopropanol mixtures. We also compared the PV performance of blend membranes with the plain NaAlg membrane. This work also explores the effect of varying water concentration in the binary feed mixture on membrane flux and selectivity. Characterization by FTIR analysis, DSC and sorption studies have been used to explain the interaction mechanisms between the polymers.

EXPERIMENTAL

Materials

Sodium alginate (NaAlg), glutaraldehyde (GA), acrylamide, analytical reagent grade (high purity) isopropanol (IPA), acetone, and hydrochloric acid (HCl) were all purchased from s.d. Fine Chemicals, Mumbai, India. Hydroxyethylcellulose (HEC) powder was purchased from Polysciences Inc., USA. Deionized water having a conductivity of $20\ \mu\text{S}/\text{cm}$ was produced in the laboratory from the Permeonics pilot plant (Vadodara, India) using the nanofiltration membrane module.

Synthesis of HEC-Grafted-Poly(Acrylamide)

HEC-grafted-poly(acrylamide) was synthesized by a solution polymerization technique using ceric ammonium nitrate (CAN) as an initiator (18). In brief, HEC solution was prepared by dissolving 5 g of solid polymer in 100 mL of HNO_3 ($5 \times 10^{-3}\ \text{M}$) under by overnight stirring. The solution was then degassed by passing nitrogen for 30 min, later 0.07 moles of acrylamide was added to this solution and stirred thoroughly for 1 h at 60°C . The initiator solution containing 5.47×10^{-4} moles of CAN was added to the mixture with a continuous stirring at 60°C for 5 h. The reaction mixture was then cooled and 10 mg of hydroquinone was added to quench the reaction. The mass obtained was precipitated in acetone and was washed with aqueous methanol to remove the formed poly(acrylamide) homopolymer. The solid copolymer was dried in an electrically controlled oven at 40°C

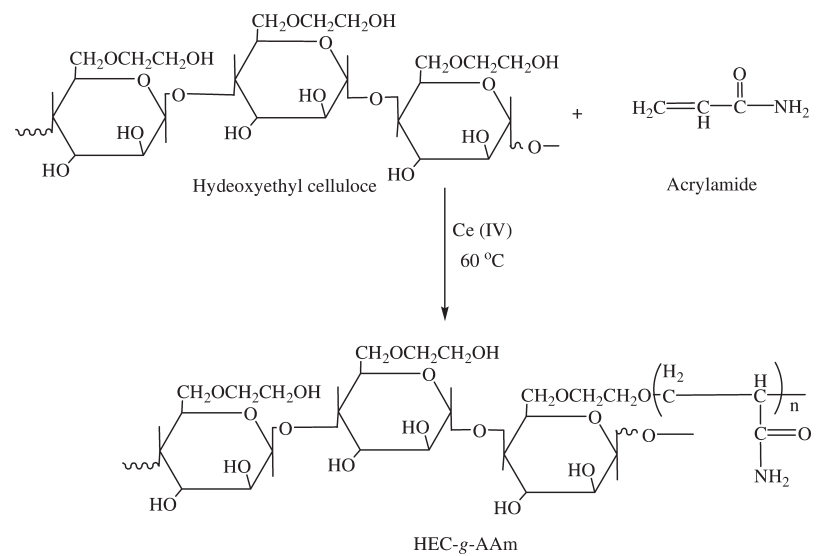
Table 1. Grafting details of HEC with poly(acrylamide)

Weight of HEC (g)	Moles of AAm	Yield (%)	Moles of initiator (10 ⁻⁴)	Grafting (%)	Grafting efficiency	Conversion of AAm (%)
5	0.07	92	5.47	84	84	184

before further use. The % grafting, grafting efficiency and % conversion were calculated by following the procedures proposed in the literature (21–23). The grafting results of HEC with poly(acrylamide) was reported in Table 1 and chemical interactions occurred during grafting was shown in Scheme 1.

Membrane Preparation

Blend membranes of sodium alginate with HEC-g-AAm were prepared by solution casting. Required amount of NaAlg (depends on the amount of HEC-g-AAm) was dissolved in 100 mL distilled water by stirring over a magnetic stirrer (Jenway, model 1103, UK) for 24 h. To this, different amounts of HEC-g-AAm (10, 20, and 30 wt.%) were added. The amount of NaAlg and HEC-g-AAm polymers present in different membranes were shown in Table 2. The solution was mixed uniformly and filtered to remove any suspended particles and then the filtrate was decanted onto a clean glass



Scheme 1. Synthesis of HEC-g-poly(acrylamide).

Table 2. Composition of NaAlg and HEC-*g*-AAm in the present membranes

Membrane	Amount of NaAlg (g)	Amount of HEC- <i>g</i> -AAm (g)
NaAlg	4.0	—
M-1	3.6	0.4
M-2	3.2	0.8
M-3	2.8	1.2

plate leveled perfectly on a tabletop kept in a dust free atmosphere and dried at room temperature. The dried membranes were peeled off carefully from the glass plate. Membranes were then crosslinked by immersing in 70% aqueous-acetone mixture containing 2.5 mL HCl and 2.5 mL GA for up to 12 h. After removing the membranes from the crosslinking bath, they were washed with water repeatedly and dried in an oven at 40°C. The thickness of the entire membranes were determined as a mean value from at least ten single measurements taken around the circumference of a membrane disk using a peacock dial thickness gauge (Model G, Ozaki Mfg. Co., Japan) with an accuracy of $\pm 5 \mu\text{m}$. The measured membrane thickness was around 35–40 μm . The membranes prepared with 10, 20, and 30 wt.% of HEC-*g*-AAm were designated as M-1, M-2, and M-3 respectively, while the plain sodium alginate membrane was designated as NaAlg.

Swelling Experiments

Equilibrium swelling experiments on all the membranes were performed in water-isopropanol mixtures ranging from 10–90 wt.% of water at $30 \pm 0.5^\circ\text{C}$ in an electronically controlled incubator (WTB Binder, Model BD-53, Tuttlingen, Germany). The detailed experimental procedure was described in elsewhere (24). Circularly cut (diameter = 2.5 cm) disk-shaped membranes were stored in a desiccator over anhydrous calcium chloride maintained at 30°C for about 48 h before performing the swelling experiments. Mass measurements were taken on a digital Mettler microbalance (Model AE 240, Greifensee, Switzerland) sensitive to $\pm 0.01 \text{ mg}$.

The degree of swelling (*DS*) of the membranes was calculated using:

$$DS = M_s/M_d \quad (1)$$

where M_s is mass of the swollen polymer in (g) and M_d is mass of the dry polymer in (g).

The diffusion coefficient was computed from sorption results using the equation (25)

$$D = \pi \left(\frac{h\theta}{4Q_\infty} \right)^2 \quad (2)$$

where θ is slope of the linear portion of the sorption curve before attainment of 60% equilibrium and h is the initial film thickness.

Weight gain, Q_∞ of the soaked polymer membranes at equilibrium is expressed in mole percent units (i.e., number of moles of solvent sorbed by 100 g of the polymer), which is calculated as (26)

$$Q_\infty = \left(\frac{W_\infty - W_i}{W_i} \right) \frac{100}{M_s} \quad (3)$$

where W_∞ and W_i are, respectively weight gains at equilibrium time and initial weight; M_s is molecular weight of the sorbed liquid.

Fourier Transform Infrared Measurements (FTIR)

FTIR measurements were taken at ambient temperature using a Nicolet, (Model Impact 410, USA). About 2 mg of the samples were grounded thoroughly by mixing with KBr and pellets were prepared under a hydraulic pressure of 600 kg/cm². Spectra were scanned between 4000 to 400 cm⁻¹.

Differential Scanning Calorimetry (DSC) Studies

DSC thermograms of the HEC and HEC-*g*-AAM copolymers were recorded using Rheometric Scientific differential scanning calorimeter, (Model-DSC SP, UK). The analysis was performed by heating the samples at the rate of 10°C/min under an inert atmosphere.

Pervaporation Experiments

Pervaporation experiments were performed in an apparatus designed indigenously (27). The PV apparatus consists of a stirred stainless steel cell through which retentate is circulated to the feed tank. The effective surface area of the membrane in the cell is 32.43 cm² with a diameter of 6.4 cm and the volume capacity of the cell is 250 cm³. Temperature of the feed mixture is kept constant using a thermostatically controlled water jacket. The PV cell is provided with an efficient three-blade stirrer powered by a DC current motor in the feed compartment. The downstream side of the PV apparatus

was continuously evacuated using a vacuum pump (Toshniwal, India) at a low pressure of 10 torr.

The test membrane was equilibrated for about 2 h with the feed mixture before starting the PV experiment. For each feed mixture PV runs lasted up to 5–6 h. After establishment of steady state, permeate vapors were collected in traps immersed in liquid nitrogen. PV experiments were performed for 10 to 50 wt.% water containing feed mixture. Each time, the depleted solvent mixture in the feed compartment was continuously enriched by adding the required amount of fresh solvent mixture. Mass of permeate collected in the trap was taken and its composition was determined by measuring its refractive index at 30°C using a refractometer (Atago, model 3T, Japan). From the PV data, selectivity, α was calculated,

$$\alpha_{PV} = \left(\frac{y_A}{1 - y_A} \right) \left(\frac{1 - x_A}{x_A} \right) \quad (4)$$

where x_A is mole fraction of water in the feed and y_A is mole fraction of water in the permeate. Flux, J (kg/m²h) was calculated from the weight of the permeate, w (kg), effective membrane area, A (m²) and time, t (h) using the relation,

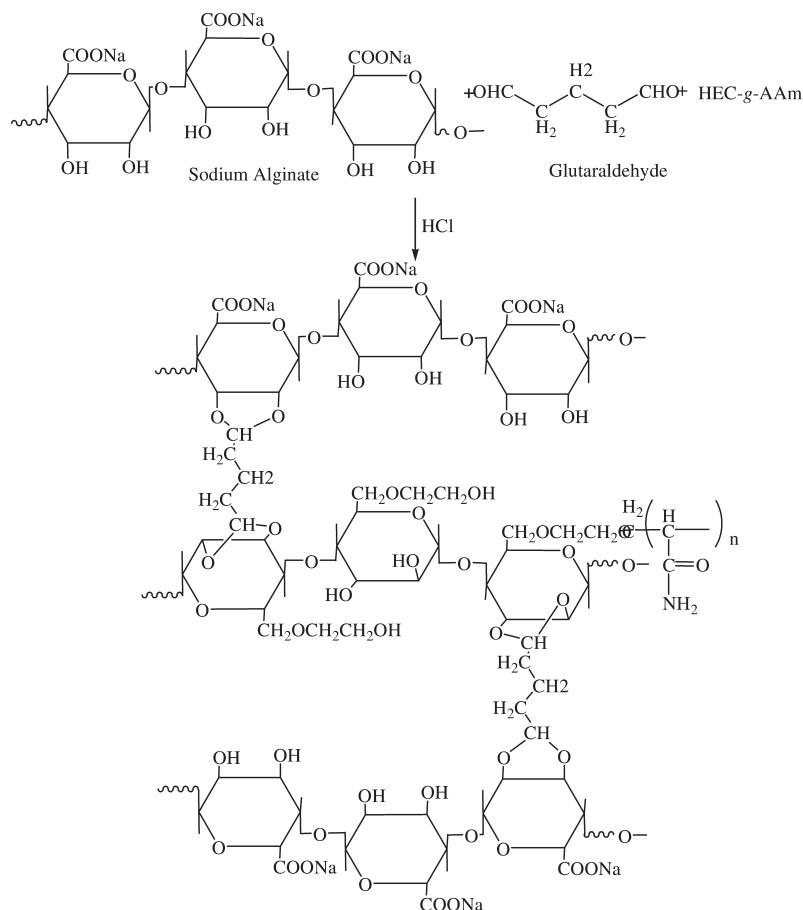
$$J = w/At \quad (5)$$

RESULTS AND DISCUSSIONS

The blend membrane formed by mixing the two polymers exhibited considerable swelling but remained insoluble in water indicating substantial chemical inertness. This insolubility of the blend can be due to crosslinking as well as the formation of interactions (hydrogen bonding between hydroxyl groups, hydroxy and amino groups of NaAlg and HEC-*g*-AAM) thus resulting in blending the two polymers. The blends were then crosslinked with glutaraldehyde (GA) to reduce the extent of swelling. During the crosslinking reaction, the hydroxyl group of NaAlg/HEC-*g*-AAM interacts with the aldehyde groups of GA resulting in the formation of acetal linkages (Scheme 2). It was noticed that both the polymers and the NaAlg/HEC-*g*-AAM blends were optically clear to the naked eye. No separation into two layers or any precipitation was noticed when allowed to stand for one month at room temperature.

FTIR Analysis

FTIR spectral studies were performed to confirm the grafting of acrylamide on HEC and also the crosslinking of NaAlg with HEC-*g*-AAM. The spectra of



Scheme 2. Interactions of NaAlg and HEC-g-AAm with glutaraldehyde.

pure HEC, HEC-g-AAm and GA crosslinked HEC-g-AAm are displayed in Figs. 1a and 1b. The appearance of broad band around $\sim 3430\text{ cm}^{-1}$ corresponds to associated -OH stretching vibrations of the hydroxyl groups in the curves of Figs. 1a and 1b. In the spectra of the copolymer (curve B in Fig. 1a), a new peak was observed at $\sim 3200\text{ cm}^{-1}$ and a peak at 1665 cm^{-1} corresponds to -NH bending of the primary amide of acrylamide. A relatively high intensity peak at 2925 cm^{-1} corresponds to aliphatic -CH stretching in the graft copolymer, which confirms the grafting of acrylamide on HEC (curve B). The new peak at $\sim 1455\text{ cm}^{-1}$ corresponding to C-N bending vibration supports the grafting reaction. A sharp peak at $\sim 1642\text{ cm}^{-1}$ corresponds to C=O stretching of the carboxylic group of NaAlg. The peaks appearing in the range $1050\text{--}1150\text{ cm}^{-1}$ in GA crosslinked membrane correspond to C-O-C linkage vibrations.

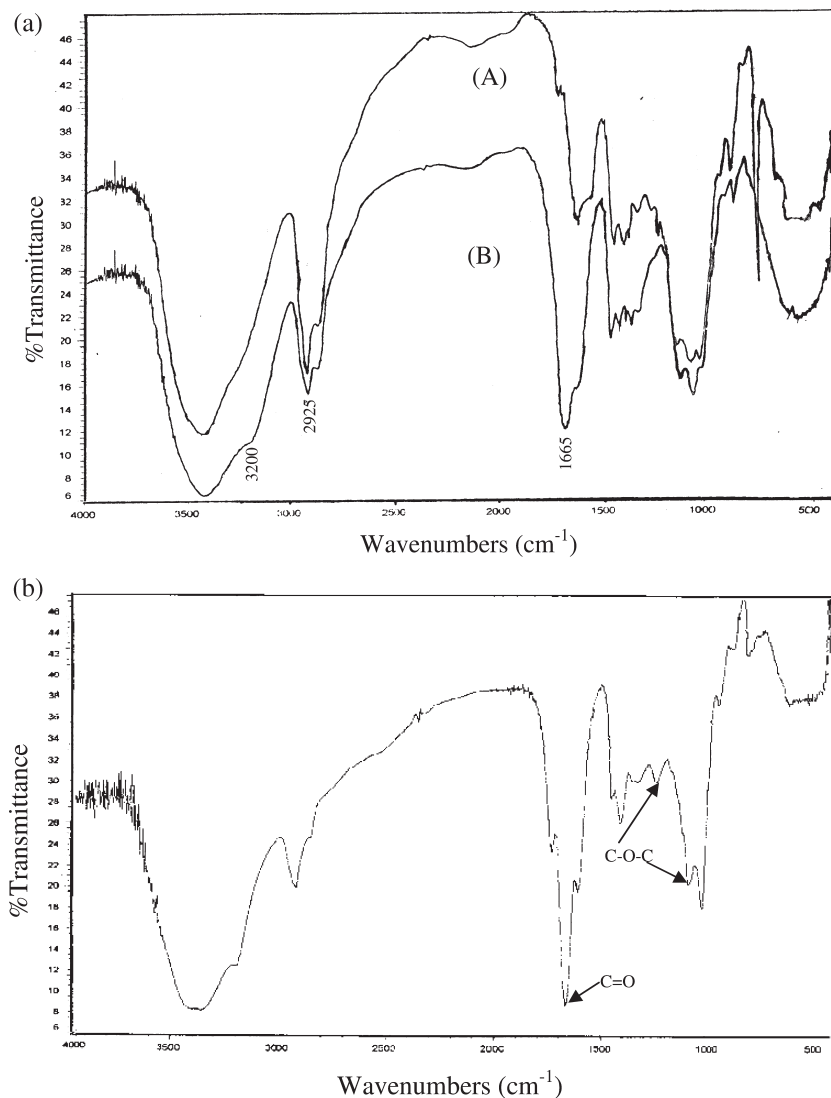


Figure 1. (a) FTIR spectra of (A) pure HEC and (B) HEC-g-AAm; (b) FTIR spectra of NaAlg/HEC-g-AAm crosslinked with glutaraldehyde.

DSC Studies

The DSC scans of the plain HEC and HEC-g-AAm are shown in Fig. 2. The values of the glass transition temperature T_g of both the polymers are determined by the DSC technique at a heating rate of 10°C/min. Plain HEC has

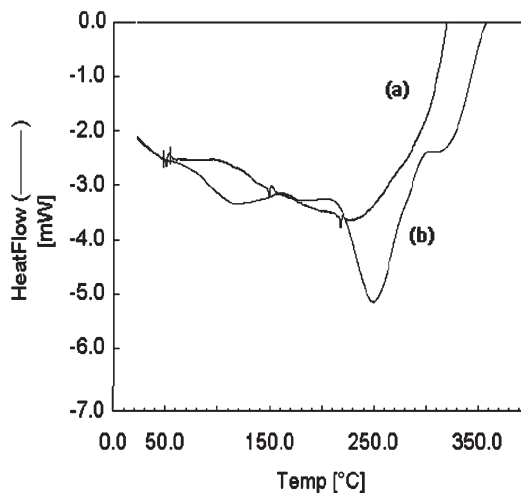


Figure 2. DSC thermograms of (a) HEC and (b) HEC-g-AAm copolymer.

a glass transition temperature around 65°C. The T_g of HEC was shifted to higher temperature (135°C) in the graft copolymer, which confirms the grafting of acrylamide on HEC.

Membrane Swelling

It has been well recognized that swelling properties exhibited by the polymers are helpful in the selection of proper membrane materials because PV performance of the membranes depends on their sorption characteristics. However, it must be pointed out that swelling data does not always necessarily correspond to permeability because diffusion through the membrane materials also contributes significantly to the overall permeation process.

Results of the degree of swelling of membranes in water-isopropanol mixtures ranging from 10 to 100 wt.% of water at 30°C are displayed in Fig. 3. *DS* of the membranes increased with an increasing amount of water in the feed and also, with increasing amount of HEC-g-AAm in the blend membrane. This could be due to increased solubilization of the carbohydrate polymers in the presence of higher amount of water of the feed mixture. As the amount of grafting in the copolymer was increased, the blend membrane became more hydrophilic because of the presence of higher amount of HEC, which is more hydrophilic than NaAlg. This effect would further increase the free volume of the matrix due to the polarization of matrix, thus leading to an increase in swelling (27). The degree of membrane swelling in water-isopropanol feed mixtures varies according to the sequence M-3 > M-2 > M-1 > NaAlg (Table 3). The least swelling of all

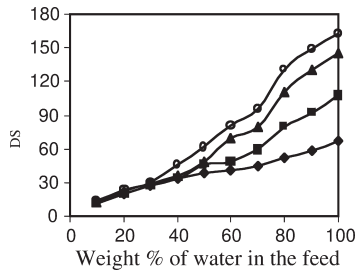


Figure 3. Equilibrium swelling curves in water-isopropanol at 30°C. Symbols: NaAlg (◆); M-1 (■); M-2 (▲); M-3 (○).

the membranes is that of NaAlg, whose behavior could be directly related to its PV performance as compared to the blend membranes.

It is well known that the separation characteristics of a membrane depend upon the interaction between the solvent to be separated and the membrane matrix. For a hydrophilic membrane like NaAlg which can develop hydrogen bond interactions, it could extract water from the organic solvent by PV. The hydrogen bond interactions between water and isopropanol forms a cluster, which has the formula $(ROH)_x \cdot yH_2O$, so that separation by the hydrophobic membrane is difficult due to the relatively large coupling of the diffusion. The influence of feed composition has been examined in order to study in detail the PV separation.

Diffusion Coefficient

Transport of molecules in PV experiments has been explained by the solution–diffusion model, (28) since molecular transport in PV depends upon sorption

Table 3. Equilibrium swelling (wt/wt) results of different membranes in water-isopropanol mixtures at 30°C

Wt.% of water	NaAlg	M-1	M-2	M-3
10	12.88	11.08	12.94	13.05
20	19.80	20.09	22.15	23.65
30	26.92	27.01	28.60	29.65
40	32.93	32.96	36.45	46.35
50	38.72	45.63	48.32	62.35
60	40.96	49.23	69.98	80.32
70	45.00	59.89	80.02	95.12
80	51.60	79.65	110.36	130.65
90	58.60	92.17	130.60	148.72
100	66.78	108.07	145.62	162.35

and diffusion of liquid molecules through the barrier membrane. Diffusion coefficients of plane NaAlg and NaAlg/HEC-*g*-AAM blend membranes at azeotropic concentration of isopropanol/water mixtures were calculated using Equation (2) and the results were presented in Table 4. From this table, it was observed that the diffusion coefficient values were increased with increasing HEC-*g*-AAM content. In order to ascertain the mechanism of liquid diffusion through NaAlg/HEC-*g*-AAM membranes, we have analyzed the mol% sorption data using the empirical equation (29)

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \tag{6}$$

where Q_t and Q_∞ are mol% uptake values at time, t and at equilibrium, respectively; k and n are the system parameters that depend upon the structural characteristics of the membranes. These values give valuable information about the nature of interactions between liquid components and NaAlg/HEC-*g*-AAM membranes. Values of k and n have been estimated by the method of regression analysis by fitting $\log(Q_t/Q_\infty)$ vs $\log t$ and were computed in Table 4. The value of n indicates the type of diffusion mechanism. The n values of NaAlg and other NaAlg/HEC-*g*-AAM membranes were found to be less than 0.5, indicating simultaneous relaxation, i.e., Case I type transport (25).

Pervaporation Results

PV results (flux and selectivity) of the blend membranes along with the plain NaAlg membrane at different wt.% of water in the feed are displayed in Fig. 4. Plain NaAlg membrane has a flux of 0.349 kg/m² · h with a removal of 99.12 wt.% of water in the permeate side when for 10 wt.% water in the feed was considered. These values are much lower than those observed for blend membranes. However, we could see considerable increase in flux up to 1.64 kg/m² · h with a somewhat higher amount of water 94 wt.% in the permeate side at higher concentrations of water in the feed. For the azeotropic

Table 4. Diffusion coefficient and n values of NaAlg and NaAlg/HEC-*g*-AAM membranes in 10 wt.% of water in water-isopropanol mixture at 30°C

Membrane	$D \text{ (m}^2\text{/s)} \times 10^8$	k	n
NaAlg	1.34	0.49	0.224
M-1	2.42	0.50	0.255
M-2	2.88	0.52	0.257
M-3	4.02	0.56	0.264

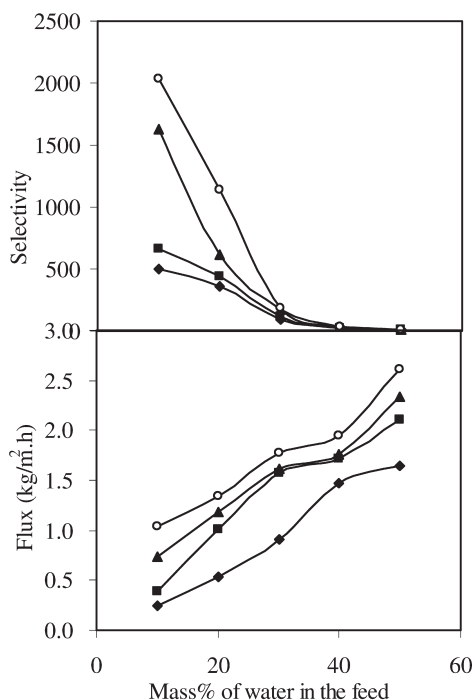


Figure 4. Water flux and selectivity vs. wt.% of water in the feed for NaAlg and its blend membranes with HEC-g-AAm. Symbols: NaAlg (◆); M-1 (■); M-2 (▲); M-3 (○).

composition, i.e., 12.5 wt.% water in the feed mixture, the flux varied from $0.317 \text{ kg/m}^2 \cdot \text{h}$ for NaAlg to $1.113 \text{ kg/m}^2 \cdot \text{h}$ for NaAlg/HEC-g-AAm-30 (Table 5). The flux yielded by the membranes synthesized in this study followed the order; $\text{M-3} > \text{M-2} > \text{M-1} > \text{NaAlg}$. This increase in flux is due to the increase in swelling of NaAlg membrane at higher concentration of water in the feed. By blending NaAlg with a graft copolymer of HEC-g-AAm, we could increase both permeation flux and water concentration on the permeate side. Among the three blend membranes prepared, NaAlg/HEC-g-AAm-30 has shown the highest flux ranging from 0.349 to $2.615 \text{ kg/m}^2 \cdot \text{h}$ with a separation of as much as 99.56 wt.% of water in the permeate side. In case of blend membranes also, the permeation flux and wt.% of water in permeate increased with increasing concentration of water in the feed. This could be the result of excessive swelling of the blend membranes at higher amount of water in the feed mixtures. At higher feed water concentrations, the membrane swells more appreciably i.e., with more water molecules available for sorption and diffusion, the polymer chains become more flexible and the transport through the membrane becomes easier for the feed components resulting in high flux.

Table 5. Flux and selectivity of NaAlg and NaAlg/HEC-*g*-AAM membranes at azeotropic concentration (12.5/87.5) of water-isopropanol mixtures

Membrane	Water flux (kg/m ² · h)	Selectivity	Water in permeate (wt.%)
NaAlg	0.317	353	98.06
NaAlg-HEC- <i>g</i> -AAM-10	0.546	586	98.82
NaAlg-HEC- <i>g</i> -AAM-20	0.845	1199	99.42
NaAlg-HEC- <i>g</i> -AAM-30	1.113	1787	99.61

From Fig. 4, the plain NaAlg membrane has shown a selectivity of 495 at 10 wt.% water in the feed, which decreased to 16 with increasing feed water concentration up to 50 wt.%. On the other hand, blend membranes of NaAlg with HEC-*g*-AAM have all shown improved selectivity than the plain NaAlg membrane. For instance, M-1 has a selectivity of 667 with a flux value of 0.39 kg/m² · h at 10 wt.% of water in the feed, whereas M-3 has a selectivity of 2036 with still higher flux value of 1.036 kg/m² · h. At azeotropic concentration also, the selectivity of the membranes follows the same trend, i.e., 353 for NaAlg and increased to 1787 for M-3. In case of blend membranes also selectivity decreases with increasing amount of water in the feed. Excessive swelling of the blend membranes at higher water content in the feed could be the cause for this effect, since both the permeate molecules would pass through the membranes giving a decrease in selectivity.

In most of the PV experiments, efforts have been directed to simultaneously increase the flux and selectivity of the membranes. It appears that all the membranes of this study have exhibited higher values of selectivity and the flux values at lower concentration (10 wt.%) of water in the feed mixture. In order to study this effect, we have displayed the plots of flux and selectivity of the membranes (see Fig. 4) obtained at 10 wt.% of water as a function of wt.% of HEC-*g*-AAM in the blend membrane. Permeation flux as well as selectivity of the membranes increased from 0.349 to 1.036 kg/m² · h and 495 to 2036, respectively with increasing the amount of HEC-*g*-AAM from 0 to 30 wt.% in the blend membrane. At higher content of HEC-*g*-AAM in the blend, the rigid polymeric chains of NaAlg become somewhat flexible, thereby increasing the free volume of the matrix, which in turn, increases the hydrophilicity of membranes facilitating more amount of water to transport through the membrane. These results bear similar trends as those of swelling data discussed before.

Comparison of Present Work with Literature

The pervaporation performance of the NaAlg/HEC-*g*-AAM blend membranes is compared with the data available in the literature and is reported in Table 6

Table 6. Comparison of performance of present work with literature data for water isopropanol mixtures

Membrane	Temperature (°C)	Water in feed (wt · %)	Flux (kg/ m ² · h)	Selectivity	Reference
Chitosan-PAAc	30	12.5	0.14	1736	(30)
PASA			0.0029	3686	(31)
PASA-bromo propane	20	10	0.0042	∞	(31)
PVA Crosslinked with GA	30	10	0.1940	116	(32)
NaAlg-Chitosan	60	10	0.554	2010	(33)
NaAlg	30	10	0.058	411	(34)
NaAlg/GG- gpAAm	30	10	0.043	891	(34)
NaAlg/ PVA(75:25)			0.025	195	(35)
Chitosan cross- linked with TDI	30	8.4	0.39	472	(36)
PERVAP-silica	70	8.2	1.9	53	(37)
Silica	80	4.5	1.9	1150	(38)
Silica	70	5.0	2.1	600	(39)
Diisocyanate crosslinked Chitosan	30	10	0.034	2423	(40)
NaAlg/HEC-g- AAm-30	30	10	1.30	2036	Present work

PAAc: Poly(acrylic acid), PASA: poly(amide sulfonamide), PVA: poly(vinyl alcohol), TDI: toluene diisocyanate, NaAlg: sodium alginate, GA: glutaraldehyde.

(30–40). From the table, it can be noted that the membranes synthesized in the study yielded higher fluxes than other researchers work but showed comparable selectivity. A marginally good selectivity combined with high fluxes render the crosslinked blend suitable for dehydration of isopropanol-water mixtures. Furthermore, the ease in fabrication of these membranes associated with low cost render them quite attractive for pervaporation of alcohols.

CONCLUSION

GA crosslinked NaAlg/HEC-g-AAm blends appear to have promising potential for dehydration of aqueous solution of isopropanol, especially at the azeotropic composition of 12.5 wt.% of water besides dehydrating the solvent to >99 wt.% purity. We have tested hydrophilic blend membranes

for dehydration of isopropanol for this we have prepared HEC-g-AAm and it was confirmed by the FTIR. The highest selectivity for M-3 was found to reach as high as 2036 at 30°C feed temperature. This is much higher than plane NaAlg membrane value obtained for 10 wt.% of water in the feed, which was due to incorporation of the hydrophilic polymer in the blend membranes. The selectivity decreased gradually and isopropanol permeation flux increased at higher wt.% of water in the feed. Permeate rate increases as the concentration of water in feed increases; this mainly includes the contribution of both increase of the swelling degree, which conduces to the expansion of the free volume, and the active effect of the diffusion coefficient of water through a membrane.

REFERENCES

1. Fleming, H.L. and Slater, C.S. (1992) *Membrane Handbook*; Van Mastrand Reinhold: New York, p. 105.
2. Aminabhavi, T.M., Khinnavar, R.S., Harogoppad, S.B., Aithal, U.S., Nguyen, Q.T., and Hansen, K.C. (1994) Pervaporation separation of organic-aqueous and organic-organic binary mixtures. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, C34: 139–204.
3. Liang, L. and Ruckenstein, E. (1995) Poly(vinyl alcohol)-polyacrylamide interpenetrating polymer network membranes and their pervaporation characteristics for ethanol-water mixtures. *J. Membr. Sci.*, 106: 167–182.
4. Aminabhavi, T.M. and Toti, U.S. (2003) Pervaporation separation of water–acetic acid mixtures using polymeric membranes. *Des. Mono. Polym.*, 6: 211–236.
5. Rao, P.S., Smitha, B., Sridhar, S., and Krishnaiah, A. (2006) Separation of acetic acid/water mixtures by pervaporation through Poly(vinyl alcohol)–sodium alginate blend membranes. *Sep. Sci. Tech.*, 41: 979–999.
6. Naidu, B.V.K., Bhat, S.D., Sairam, M., Wali, A.C., Sawant, D.P., Halligudi, S.B., Mallikarjuna, N.N., and Aminabhavi, T.M. (2005) Comparison of the pervaporation separation of a water-acetonitrile mixture with zeolite-filled sodium alginate and poly(vinyl alcohol)-polyaniline semi-interpenetrating polymer network membranes. *J. Appl. Polym. Sci.*, 96 (5): 1968–1978.
7. Kanti, P., Srigowri, K., Madhuri, J., Smitha, B., and Sridhar, S. (2004) Dehydration of ethanol through blend membranes of chitosan and sodium alginate by pervaporation. *Sep. Purif. Technol.*, 40: 259–266.
8. Yang, G., Zhang, L., Peng, T., and Zhong, W. (2000) Effects of Ca^{2+} bridge cross-linking on structure and pervaporation of cellulose/alginate blend membranes. *J. Membr. Sci.*, 175: 53–60.
9. Kulkarni, A.R., Soppimath, K.S., Aminabhavi, T.M., Dave, A.M., and Mehta, M.H. (2000) Glutaraldehyde crosslinked sodium alginate beads containing liquid pesticide for soil application. *J. Contr. Rel.*, 63: 97–105.
10. Xing, L., Dawei, C., Liping, X., and Rongquing, Z. (2003) Oral colon-specific drug delivery for bee venom peptide: development of a coated calcium alginate gel beads-entrapped liposome. *J. Contr. Rel.*, 93: 293–300.
11. Kurkuri, M.D., Kumbar, S.G., and Aminabhavi, T.M. (2002) Synthesis and characterization of polyacrylamide-grafted sodium alginate copolymeric membranes and

- their use in pervaporation separation of water and tetrahydrofuran mixtures. *J. Appl. Polym. Sci.*, 86: 272–281.
12. Savage, A.B. and Ethers, C. (1971) *Cellulose and Cellulose Derivatives*; John Wiley & Sons: USA.
 13. Nicholson, M.D. and Merritt, F.M. (1985) Cellulose ethers. In *Cellulose Chemistry & its Applications*; Nevell, T.P. and ShZeronian (eds.); Ellis Horwood: U.K. pp. 363–383.
 14. Chanachai, A., Jiratananon, R., Uttapap, D., Moon, G.Y., Anderson, W.A., and Huang, R.Y.M. (2000) Pervaporation with chitosan/hydroxyethylcellulose (CS/HEC) blended membranes: I. Effect of operating conditions. *J. Membr. Sci.*, 166 (2): 271–280.
 15. Jiratananon, R., Chanachai, A., Huang, R.Y.M., and Uttapap, D. (2002) Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose composite membranes: I. Effect of operating conditions. *J. Membr. Sci.*, 195 (2): 143–151.
 16. Jiratananon, R., Chanachai, A., and Huang, R.Y.M. (2002) Pervaporation dehydration of ethanol-water mixtures with chitosan/hydroxyethylcellulose (CS/HEC) composite membranes: II. Analysis of mass-transport. *J. Membr. Sci.*, 199: 211–222.
 17. Mino, G. and Kaizerman, S. (1958) A new method for the preparation of graft copolymers. Polymerization initiated by ceric ion redox systems. *J. Polym. Sci.*, 31: 242–243.
 18. Lepoutre, P., Hui, S.H., and Robertson, A. (1973) The water absorbency of hydrolyzed polyacrylonitrile-grafted cellulose fibers. *J. Appl. Polym. Sci.*, 17: 3143–3156.
 19. Lepoutre, P. and Hui, S.H. (1975) Grafting acrylonitrile onto wood pulp: Influence of process variables. *J. Appl. Polym. Sci.*, 19: 1257–1268.
 20. Zhuran, A.H., Williams, J.L., and Stannet, V.T. (1980) Radiation grafting of acrylic and methacrylic acid to cellulose fibers to impart high water sorbency. *J. Appl. Polym. Sci.*, 25: 535–542.
 21. Sun, T.P., Xu, Q., Liu, Q., Xue, J., and Xie, W. (2003) Graft copolymerization of methacrylic acid onto carboxymethyl chitosan. *Euro. Polym. J.*, 39: 189–192.
 22. Hayashi, T., Takeuchi, Y., Eguchi, M., Lida, T., and Tsubokawa, N. (1999) Graft polymerization of vinyl monomers initiated by peroxy carbonate groups introduced onto silica surface by Michael addition. *J. Appl. Polym. Sci.*, 71: 1491–1497.
 23. Vandana, S., Ashutosh, T., Devendra, N.T., and Rashmi, S. (2005) Poly(acrylonitrile) grafted *Ipomoea* seed-gums: A renewable reservoir to industrial gums. *Biomacromolecules*, 6: 453–456.
 24. Aminabhavi, T.M., Phayde, H.T.S., Ortego, J.D., and Vergnaud, J.D. (1996) A study of sorption/desorption profiles and diffusion anomalies of organic haloalkanes into a polymeric blend of ethylene-propylene random copolymer and isotactic polypropylene. *Polymer*, 37: 1677–1684.
 25. Rao, P.S., Sridhar, S., Krishnaiah, A., and Wey, M.Y. (2007) Pervaporative separation of ethylene glycol/water mixtures by using cross-linked chitosan membranes. *Ind. Eng. Chem. Res.*, 45: 2155–2163.
 26. Harogopad, S.B. and Aminabhavi, T.M. (1991) Diffusion and sorption of organic liquids through polymer membranes. II. Neoprene, SBR, EPDM, NBR, and natural rubber versus n-alkanes. *J. Appl. Polym. Sci.*, 42: 2329–2336.
 27. Duda, J.L. and Zielinski, J.M. (1996) *Free-volume Theory in Diffusion Polymers*; Marcel Dekker, Inc.: New York.

28. Wijmans, J.G. and Baker, R.W. (1995) The solution-diffusion model: a review. *J. Membr. Sci.*, 107: 1–21.
29. Lucht, L.M. and Peppas, N.A. (1987) Transport of penetrants in the macromolecular structure of coals. V. Anomalous transport in pretreated coal particles. *J. Appl. Polym. Sci.*, 33: 1557–1566.
30. Dhanuja, G., Smitha, B., and Sridhar, S. (2005) Pervaporation of isopropanol–water mixtures through polyion complex membranes. *Sep. Purif. Technol.*, 44: 130–138.
31. Chan, W.H., Ng, C.F., Lam-Leung, S.Y., and He, X. (1999) Water–alcohol separation by pervaporation through chemically modified poly(amidesulfonamide). *J. Membr. Sci.*, 160: 77–86.
32. Brushe, M.C., Netke, S.A., Sawant, S.B., Joshi, J.B., and Pangarkar, V.G. (1997) Pervaporative dehydration of organic solvents. *Sep. Sci. Technol.*, 32: 1335–1349.
33. Moon, G.Y., Pal, R., and Huang, R.Y.M. (1999) Novel two-ply composite membranes of chitosan and sodium alginate for the pervaporation dehydration of isopropanol and ethanol. *J. Membr. Sci.*, 156: 17–27.
34. Toti, U.S. and Aminabhavi, T.M. (2002) Pervaporation separation of water-isopropyl alcohol mixtures with blend membranes of sodium alginate and poly(acrylamide)-grafted guar gum. *J. Appl. Polym. Sci.*, 85: 2014–2024.
35. Kurkuri, M.D., Toti, U.S., and Aminabhavi, T.M. (2002) Syntheses and characterization of blend membranes of sodium alginate and poly(vinyl alcohol) for the pervaporation separation of water + isopropanol mixtures. *J. Appl. Polym. Sci.*, 86: 3642–3651.
36. Devi, D.A., Smitha, B., Sridhar, S., and Aminabhavi, T.M. (2005) Pervaporation separation of isopropanol/water mixtures through crosslinked chitosan membranes. *J. Membr. Sci.*, 262: 91–99.
37. Gallego-Lizon, T., Ho, Y.S., and Santos, L.F.D. (2002) Comparative study of commercially available polymeric and microporous silica membranes for the dehydration of IPA/water mixtures by pervaporation/vapour permeation. *Desalination*, 149: 3–8.
38. Gemert, R.W.V. and Cuperus, F.P. (1995) Newly developed ceramic membranes for dehydration and separation of organics by pervaporation. *J. Membr. Sci.*, 105: 287–291.
39. Verkerk, A.W., Male, P.V., Vorstman, M.A.G., and Keurentjes, J.T.F. (2001) Properties of high flux ceramic pervaporation membranes for dehydration of alcohol/water mixtures. *Sep. Purif. Tech.*, 22–23: 689–695.
40. Choudhari, S.K., Kittur, A.A., Kulkarni, S.S., and Kariduraganavar, M.Y. (2007) Development of novel blocked diisocyanate crosslinked chitosan membranes for pervaporation separation of water-isopropanol mixtures. *J. Membr. Sci.*, 302: 197–206.