

Characterization and Performance Evaluations of Sodium Zeolite-Y Filled Chitosan Polymeric Membrane: Effect of Sodium Zeolite-Y Concentration

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Received 2 September 2004; accepted 8 April 2005

DOI 10.1002/app.22703

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Sodium zeolite-Y (NaY zeolite) filled chitosan polymeric membranes were developed and characterized. The impact of adding different concentrations of NaY zeolite into the homogeneous chitosan membrane was investigated. The surface morphology, mechanical-physical properties, sorption, and pervaporation performance for the dehydration of isopropanol-water mixture separation by the pervaporation process were studied and evaluated. A homogeneous chitosan membrane showed preferential water sorption and permeation compared to isopropanol. The optimum concentration of NaY zeolite added to the homogeneous chitosan membrane was 0.4 wt %, which showed that the dispersion of the NaY zeolite was the most homoge-

neous and finely covered by the chitosan polymer in the zeolite-chitosan polymer interface. The tensile strength and percent strain at maximum of this membrane were 59.347 MPa and 27.5%, respectively. The sorption experiments showed that the degree of swelling was 6.54% with 1.01 wt % isopropanol sorbed in these membranes. The pervaporation separation tests demonstrated that the NaY zeolite filled chitosan membrane was capable for isopropanol-water mixture separation and improved the pervaporation separation index from 272 (homogeneous chitosan membrane) to 2687. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1740–1751, 2006

Key words: swelling; membranes; zeolites; strain

INTRODUCTION

Pervaporation can be used for selective separation based on selective sorption and diffusion of one component through a dense membrane. The process involves a phase change of permeate from the liquid phase to the gas phase. Consequently, energy is needed for the vaporization of the permeate. Pervaporation appears to be promising, especially when the preferential permeable component present in the feed is at a low concentration. Transport through the membrane is induced by maintaining a vapor pressure on the permeate side of the membrane that is lower than the partial pressure on the feed liquid. Applying a vacuum pump can create the pressure difference as the driving force. It is also achieved by cooling the permeate vapor to a temperature that is lower than the feed stream, causing it to condense.

The pervaporation process is used for the dehydration process to remove low concentrations of water in solvent-water mixtures. Among the applications are the dehydration of ethanol using different types of

water selective membranes such as (HY) zeolite filled (CS),¹ an asymmetric polysulfone membrane,² a CS/poly(acrylic acid) membrane,³ a composite membrane of poly(acrylic acid) and plasma-treated polycarbonate,⁴ metal ion exchanged poly(vinyl alcohol) (PVA)/sulfosuccinic acid,⁵ and sulfonated zirconia-PVA.⁶ It is also applied in the dehydration of the following: alcohol using a surface resintering expanded poly(tetrafluoroethylene),⁷ butanol using an asymmetric sulfonated polystyrene sulfonated poly(ether sulfone),⁸ phenol using a polyamide membrane,⁹ isopropanol using a sodium alginate (SA)/polyacrylamide blend membrane,¹⁰ isopropanol using an polyacrylonitrile/alginate membrane,¹¹ isopropanol using a sodium zeolite-Y (NaY zeolite) incorporated SA membrane,¹² light oil using a PVA/poly(acrylic acid-co-maleic acid) membrane,¹³ toluene using a composite membrane,¹⁴ hydrazine using an ethylcellulose membrane,¹⁵ and dehydration of tetrahydrofuran using a polyacrylamide-grafted SA copolymeric membrane.¹⁶

Pervaporation is also used in the removal of small quantities of volatile organic solutes or organic solvents from water using hydrophobic membranes.¹⁷ The application of this method was investigated in relation to the removal of volatile organic pollutants such as halogenated hydrocarbons from water.¹⁸

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Mishima and Nakagawa¹⁹ adopted analytical pervaporation through a poly(dimethylsilazane) membrane for environmental samples to analyze hydrophilic organic compounds in the water. Cui et al.²⁰ used the zeolite-T membrane to separate organic liquid and acetic acid from water by pervaporation. Therefore, the removal of low contents of organic solvents from aqueous solutions provides numerous opportunities for applications in wastewater treatment and solvent recovery. There are also other promising applications in the food industry such as aroma recovery and beer dealcoholization.^{21,22} Other applications of pervaporation are for separation of mixed organic solvents^{23,24} and organic vapor separation from contaminated air.^{25,26}

Zeolites have been conventionally used as catalysts, ion exchangers, and adsorbents. Only in recent years has the potential of using these materials for membrane-based pervaporation been realized. Types of zeolite in common used are A, X, Y, silicate, and ZSM-5. When sodium is present as the counterion in the membrane lattice, the zeolites are termed NaA, NaX, and NaY. These zeolites are mainly classified based on their cage size and hydrophilicity. By changing the ratio of the various oxides (Na_2O , SiO_2 and Al_2O_3) in the membranes, the cage size and hydrophilicity are both varied.

Synthetic zeolites have a highly crystalline ordered structure and hence offer the unique advantage of a narrow pore size distribution, which provides higher molecular sieving properties. These materials also have higher resistance to a variety of solvents and stability at elevated temperature because of their inorganic nature. Zeolites can be classified into hydrophilic and organophilic membranes, depending on the silica (Si_2O) content. Higher silica content indicates a higher hydrophobic character.²⁷

A zeolite cage has positively charged metal ions (Na^+ and K^+) that are electrostatically bound to the aluminosilicate framework. Jafar and Budd²⁸ used the Na and K forms of the zeolite-A membrane to investigate the effects of the type of counterions on the separation properties of the zeolite-A membrane. The separation is not dramatically affected by the different forms of zeolite-A membranes. However, there is a distinct possibility that the membrane properties could change into other forms such as Mg, Ca, and so forth. Silicate and ZSM-5 are the two materials that are usually studied for their organic permeation behavior. The addition of these types of zeolites to silicone rubber membranes can improve the alcohol to water selectivity.

The objective of the current work is to develop and compare the effect of adding NaY zeolite into a chitosan membrane as a filler to improve the membrane properties. NaY zeolite was chosen because of its hydrophilic characteristics. Two types of chitosan mem-

branes (homogeneous chitosan membrane without NaY zeolite and NaY zeolite filled chitosan membrane) were developed and characterized. These membranes were characterized in term of their surface structure morphologies; mechanical-physical properties, including the tensile strength and strain at maximum; and sorption tests, including the degree of swelling and selectivity. The membranes were further characterized using the pervaporation process for the dehydration of an isopropanol-water mixture; the overall flux, individual flux, composition in the feed and permeate, separation factor, and pervaporation separation index (PSI) were evaluated and compared.

EXPERIMENTAL

Materials

Chitosan polymer (molecular weight = 50,000–100,000) was used. Reagent grade acetic acid was supplied by Mallinckrodt Baker. NaY zeolite with an average particle size of $\sim 2 \mu\text{m}$ in powder form was purchased from Aldrich Chemical Company. The isopropanol-water mixture (90 wt %) used for the pervaporation tests was prepared by mixing a known quantity of isopropanol and deionized water. The isopropanol was purchased from Merck.

Membrane preparation

Preparation of homogeneous chitosan membrane

Figure 1 provides a flowchart to prepare both types of membranes. Preweighed chitosan powder was dissolved in a 10 wt % aqueous acetic acid solution for 24 h at room temperature to produce a casting solution consisting of 2 wt % chitosan. The polymer solution was filtered to remove the undissolved chitosan and impurities using a vacuum pump. The solution was left overnight at room temperature to release the effervescence and to produce a homogeneous solution. A petri dish was washed carefully with distilled water and then dried in an oven. The casting solution was poured onto the petri dish, allowing the casting solvent to spread slowly, and evaporated in a dust-free atmosphere for 3–4 days at room temperature to form an even liquid film. The membrane that was formed was peeled off the plate. Three weight percent of a NaOH solution containing 47 wt % ethanol and 50 wt % deionized water was used to treat the membrane at room temperature for 24 h. Then, the membrane was washed thoroughly with deionized water to completely remove the NaOH and dried at room temperature. The thickness of the membrane was 20–30 μm .

Preparation of NaY zeolite filled chitosan membranes

The NaY zeolite filled chitosan membrane was prepared by adding a calculated amount of NaY zeolite

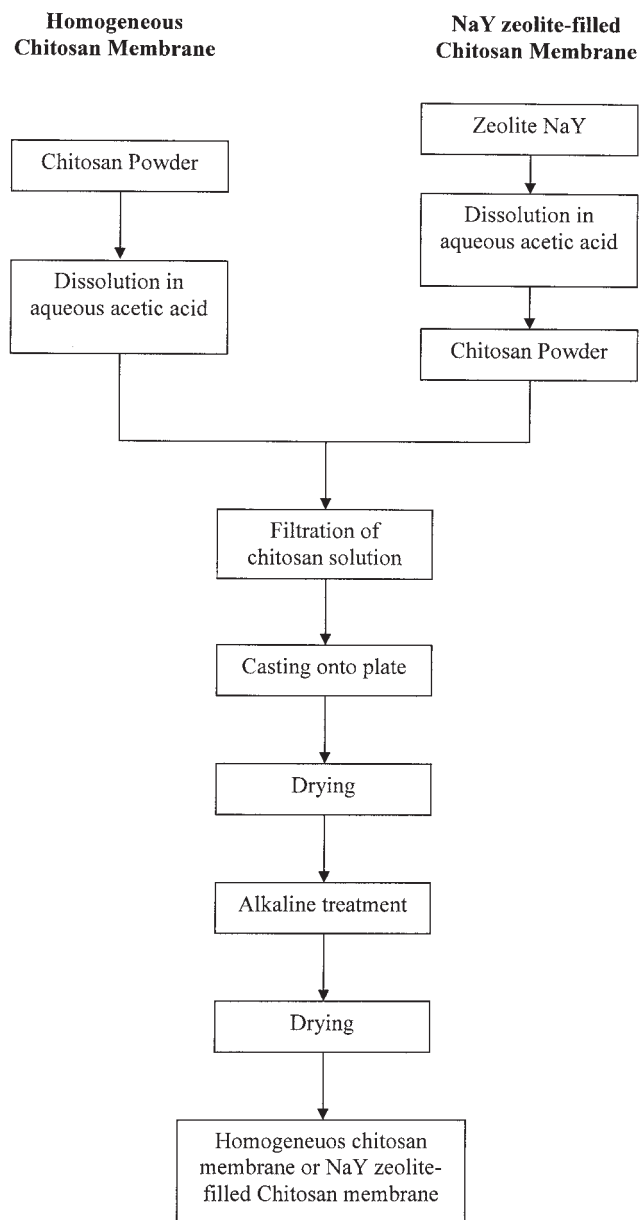


Figure 1 A flowchart showing the preparation of both types of membranes.

into the casting solution and mixing thoroughly before casting. The quantity of NaY zeolite that was used was 0.1–0.5 wt %. As shown in Figure 1, the NaY zeolite were dispersed well in the 10 wt % acetic acid solution before 2 wt % chitosan powder was added for 24 h at room temperature to produce the casting solution. The latter procedures were the same as the homogeneous chitosan membrane.

Performance study of membranes

Scanning electron microscopy (SEM)

The morphology of the chitosan-based membrane was determined with a Philips XL-40 scanning electron

microscope at a 15-kV accelerating voltage. The membrane was freeze-fractured in liquid nitrogen and then mounted on the aluminum stub. The specimen was sputter coated with gold prior to macroscopic observation. The membrane was examined to determine if the zeolite particles were dispersed homogeneously and if there were any defects or flaws in the membrane using the surface and cross section of the SEM micrographs.

Mechanical strength of membranes

The tensile strength test for the membrane was performed with a Lloyd EZ 50 instrument. The membrane was cut into several dumbbell-shaped specimens. Then, the widths and thicknesses of the specimens at several points along their narrow sections were measured with an electronic digital calliper and a digimatic micrometer. The width of a specimen was measured as the distance between the cutting edges of the die in the narrow section. The specimen was placed in the grips of the testing machine, and the grips were tightened evenly and firmly to the degree necessary to prevent slippage of the specimen during the test. Then, the extension indicator was attached. The cross-head speed was fixed at 10 mm/min for the tensile strength and percent strain at maximum tests. The minimum number of specimens needed for each sample was five (ASTM D 638).

Tensile strength

The tensile strength of the membrane was calculated by dividing the maximum load in Newtons (or lbf) by the original minimum cross-sectional area of the specimen in square meters (or in.²). The result was expressed in Pascals (or lbf/in.²; ASTM D 638).

$$\text{tensile strength} = \frac{\text{load at maximum}}{\text{area of membrane sample}} \quad (1)$$

The percent strain at maximum of the membrane was calculated by reading the extension (change in gage length) at the moment the applicable load was reached. Then, the extension was divided by the original gauge length and multiplied by 100. The percent strain at maximum was reported to two significant figures (ASTM D 638).

percentage strain at maximum =

$$\frac{\text{extension at maximum}}{\text{gauge length}} \times 100 \quad (2)$$

Liquid sorption experiments

The preweighed membrane was kept in a desiccator to desorb any moisture absorbed from the air, and then it

was immersed in a known composition of an isopropanol–water mixture in a closed bottle at room temperature for 48 h for equilibrium swelling. The swollen membrane was removed and weighed immediately after being pressed between tissue papers. The amount of sorbed liquid in the membrane was expressed as the degree of swelling (DS %), which was calculated using the following equation:

$$\text{DS \%} = \frac{(w_f - w_i)}{w_i} \times 100\% \quad (3)$$

where w_f and w_i denote the final (swollen) and initial (dry) weights of the membrane, respectively.

The sorption selectivity ($\alpha_{\text{sorption water/IPA}}$) was calculated as follows¹⁸:

$$\alpha_{\text{sorption water/IPA}} = \frac{C_w/C_{\text{IPA}}}{X_w/X_{\text{IPA}}} \quad (4)$$

where C_w and C_{IPA} are the weight fractions of the permeate water and isopropanol component in the membrane at equilibrium sorption, respectively, and X_w and X_{IPA} are the weight fractions of the feed water and isopropanol component at equilibrium sorption, respectively.

The membrane was then immediately placed in a desorption cell that was connected to a cold trap followed by a vacuum pump. The liquid sorbed by the membrane was desorbed under vacuum and collected in the trap. The collected liquid was then weighed, removed, and analyzed for composition using the measurement of the refraction index. The membrane was periodically weighed until the mass was constant. The individual sorbed amount was calculated from the total sorbed amount and the sorbed composition.

Pervaporation experiments

The pervaporation schematic diagram is shown in Figure 2. The feed mixture entered the cell through the inlet opening and left the cell through the outlet opening at the opposite side. The feed mixture was circulated through the cell by a Masterflex peristaltic circulation pump. The vapor permeated through the membrane was withdrawn from the lower part of the cell, which was kept under a vacuum and condensed in a cold trap that was immersed in liquid nitrogen. A control valve was used to control the downstream pressure. The pervaporation was run for at least 1 h to get the system up to a steady state before condensing collection was started. The permeate was warmed to ambient temperature, weighed, removed, and analyzed for permeate composition using the refraction index. The composition of the feed and the trap retentate were also measured to verify the constancy of the

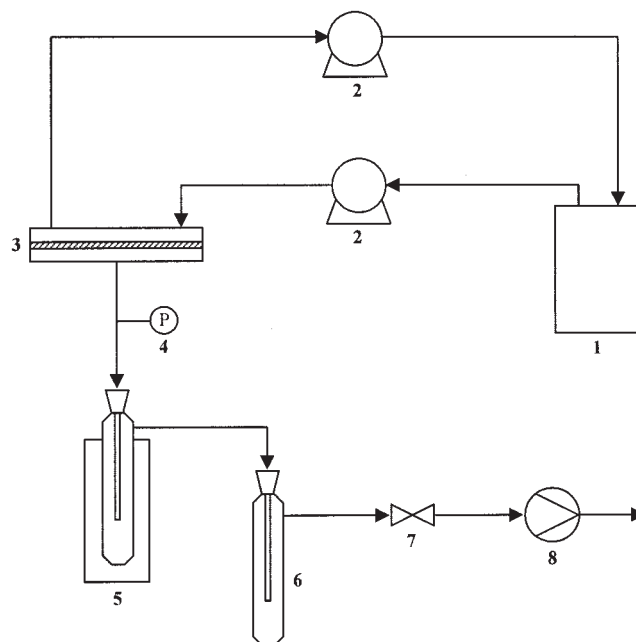


Figure 2 A schematic diagram of the pervaporation apparatus.

composition. However, it could be assumed that the feed composition remained constant during the duration of the experiment because the weight of the permeate collected was less than 1% of the weight of the feed charged to the tank. The temperature of the permeate cell was at room temperature for all experiments. The upstream pressure of the pervaporator was at atmospheric pressure, whereas the downstream pressure was maintained at 60 mmHg with a vacuum pump. The effective membrane area was $4.66 \times 10^{-3} \text{ m}^2$.

The total flux of the permeating component and the selectivity of the membrane are two parameters that are generally used to characterize a pervaporation process. The total permeation flux (J_t) through the membrane is defined as

$$J_t = \frac{W}{\Delta t A} \quad (5)$$

where W is the weight (g) of the permeate, t is the permeation time (h), and A is the membrane area (m^2).

The separation factor (α_{ij}) is defined as

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (6)$$

where y_i and y_j are the weight fractions of components i and j in the permeate, respectively, and x_i and x_j are the feed phase weight fractions of components i and j , respectively. In both cases, component i is the more

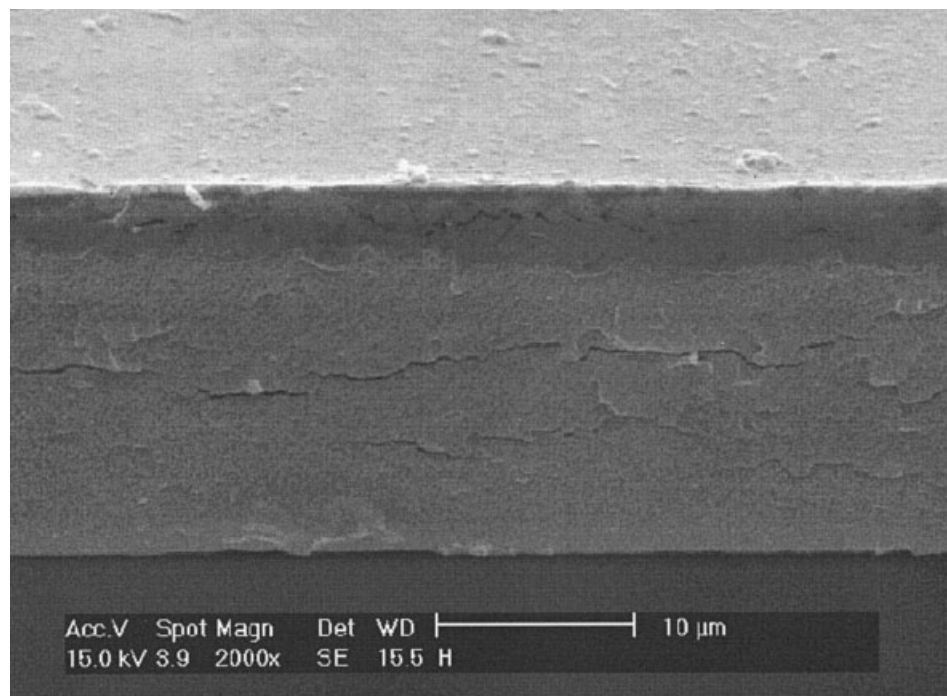


Figure 3 The cross-sectional morphology of the homogeneous chitosan membrane.

preferentially permeating component in i and j mixtures. When the separation factor is unity, no separation occurs; the membrane becomes perfectly semipermeable when it approaches infinity. For the current study, water is the preferential component.

In a practical sense, the membrane must have a high permeation flux and good separation factor. Nevertheless, in the actual pervaporation process, there is normally a trade-off between the permeation flux and separation factor, where there is a high permeation flux with a low separation factor and vice versa. Thus, Huang and Rhim²⁹ developed a new formula for the PSI for the measurement of the membrane separation ability. It can be defined as follows:

$$PSI = J_i(\alpha_{ij} - 1) \quad (7)$$

where α_{ij} must be >1 for separation to happen; when $\alpha_{ij} = 1$, no separation occurs; and when $PSI = 0$, it means zero flux or zero separation.

RESULTS AND DISCUSSION

Surface morphology of membrane

SEM was used to study the morphology of the homogeneous and NaY zeolite filled chitosan membranes with the same level of magnification ($\times 2000$).

Homogeneous chitosan membrane

Figure 3 shows the cross-sectional morphology of the homogeneous chitosan membrane. The micrograph of

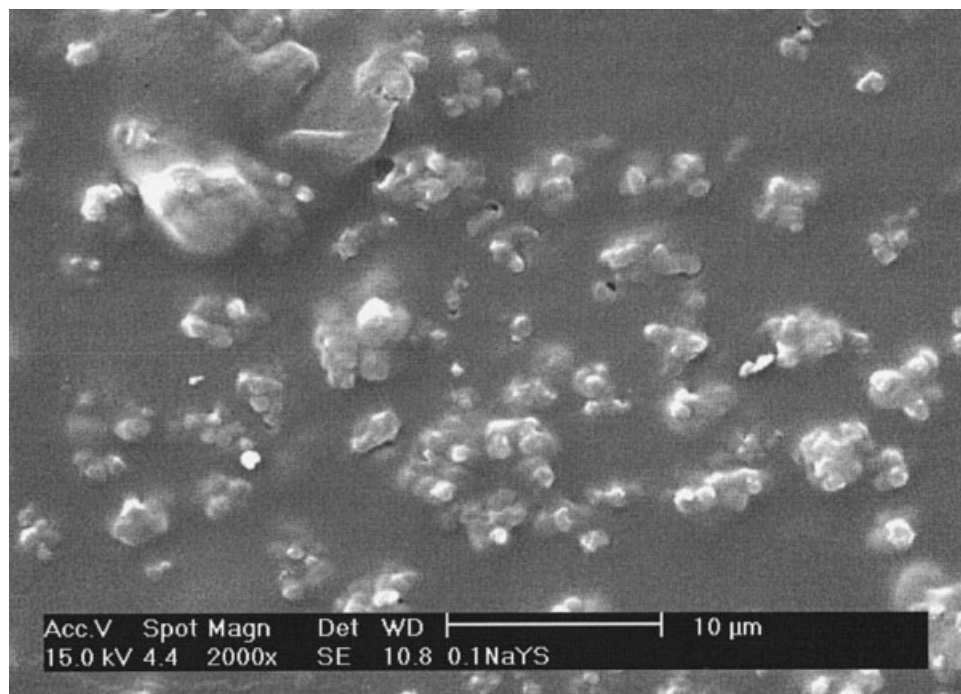
the homogeneous membrane shows that the membrane's structure was uniform and no pores were observed. This shows that the homogeneous chitosan membrane was a dense membrane. The SEM micrograph was used as a comparison to the different concentrations of NaY zeolite filled chitosan membranes.

NaY zeolite filled chitosan membranes

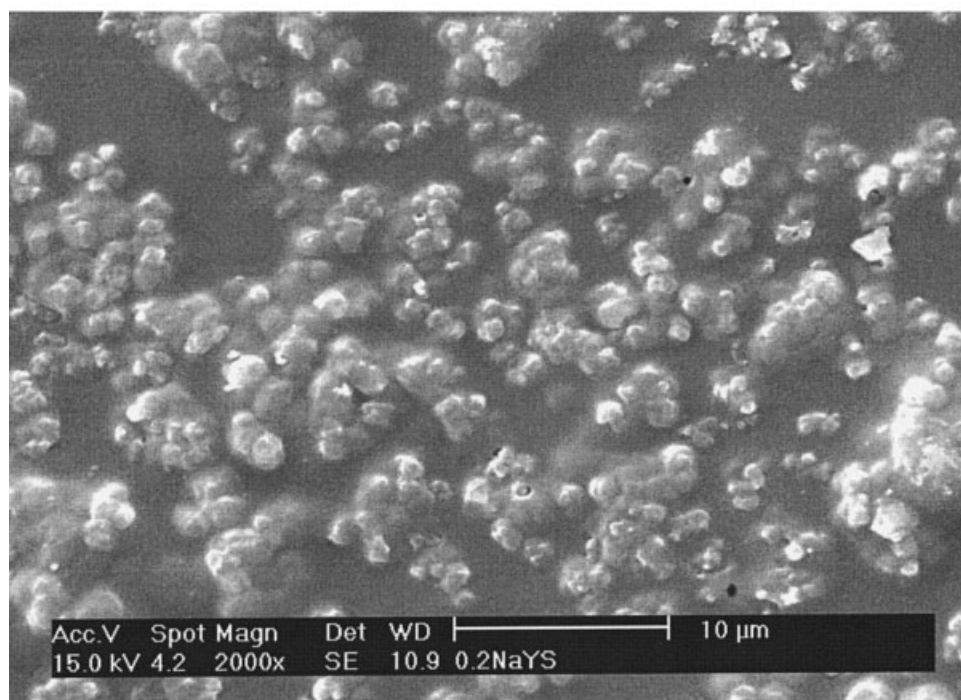
The bottom surface view of 0.1–0.3 wt % NaY zeolite filled chitosan membranes [Fig. 4(a–c)] shows a non-homogeneous dispersion of NaY zeolite in which the NaY zeolite particles were not completely covered by the chitosan polymer. As a result, nonselective voids were observed at the zeolite–chitosan polymer interfaces.³⁰ However, when 0.4 wt % NaY zeolite was added, the dispersion of this zeolite in the chitosan polymer was the most homogeneous [Fig. 4(d)] compared to the other concentrations of NaY zeolite filled membranes because the NaY zeolite was dispersed well and evenly in the chitosan polymer. Thus, the NaY zeolite was finely covered by the chitosan polymer and free from interface defects. Increasing the zeolite concentration to 0.5 wt % [Fig. 4(e)] caused some aggregation of zeolites.

Mechanical properties of membranes

Table I shows the mechanical properties of the membranes (tensile strength and percentage of strain at maximum), which indicate the membrane's plasticity. The membrane's tensile strength increased to the max-



4(a)

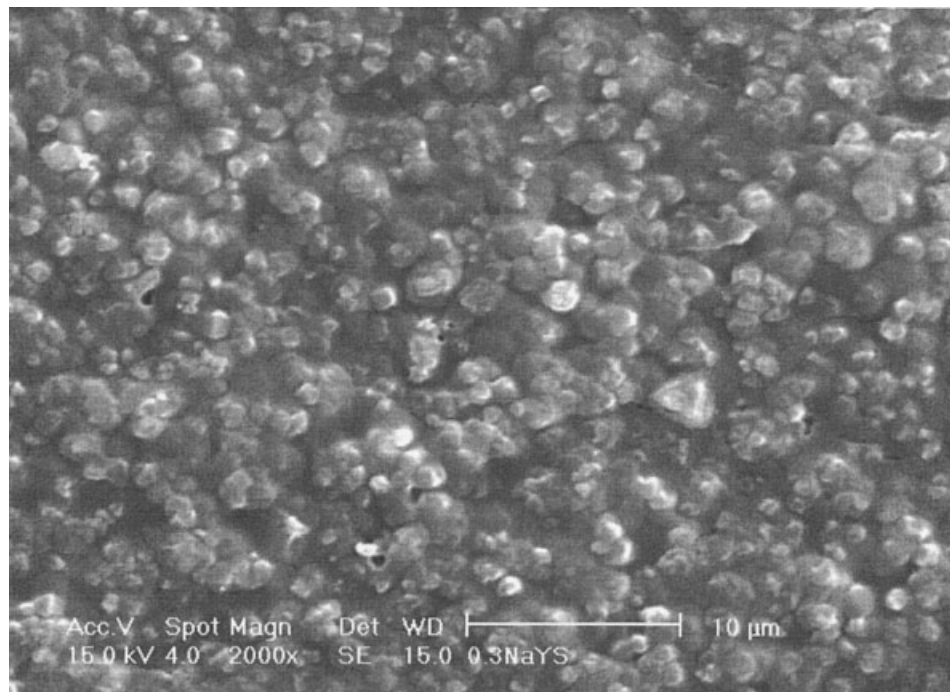


4(b)

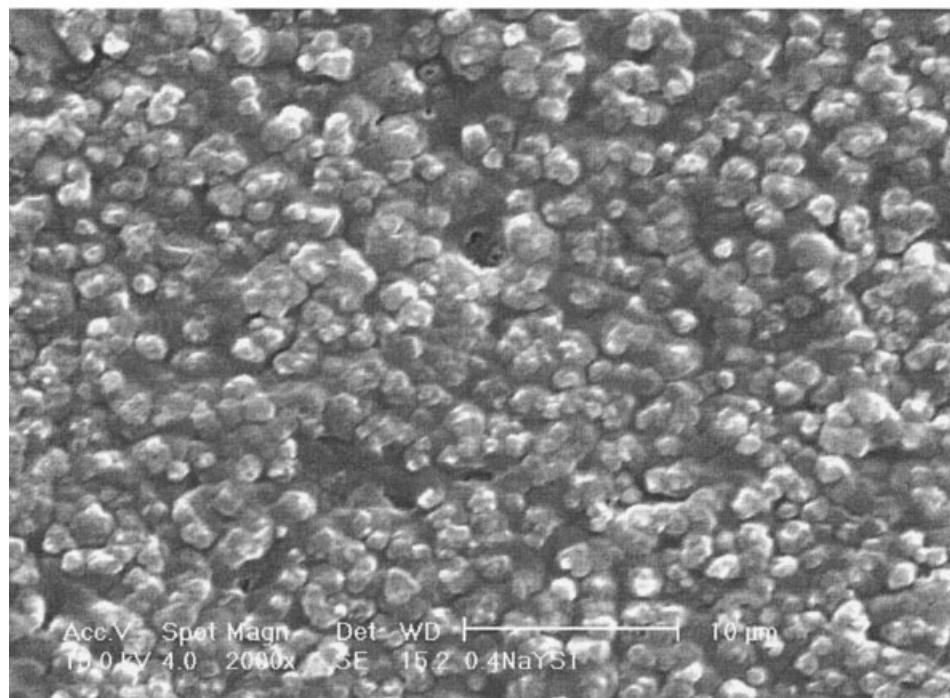
Figure 4 A bottom surface view of (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, and (e) 0.5 wt % NaY zeolite-filled chitosan membranes.

imum value of 59.4 MPa at 0.4 wt % NaY zeolite. The improvement of the tensile strength for the chitosan membrane was effected by the strong chain interaction between the NaY zeolite and chitosan polymer.

However, the tensile strength was decreased to the minimum value of 50.946 MPa for the 0.5 wt % NaY zeolite filled chitosan membrane. This was due to the aggregation of the NaY zeolite, which caused a



4(c)

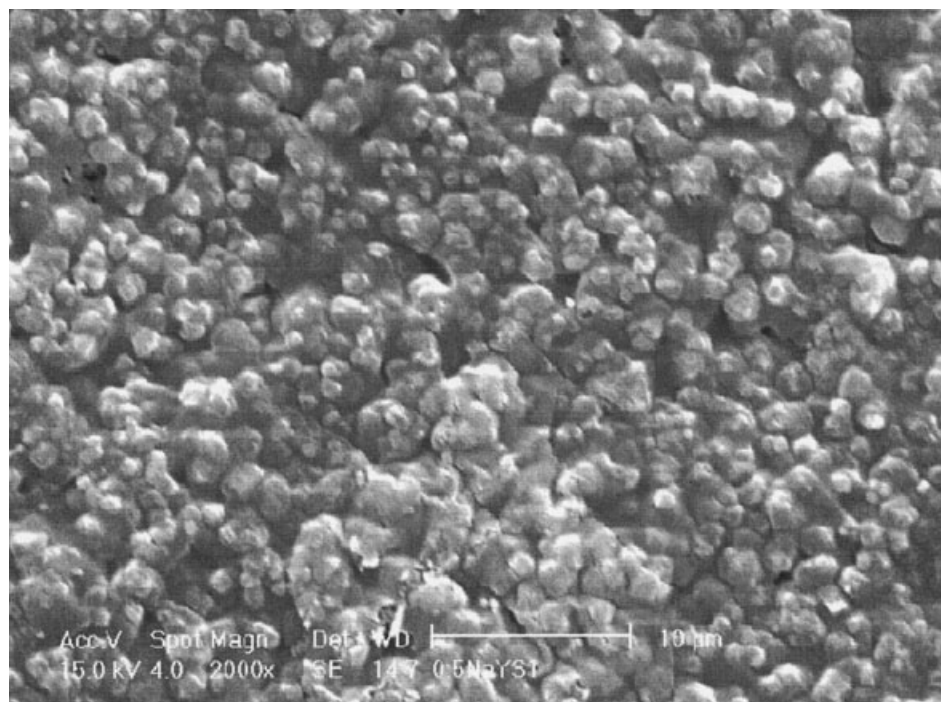


4(d)

Figure 4 (Continued from the previous page)

weaker interaction between the NaY zeolite and the chitosan polymer. The weaker interaction between the zeolite and polymer formed nonselective voids at the zeolite–chitosan interface where the NaY zeolite was not finely covered by chitosan polymer.

The percentage of strain at maximum of the NaY zeolite filled chitosan membrane shows that the 0.2 wt % NaY zeolite filled chitosan membrane had the highest percentage of strain at maximum (32.75%). The percentage of strain at maximum then decreased to



4(e)

Figure 4 (Continued from the previous page)

20% when 0.5 wt % NaY zeolite was added. This was attributable to the chitosan polymer–zeolite chains joined together and this decreased the chain mobility and the percentage of strain at maximum for the membrane. As the result, the plasticity of the membrane decreased.

Sorption experiments

Table II shows the degree of swelling and sorption selectivity for different concentrations of NaY zeolite. The degree of swelling increased to maximum (6.80%) when 0.3 wt % NaY zeolite was added. After this maximum point, the degree of swelling decreased to 6.19% with 0.5 wt % NaY zeolite. The addition of NaY zeolite increased the degree of swelling because of the

hydrophilic properties of zeolite. However, the leaching out of NaY zeolite particles at higher concentration (0.4 and 0.5 wt %) led to the reduction in the degree of swelling.

Figure 5 shows the percentage of isopropanol in the sorbed phase, which was calculated from the desorption test. The percentage of isopropanol sorbed in the NaY zeolite filled chitosan membrane increased with increasing NaY zeolite concentration. However, water was the major composition in the membrane sorbed amount, which varied from 98.54 to 99.28%. According to the solution–diffusion model, the permeation flux is a function of solubility and diffusivity. Preferential sorption at the liquid–membrane interface and diffusion through the membranes played an impor-

TABLE I
Effect of NaY Zeolite Concentration on Tensile Strength and Strain at Maximum

Concn of zeolite NaY (wt %)	Tensile strength (MPa)	Strain at maximum (%)
0	53.664	16.08
0.1	55.395	29.94
0.2	57.249	32.75
0.3	58.054	27.50
0.4	59.347	27.56
0.5	50.946	20.15

TABLE II
Degree of Swelling and Sorption Selectivity at Different NaY Zeolite Concentration

Concn of zeolite NaY (wt %)	Degree of swelling (%)	$\alpha_{\text{sorption water/IPA}}$
0	6.12	1352.17
0.1	6.35	1330.43
0.2	6.33	1213.04
0.3	6.80	891.00
0.4	6.54	933.78
0.5	6.19	678.26

Atmospheric pressure and temperature, 90 wt % isopropanol–water feed solution.

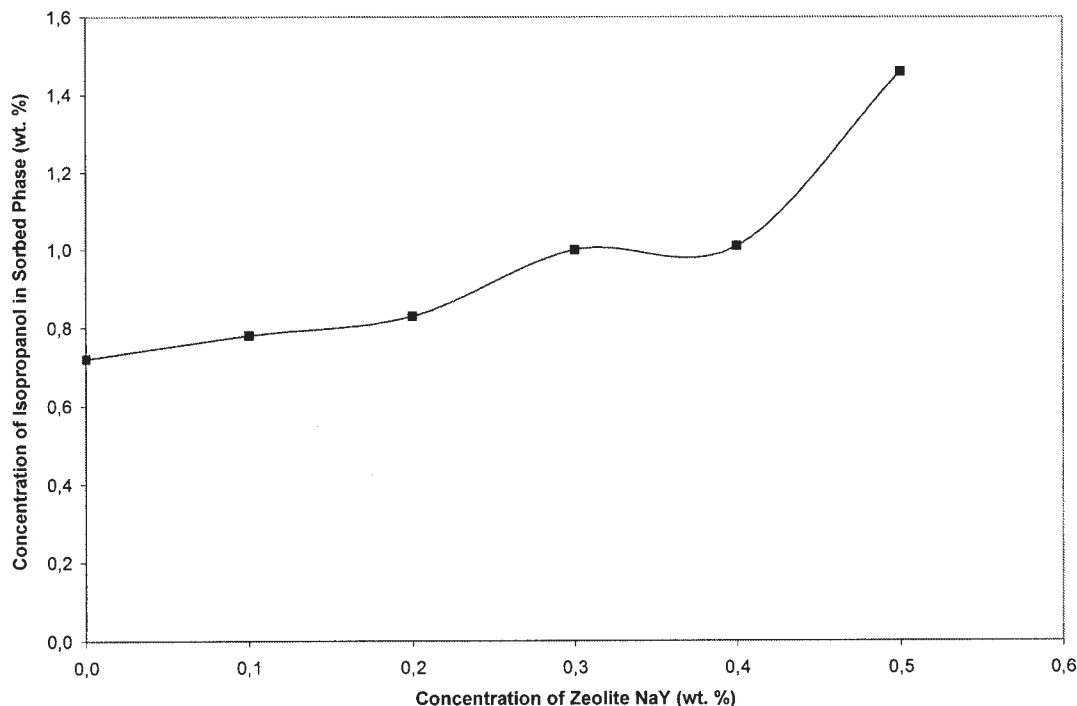


Figure 5 The concentration of isopropanol in the sorbed phase versus the concentration of NaY zeolite.

tant role in determining the permselectivity in the pervaporation process.³¹

The overall relationship between the degree of swelling and sorption selectivity for the NaY zeolite filled chitosan membrane showed that when the degree of swelling increased the sorption selectivity decreased and vice versa. When the water molecules diffused into the membrane, the crystallinity of chitosan decreased; consequently, the membrane became swollen. The swelling decreased the interaction between the zeolite and chitosan, and this resulted in some tiny cracks. These defects allowed isopropanol molecules and water to be sorbed into the membrane.¹

Pervaporation experiments

The feed concentration was 90 wt % isopropanol and 10 wt % water in the pervaporation experiments. Figure 6 shows the total and individual component (water and isopropanol) permeation flux. The NaY zeolite in the chitosan membrane facilitated the permeation of water while it hindered the passage of bigger molecules (isopropanol). The addition of 0.1 wt % NaY zeolite in the chitosan membrane improved the total permeation flux from 30.49 (for the homogeneous chitosan membrane) to 76.11 g/m² h. In the extreme case of hindrance, the dependence of the facilitation permeation on the molecular size was no longer observed in this region.³² The total permeation flux decreased when increasing the NaY zeolite concentration from

0.1 to 0.4 wt %. Although the total permeation flux for 0.2–0.4 wt % NaY zeolite filled chitosan membrane decreased, the values were still higher compared to the homogeneous chitosan membrane. Modification via the NaY zeolite improved the total permeation flux. However, at 0.5 wt % zeolite, the total flux increased to the maximum value of 92.65 g/m² h. The zeolite was observed to aggregate, having pinholes and nonselective voids.³³ Thus, water and isopropanol were easier to diffuse through these voids, without following the molecular sieve effect, which enhanced the total flux.

Figure 7 shows the separation factor (α) and PSI. High permeation flux gave a low separation factor and vice versa.²⁹ The separation factor increased once the water concentration in the permeate increased or the concentration of isopropanol in the permeate decreased. The separation factor increased from 9.95 to 47.83 when the zeolite concentration was increased from 0.1 to 0.4 wt % because of the reduced isopropanol concentration in the permeate of these regions (Fig. 8). However, at 0.5 wt % zeolite the separation factor dropped to 14.93 because of the unexpected increase of the isopropanol concentration in the permeate at this zeolite concentration because of the formation of pinholes and microvoid structures. The calculated PSI showed that the highest PSI was obtained at 0.4 wt % zeolite concentration.

The concentration of isopropanol and water in the permeate stream after the pervaporation process is

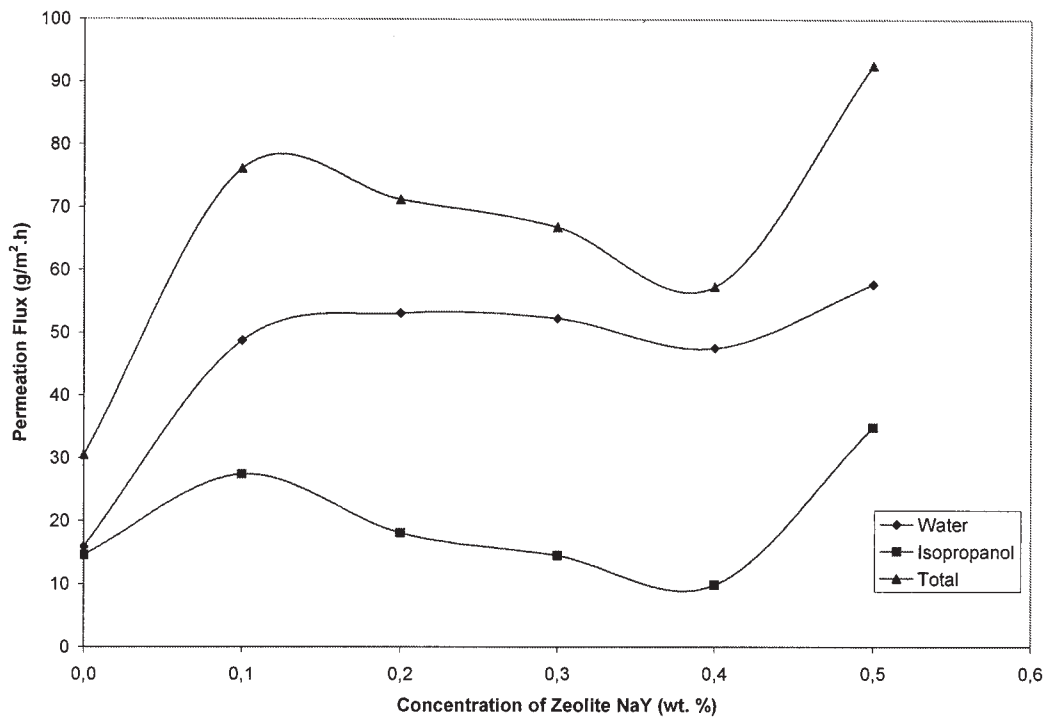


Figure 6 The permeation flux versus the concentration of NaY zeolite for each component.

shown in Figure 8. The water was the preferential permeate component and enriched in the permeate phase. These results confirmed that the introduction of the NaY zeolite with smaller particle size and higher

specific pore volume led to a decrease in the diffusion resistance during pervaporation, which resulted in an improvement of the membranes' pervaporation properties.²⁷ When the retentate of the isopropanol–water

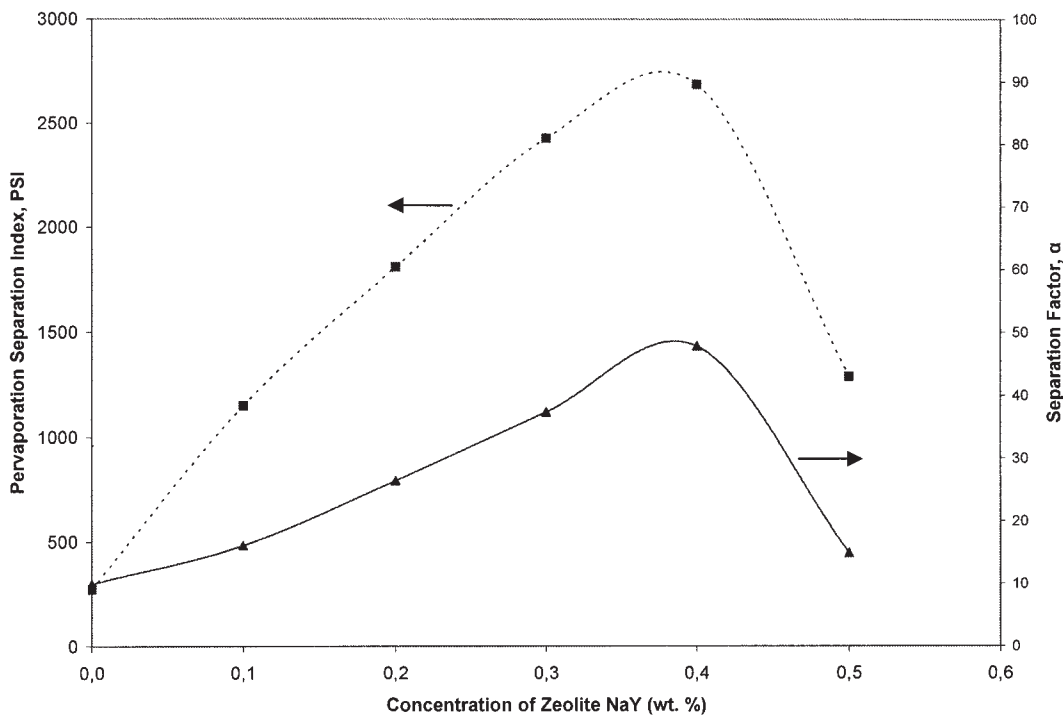


Figure 7 The total permeation flux and separation factor versus the concentration of NaY zeolite.

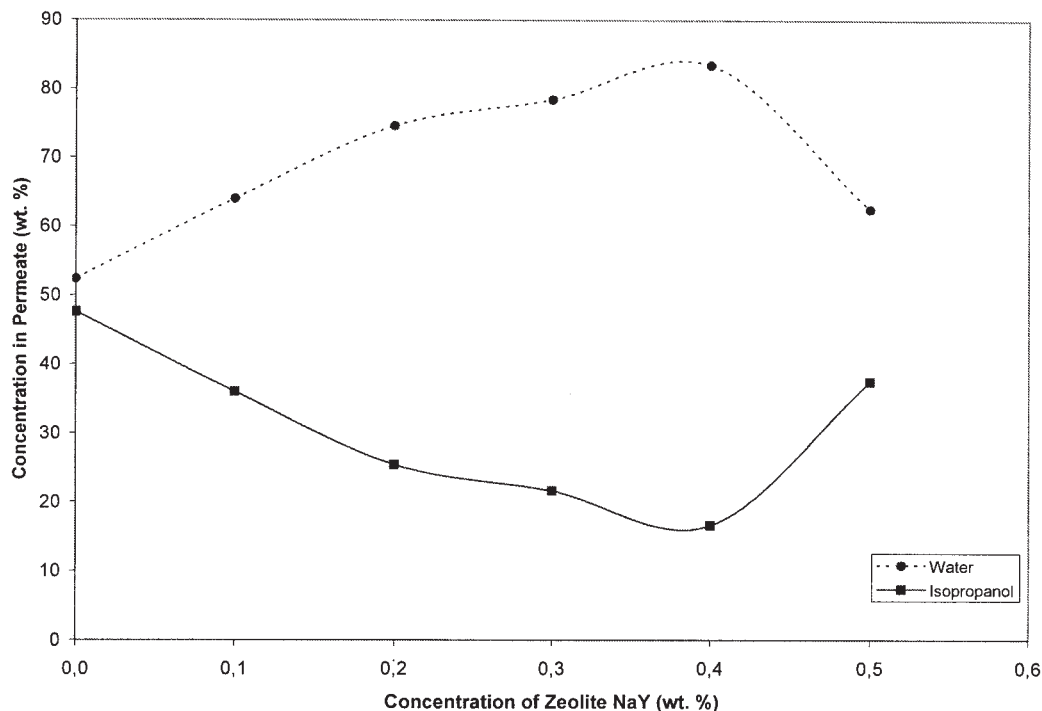


Figure 8 The concentration of isopropanol and water in the permeate versus the concentration of NaY zeolite.

mixture was recycled back to the feed side of the separation process, the concentration of isopropanol increased from 95 to 99 wt %.

CONCLUSION

NaY zeolite filled polymeric chitosan was successfully developed and well characterized in terms of the surface morphology, mechanical properties, sorption, and pervaporation of dehydration of an isopropanol–water mixture. The characterizations were compared to an ordinary homogeneous chitosan polymeric membrane. Results showed that, by adding NaY zeolite to the chitosan polymeric membrane, the membrane properties were improved, especially toward an effective pervaporation of dehydration of the isopropanol–water mixture. NaY zeolite formed a strong interaction with the amino groups of the chitosan polymeric membrane, hence increasing the hydrophilicity of the membrane. However, adding too much NaY zeolite (0.5 wt %) formed an aggregation of zeolite, which led to pinholes and nonselective microvoids. The results demonstrated that adding 0.4 wt % NaY zeolite gave optimum results. The dehydration of the isopropanol–water mixture was enhanced using the optimum NaY zeolite concentration as the chitosan membrane filler where the water concentration was increased from 10 to 84 wt % and the isopropanol concentration was reduced from 90 to 16.59 wt % in the permeate. The enrichment of isopropanol reached

95–99 wt % purity when the retentate was recycled back to the feed stream.

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