

Incorporation of Multiwalled Carbon Nanotubes into Poly(vinyl alcohol) Membranes for Use in the Pervaporation of Water/Ethanol Mixtures

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ABSTRACT: Multiwalled carbon nanotube (MWNT)/poly(vinyl alcohol) (PVA) blend membranes were prepared by the solution-casting method to determine the effect of MWNTs with nanoscale empty inner space along the tube length on the pervaporation performance of a PVA membrane in the separation of alcohol/water mixtures. The blend membranes were then characterized with several analytical methods such as transmission electron microscopy, differential scanning calorimetry, and X-ray diffractometry. Transmission electron microscopy showed that the MWNTs were homogeneously distributed through the PVA matrix. The glass-transition temperature of the PVA membrane was increased from 69.21 to 78.53°C via blending with MWNTs. The crystallinity of the PVA matrix decreased with increas-

ing MWNTs up to 5 wt % from 41 to 36%. The pervaporation properties of the blend membranes were completely different from those of the pure PVA membrane in the separation of water/ethanol mixtures. The flux of the membrane was increased with the amount of MWNTs, whereas the separation factor was maintained up to 1.0 wt % MWNTs. However, beyond that, it was reduced. These results suggested that two factors, the crystallinity of the membrane and the diameters of the MWNTs, affected the performance of the membranes. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2186–2193, 2009

Key words: compatibility; hydrophilic polymers; nanotechnology; selectivity; separation techniques

INTRODUCTION

Membrane separation techniques have attracted considerable attention in a wide variety of medical, food, industrial, energy, and environmental applications. In particular, a pervaporation process is very useful for the separation of liquid mixtures, such as aqueous organic azeotropic mixtures and close-boiling-point chemicals, and in addition, it can offer many advantages in energy savings.^{1–6}

The dehydration of alcohols with pervaporation processes has received intense attention because of its vigorous potential in industrial applications. In general, low-molecular-weight alcohols are miscible with water and form azeotropic mixtures (96.5 wt % ethanol) that cannot be easily separated by simple distillation. Therefore, pervaporation technology

using membranes can be applied to separate azeotropic water/ethanol mixtures.

Many attempts have been made to develop various membranes (asymmetric, composite, or mixed matrices) for pervaporation applications.^{7–11} A good pervaporation membrane material should have a high permeation flux and separation factor for the pervaporation dehydration of alcohol. Most studies on pervaporation dehydration of alcohols have focused on highly hydrophilic materials because of their strong affinity to water molecules.^{12–14} In particular, poly(vinyl alcohol) (PVA) is widely used as a membrane material for the separation of water/ethanol solutions by pervaporation because the PVA membrane shows remarkable selectivity toward water and has excellent film-forming characteristics with good resistance to organic mixtures, even though it has poor stability in aqueous mixtures.

However, like the PVA membrane, current polymeric membrane materials commonly suffer from the inherent drawback of a tradeoff between permeability and selectivity, and this means that more permeable membranes are generally less selective and vice versa. Thus, many researchers have studied organic–inorganic membranes, which are prepared by

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the simple incorporation of inorganic particles, such as zeolite, carbon molecular sieves, silica, and carbon graphite, into organic materials.^{15–17} Recently, carbon nanotubes (CNTs) have also been applied to filters and membranes used to separate various gases and liquids.^{18–20} For example, Hinds et al.¹⁹ reported nanotube-based membranes consisting of vertically aligned nanotubes embedded in a polymer host. The hollow nanotube cores represented the only conduction path during molecular transport through the membranes. Because of their arrangement, the termini of the aligned CNTs were accessible to the outer molecules from both sides of the formed membranes. From their results, we saw the possibility of CNTs for membrane applications by using the empty inner space.

Therefore, we tried multiwalled carbon nanotube (MWNT)/PVA blend membranes in this study and formed the blend membranes by a simple solution-casting method using MWNT/PVA blend solutions with different compositions. To make the MWNTs miscible with water, we treated them with strong acids such as sulfuric acid (H₂SO₄) and nitric acid (HNO₃). The prepared blend membranes were then characterized with various analytical methods to figure out the effect of MWNTs on the PVA pervaporation membranes. The results of the membrane characterization and effect of the MWNTs on the permeation properties of the PVA membranes are elaborated here.

EXPERIMENTAL

Materials

PVA, purchased from Aldrich, was 99% hydrolyzed with a molecular weight of 50,000 g/mol. MWNTs with a purity of 95%, manufactured by the chemical vapor deposition process and supplied by Iijin Nanotech (Korea), were treated with a strong acid before use. The general shape of the MWNTs was cylindrical, and it was composed of six-member carbon rings. The MWNTs were known to consist of several sheets of graphite rolled up into tubes. The average diameters and lengths of the MWNTs were about 10–20 and 10–50 μm, respectively, but their inner-core diameter was 4.3 ± 2.3 nm. The modification of MWNTs was based on a mixture of concentrated HNO₃ and H₂SO₄ in a volume ratio of 1 : 3.²¹ In a typical experiment, 1 g of raw MWNTs was added to 150 mL of the acid mixture in a round-bottom flask, and then the mixture was refluxed at 80°C for 1 h. On cooling, the mixture was washed with distilled water until nearly neutral water was obtained. The collection was then freeze-dried *in vacuo* at –80°C for further use. High-performance liquid chromatography grade ethanol was purchased

from Merck Co. and was used without further purification.

Membrane preparation

MWNT/PVA blend membranes were prepared through the casting of blend PVA solutions containing different contents of MWNTs (1–5 wt %) onto a glass plate followed by drying at room temperature. The detailed procedure was as follows: To prepare a 15 wt % PVA solution in water, 15 g of PVA was dissolved in 85 g of distilled water at 90°C with continuous stirring for more than 4 h. The 5 wt % MWNT solution was prepared by the dispersion of 5 g of modified MWNTs into 95 g of water. It was sonicated for 80 s with a high-power sonic tip (SKB-2000, Sonics Korea; 2 kW) (Seoul, Korea) for better dispersion. The exact amount of the MWNT solution was then added dropwise to the PVA solution with continuous stirring with a mechanical stirrer to prepare blend solutions with different compositions of MWNTs. For all the blend solutions, the MWNT/PVA mixture to water ratio was 10/90, but the ratio of PVA to MWNTs was varied: 99/1.0, 98/2.0, 97/3.0, 96/4.0, 95/5.0, and 90/10 wt %. After this, the blend solutions were kept at room temperature for at least 24 h to remove air bubbles from the solutions. The PVA/MWNT blend solutions were then cast onto a glass plate with a Baker applicator and dried at room temperature. The membrane thickness was about 20–25 μm.

Characterization

To characterize the modified MWNT solution in water and the blend membranes, ζ potentiometry, transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and X-ray diffractometry (XRD) were used. To evaluate the dispersivity of the MWNTs in water, a ζ-potentiometer (electrophoretic light scattering model ELS-8000, Otsuka, Tokyo, Japan) was used. The pH values of the MWNT solutions were varied from 2.0 to 10.0 by the addition of certain amounts of a 10 mM hydrochloric acid or 10 mM sodium hydroxide solution to water. The structure of the blend membranes was observed by TEM. The blend membranes were embedded in epoxy resin and sliced into thin films (thickness ≈ 50 nm) with a Leica EM UC6 microtome. The TEM apparatus was an FEI Tecnai G2 20 operated at 200 kV. The crystallinity and polymer structure of the blend membranes were studied with a Rigaku D/MAX-2200 V X-ray diffractometer using nickel-filtered Cu-Kα radiation (40 kV, 40 mA) with a wavelength of 1.54 Å. The scanning range was 2–50° with a scanning rate of 1°/min. Thermal properties of the membranes were studied with DSC (DSC2910, TA

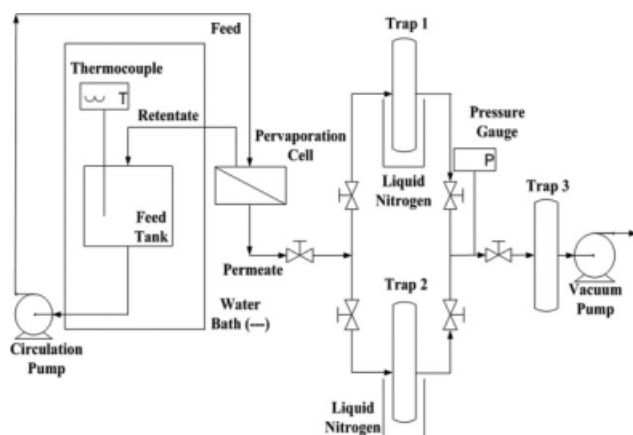


Figure 1 Schematic diagram of the pervaporation test setup.

Instruments, United States). The conditions for the DSC measurement were as follows: first heating to 250°C at a rate of 10°C/min and holding there for 1 min, then cooling to room temperature, and finally heating again to 250°C at the same rate under nitrogen. Before the measurements, all the samples were vacuum-dried for 24 h at room temperature.

Degree of swelling of the membranes

The PVA and blend membranes were completely dried *in vacuo* at 40°C and weighed. After that, the prepared membranes were immersed into a water/ethanol (10/90 wt %) mixture in a sealed vessel at 40°C for 48 h. When the membranes maintained a constant weight, they were wiped quickly with filter paper, and then the weight of the swollen membranes was measured. All experiments were repeated at least three times, and the results were averaged. The degree of swelling (DS) was calculated as follows:

$$DS(\%) = \left(\frac{W_s - W_d}{W_d} \right) \times 100$$

where W_s and W_d are the masses of the swollen and dried membranes, respectively.

Permeation measurements

The pervaporation experiments were carried out with the apparatus shown in Figure 1 under the following conditions: permeation temperatures of 30, 40, 50, and 60°C and a permeate side pressure of 1×10^{-1} Torr. The effective membrane area was 18.8 cm². The feed solution was 90 wt % ethanol with a volume of 2 L. The permeate was collected in a U-tube at the temperature of liquid nitrogen. The total permeation (water plus ethanol) rates of aqueous

alcohol solutions during pervaporation were determined from the weight of the permeate collected in the U-tube per the permeation time and the effective membrane area. To facilitate a comparison of the permeation rates of membranes with different thicknesses, the normalized permeation rate (m kg/m² h) was used, which was the product of the permeation rate and the membrane thickness. The compositions of the feed solution and permeate were determined with a Shimadzu GC-14B gas chromatograph equipped with a flame ionization detector (Tokyo, Japan). The separation factor (α) was defined as follows:

$$\alpha = (W_{H_2O}/W_{ethanol})_{Permeate} / (W_{H_2O}/W_{ethanol})_{Feed}$$

where W_{H_2O} is the weight fraction of water and $W_{ethanol}$ is the weight fraction of ethanol. It was assumed that α for each membrane was not dependent on the membrane thickness.

RESULTS AND DISCUSSION

Characterization of the CNT dispersions

ζ potentials as a function of the pH of the MWNTs before and after modification dispersed in water are given in Figure 2. The ζ potential was calculated with the Smoluchowski equation:

$$\zeta = \frac{4\pi\eta\mu}{\epsilon}$$

where μ is the electrophoretic mobility and η and ϵ are the viscosity and dielectric constant of the liquid in the boundary layer, respectively. The mobility of the particle is determined from the velocity:

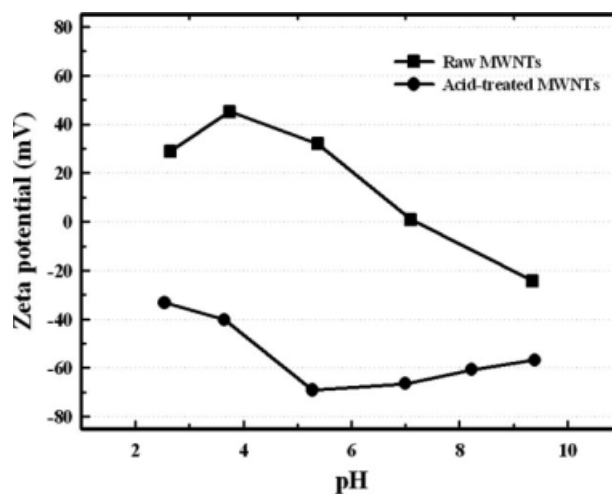


Figure 2 ζ potentials of aqueous solutions of raw and acid-treated MWNTs as a function of the pH.

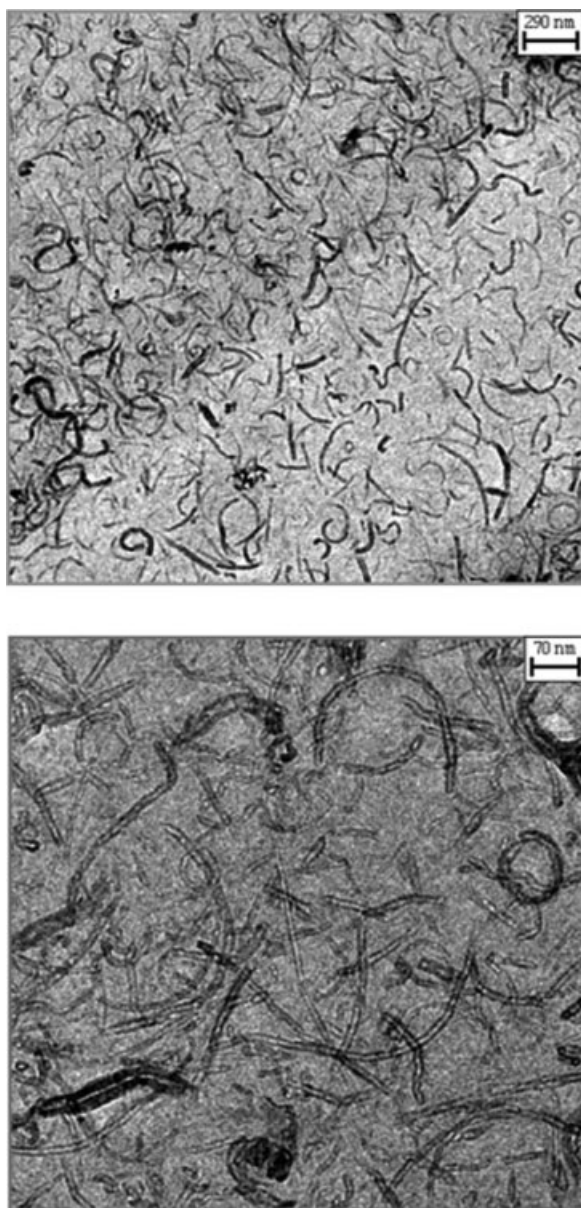


Figure 3 TEM images of a specimen from the cross-sectional microtomy of the MWNT/PVA (10/90 wt %) blend membrane.

$$\mu = v/E$$

where μ and v are the mobility and velocity of the particle under electric field E . These measurements are of interest because they provide information on the dispersibility of MWNTs.^{22,23} A larger absolute value of the ζ potential means that MWNTs are better dispersed in the solution. That is, when MWNTs are aggregated, they move slowly under the same electric field because of their increased mass, and this results in a smaller absolute value of the ζ potential. From this point of view, Figure 2 shows that acid-treated MWNTs have higher absolute values of the ζ potential over a wide pH range of 2–10;

at the pH values of 2.5, 7, and 9.3, the ζ potentials of acid-treated MWNTs are -33 , -66 , and -56 mV, respectively. These results indicate that the treatment with acid introduces abundant hydroxyl and carboxyl groups at the open ends and defect sites of the MWNTs,^{24,25} and these functional groups are charged negatively when dispersed in deionized water. Therefore, the MWNT bundles are fairly stable individually by the repulsive forces exerted among the MWNTs in water. However, the ζ potential of the raw MWNTs was 0 mV at pH = 7, and this means that the MWNTs cannot prevent themselves from aggregating and precipitating in water. Therefore, we can conclusively state that the acid-treated MWNTs are good enough to disperse well in water, not precipitating for several days without agitation.

Moreover, the modified MWNTs turned out to be well dispersed in a PVA matrix. This result is in good agreement with the TEM observations of the MWNT/PVA blend films. Figure 3 shows the distribution behavior of MWNTs in an MWNT/PVA blend film when the content of MWNTs was 10 wt %. It certainly proves that a fairly large number of MWNTs are well dispersed through a PVA matrix. The images reveal that by incorporation with the polymeric matrix, the defects and functional groups of MWNTs provide stronger interactions with hydroxyl groups of PVA, thus resulting in a significant increase in the dispersibility of the MWNTs in the blend film. Also, MWNTs dispersed in a blend film will affect the mobility of PVA polymer chains.

Characterization of the MWNT/PVA blend membrane

DSC

Table I exhibits physical data, such as the glass-transition temperature (T_g), melting point (T_m), and crystallinity, of the PVA membranes containing different amounts of MWNTs; these data were obtained from the DSC study. To avoid the effect of the sample preparation procedure, all the data were obtained from the second heating of DSC.

With increasing contents of MWNTs, T_g of the blend membranes increased from 69.21 to 78.53°C. It is well known that the addition of solid fillers to a polymer causes an increase in T_g if there are strong attractive forces working between the polymer and surface of the solid fillers. Similar effects have also been reported: the incorporation of a polymer and CNTs, zeolite, or silica has resulted in an increase in T_g .^{26–28} In the same manner, T_g of the blend membranes increased in this study, and this suggests that there were substantial interactions between the

TABLE I
DSC Results for a PVA Membrane and MWNT/PVA Blend Membranes

	T_g (°C)	T_m (°C)	ΔH (J/g)	χ_c (%)
PVA	69.21	224.44	64.27	41.08
MWNT/PVA (1.0/99.0)	73.53	224.75	66.13	42.27
MWNT/PVA (2.0/98.0)	75.61	224.44	62.63	40.03
MWNT/PVA (3.0/97.0)	77.27	224.33	61.39	39.24
MWNT/PVA (4.0/96.0)	77.63	224.04	60.45	38.64
MWNT/PVA (5.0/95.0)	78.53	223.74	57.02	36.44

functional groups developed on the surface of the MWNTs by the acid treatment, such as carboxylic acid and hydroxyl groups, and the hydroxyl groups of PVA via the formation of hydrogen bonds, affecting the mobility of the molecular chains of PVA.

The behavior of the T_m and crystallinity of the blend membranes according to the contents of MWNTs appeared to be different from that of T_g . T_m appeared not to be affected by the MWNTs, with a slight decrease beyond 3 wt % MWNTs.

On the other hand, the melting enthalpy was substantially affected. With increasing contents of MWNTs, it increased and then decreased, but overall it decreased, reflecting the lower crystallinity of the blend membranes. Except for 1.0 wt % MWNTs, it decreased gradually from 64.27 to 57.02 J/g. The crystallinity of the membranes, calculated from the melting enthalpy obtained from the DSC study with the following equation, also decreased as shown in Table I:

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

where χ_c is the crystallinity of the PVA matrix, ΔH_m is the measured melting enthalpy, and ΔH_m^0 is the 100% melting enthalpy of PVA. According to literature data,²⁹ we assumed $\Delta H_m^0 = 156.46$ J/g.

The dependence of the crystallinity on the contents of MWNTs can be explained by the interaction between the PVA molecules and the MWNTs in the blend membranes. When a small amount of MWNTs (1 wt %) was added, they acted like nucleating agents and then induced a small increase in the crystallinity. However, as the content of MWNTs increased further, the effect of MWNTs, which through strong interactions with PVA molecules made PVA molecules not easy to pack together to form crystals, became dominant, and this resulted in the decrease in the crystallinity. This kind of phenomenon was more or less the same as the result reported in another study.³⁰ The effect of MWNTs on the micromorphology of the blend membranes

can also be found in Figure 4, which presents the XRD data of the blend membranes.

XRD

XRD data of the PVA and MWNT/PVA blend membranes under different conditions are shown in Figure 4. The PVA membrane was found to be semi-crystalline with the d -spacing (4.55 Å) of crystallites, and the typical peak of the PVA membrane appeared at $2\theta = 19.5^\circ$ because of a mixture of (101) and (200) crystalline planes.³¹ Interestingly, when the PVA membrane was elongated [length/initial length (L/L_0) = 200%], its XRD pattern became different; a new broad peak appeared around $2\theta = 8.5^\circ$ (d -spacing ≈ 10 Å), and the original peak at 19.5° was reduced in its intensity. From this result, it can be speculated that by stretching in one direction, the PVA molecules, which were randomly distributed, were oriented along the stretching direction, and the range of the intermolecular distance between the ordered molecules became narrow; they behaved like pseudocrystals, showing a new peak around $2\theta = 8.5^\circ$ with a d -spacing of about 10 Å. On the other hand, the PVA molecules composing the crystals were also elongated, and the crystals were partially

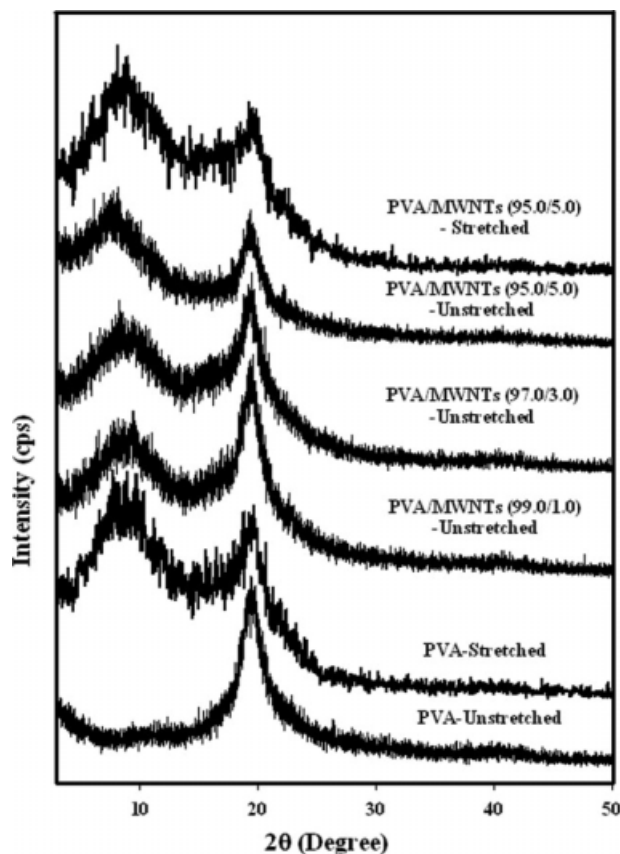


Figure 4 XRD patterns of original and stretched ($L/L_0 = 200\%$) MWNT/PVA blend membranes with different amounts of MWNTs (wt %).

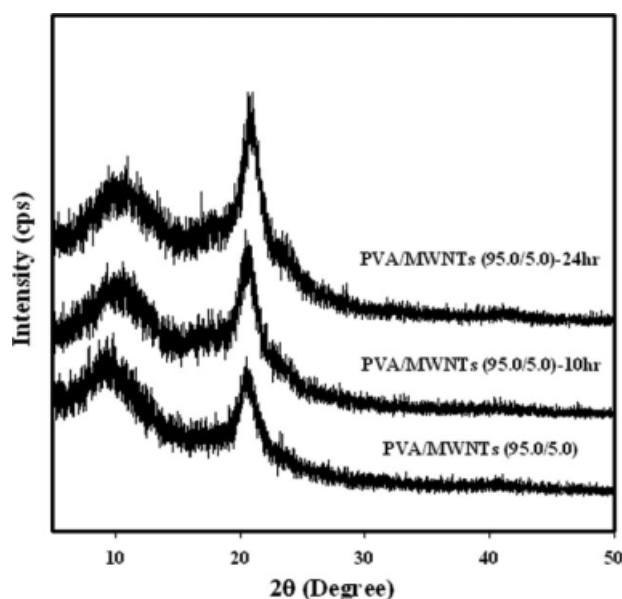


Figure 5 XRD patterns according to the annealing time at 130°C for MWNT/PVA (95.0/5.0 wt %) blend membranes.

destroyed; as a result, the intensity of the original crystal peak at 19.5° appeared to be reduced, as shown in Figure 4.

When MWNTs were blended with PVA to form blend membranes, the same phenomenon found for the elongated PVA membrane was found for the blend membranes. When MWNTs were added at a concentration of 1 wt %, the peak centered at $2\theta = 8.5^\circ$ started to appear, and then it increased in its intensity with the content of the MWNTs increasing to 5 wt %, whereas the peak centered at $2\theta = 19.5^\circ$ decreased. When the blend membrane with 5 wt % MWNTs was stretched by the same elongation ratio ($L/L_0 = 200\%$), this phenomenon became even more distinct.

From these results, how the MWNTs affect the micromorphology of the blend membranes became clear; the MWNTs, randomly distributed through the PVA matrix and interacting with the PVA molecules, induced the PVA molecules to orient one another in a limited area and reduced the crystallinity by disturbing the PVA molecules.

Figure 5. exhibits the effect of annealing on the micromorphology of the blend membranes. For this experiment, blend membranes with 5 wt % MWNTs were annealed at 130°C (above T_g) for 10–24 h. With an increasing annealing time, the peak centered at $2\theta = 8.5^\circ$ decreased, whereas the peak at $2\theta = 19.5^\circ$ increased. It was found from this result that by annealing, the PVA molecules rearranged to form more crystals.

Effect of MWNTs on the swelling of the membranes

Figure 6 shows the effect of MWNTs on the degree of swelling of the MWNT/PVA blend membranes in

a water/ethanol (10/90 wt %) mixture. The membranes used for this experiment were the ones without any crosslinking. With increasing contents of MWNTs, the swelling ratio of the blend membranes decreased, and this may have been the result of the PVA molecules stiffened by the MWNTs, as elaborated previously, which explains the effect of MWNTs on T_g . The PVA molecules, interacting strongly with the functional groups of MWNTs, were not as easy to swell in a water/ethanol mixture solution as the PVA molecules without MWNTs, and this reduced the swelling ratios.

Pervaporation performances of the blend membranes: effect of the presence of the MWNTs

Fluxes

The pervaporation performance of the blend membranes was studied with an ethanol solution containing 10 wt % water as a feed solution. As shown in Figure 7, the fluxes (water plus ethanol) depended on the composition of the blend membranes and increased with the content of MWNTs increasing. Generally, free volume reduction leads to lower flux, producing an increase in selectivity. However, in this study, with an increasing amount of MWNTs, despite the reduction of free volume (increase in T_g) found in the DSC study, as shown in Table I, the fluxes of the blend membranes increased. This unusual tendency makes it possible to suggest that both the water and ethanol may transport through the inner spaces of MWNTs without serious resistance, helping them to penetrate the blend membranes easily. As mentioned in the Experimental section, the inner diameter of the MWNTs is about 4.3 ± 2.3 nm, which is larger than the kinetic diameter of a water molecule (0.30 nm) or an ethanol

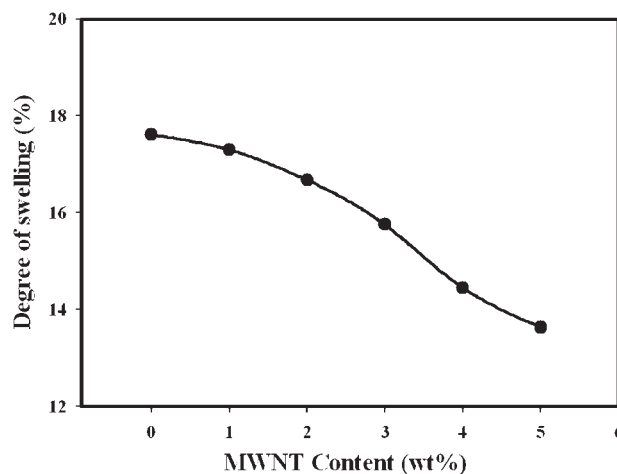


Figure 6 Degree of swelling of MWNT/PVA blend membranes in a 90 wt % ethanol aqueous solution as a function of the contents of the blended MWNTs.

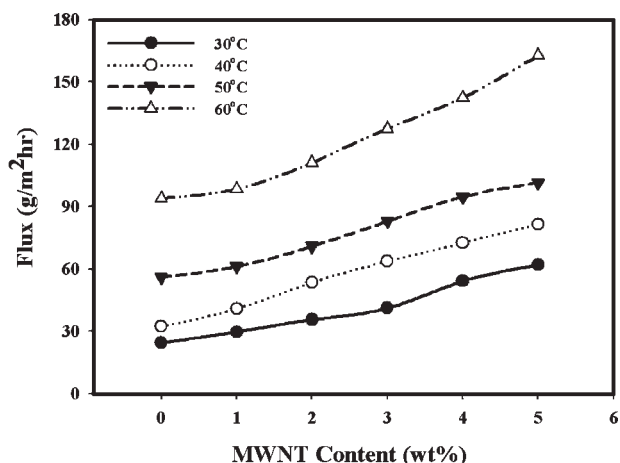


Figure 7 Flux of MWNT/PVA blend membranes in the pervaporation separation of a water/ethanol mixture (10/90 wt %) as function of the contents of the MWNTs used.

molecule (0.430 nm), so the water and ethanol molecules can pass through the inner spaces of the MWNTs, improving the flux of the blend membranes.^{32,33} Also, another factor that can explain the flux increase is the decrease in the crystallinity. Because the crystalline regions are inaccessible to the penetrant, the decrease in the crystallinity of the blend membranes by the MWNTs might induce the increase in the flux.^{34,35}

Separation factors

Figure 8 presents the behavior of the separation factor toward water of the blend membranes according to the contents of the MWNTs. The overall separation factor was found to be very dependent on the contents of the MWNTs, decreasing with the content of the MWNTs. The separation factors remained without a serious decrease up to 3 wt % MWNTs and then decreased rather drastically with a further increase in the MWNTs. This kind of behavior of the separation factors might be due to the combined effect of the characteristics of the MWNTs themselves, such as the empty inner space and the hydrophilic functional groups attached to the surface of the MWNTs, and the micromorphology change of the PVA matrix induced by the added MWNTs, as explained in the section on the characterization of the MWNT/PVA blend membrane (XRD).

Effect of the operating temperature

Figures 7 and 8 also show the temperature dependence of the fluxes and separation factors of the blend membranes. With the temperature increasing from 30 to 60°C, the fluxes increased, but the separation factors decreased. The temperature effect can be

explained by the expansion of the free volume in the polymer matrix and the mobility of the penetrants. With the temperature increasing from 30 to 60°C, the PVA free volume increased remarkably as a result of random thermal motion of the polymer chains. As the free volume increased, both water and ethanol molecules more easily penetrated the membranes; thus, the flux increased, and the selectivity decreased. In other words, at higher temperatures, the plasticizing effect on the membranes facilitated the transport of water along with ethanol because of the weaker interactions between the water, ethanol, and membranes.

CONCLUSIONS

MWNT/PVA blend membranes were prepared through the casting of PVA solutions in water containing different amounts of MWNTs (1.0–5.0 wt %) followed by drying at room temperature. It was found from TEM pictures of the blend membranes that the MWNTs treated with strong acids were good enough to be dispersed well in the aqueous PVA solutions, resulting in good dispersions in the blend membranes. The MWNTs dispersed through the blend membranes appeared to affect physical and chemical properties of the PVA membranes: with the content of the MWNTs increasing, T_g of the PVA membranes increased, T_m decreased with decreased crystallinity, and they induced micro-orientation of the PVA molecules in their vicinity in the membranes. The pervaporation properties of the PVA membranes for the dehydration of an ethanol/water mixture were also found to be affected by the MWNTs in the blend membranes: according to the

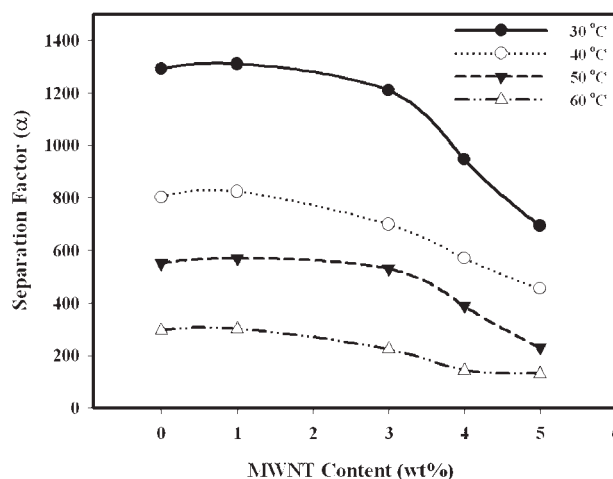


Figure 8 Separation factor of MWNT/PVA blend membranes in the pervaporation separation of a water/ethanol mixture (10/90 wt %) as function of the contents of the MWNTs used.

increase in the MWNT content, the flux increased, but the rejection decreased, especially with high contents of MWNTs, such as more than 4.0 wt % MWNTs, because of the inner empty space of the MWNTs, which could act as a path for the penetration of water and alcohol with relatively less resistance.

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