SHIFTING THE PROPERTIES OF MODIFIED PA-PVA MEMBRANES INTO THE RO REGION AND THE EFFECT OF MODIFICATION ON THEIR MORPHOLOGY AND ION REJECTION

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(Received October 2008 and accepted December 2008)

In this work, shifting the properties to reverse osmosis (RO) region, morphology and ion rejection of modified membranes based on polyamides/poly(vinyl alcohol), PA/PVA, blends were studied. The solubility parameters of the polymeric materials, \( \delta_h \) and \( \delta_d \), which represent hydrophobic and hydrophilic properties can be employed to choose the polymeric materials for the RO membranes. Large void cavities (between 150 to 250 nm) were observed in the substructure for the lower polymer concentrations in the casting solution. Feed water samples exhibited high concentrations of Cl\(^{-}\) and HCO\(_3\)\(^{-}\) – as the major anions and Ca\(^{2+}\) as the major cation. The observed rejection varied from 69\% to 100\% for Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^{-}\), SO\(_4\)\(^{2-}\), Yeast & Mold and Total Coliform. Nitrate showed lower rejection.

**Keywords:** Polyamides; Poly(vinyl alcohol); RO membranes; Morphology; Solubility parameters; Ion rejection.

1. INTRODUCTION

Since the first membrane materials were described by Loeb and Sourirajan in the late 1950's\[^1\] numerous materials have been developed to improve the performance and fouling mitigation of membrane filters. For a given treatment stream, a certain membrane material can be selected from an assortment of candidates. Inorganic, ceramic, and polymeric synthetic membranes are growing in use across the world for both municipal and industrial processes.

In order to increase the strength of the material with improved chemical resistance, polyamide (PA) type materials were developed with new techniques, originally developed by Cadotte in the early 1970's, in interfacial polymerization. Micron thin layers of PA can be applied to porous materials of increased structural strength\[^2\]. The PA substance can withstand pH between 3 and 11 and temperatures up to 40°C. Compared to cellulose acetate (CA) RO elements, PA elements show higher rejection of salts (>97\%) at lower pressures (200-400 psig). Polyamide is even more resilient to chemical and biological attacks. However, should free chlorine exist in the feed water, care should be taken to dechlorinate the water fully to prevent damage of the material which could lead to decreased rejection of dissolved materials.

Poly(vinyl alcohol), PVA, a hydrophilic water-soluble polymer, can be used to develop a new type of membranes with good anti-fouling characteristics. Better mechanical properties, low fouling potential, long-term thermal resistance and pH stability can be achieved by preparing miscible blends of PA and PVA. Na and Liu\[^3\] reported that a PVA-composite material could develop hydrophilic membranes with better fouling resistance. CA membranes, coated by a PVA gel, were found to be hydrophilic membranes with a smooth surface and have good anti-fouling properties, especially in preventing protein fouling\[^4\].

Recently, membranes based on PA/PVA blends were prepared and their interaction (miscibility) and crystallization were studied\[^5,6\]. Zhang et al\[^1\] reported that modified UF PVA membranes exhibited a high level of water permeation along with good retention of Bovine serum albumin (BSA). The membranes were hydrophilic and showed a good tendency to relieve protein fouling. Addition of nano-sized silica to PVA were found to help in preparation of PVA-based UF membranes by phase inversion method which have
good anti-fouling properties and better mechanical strength[3].

The purpose of this work is to investigate the blending of polyamides/poly(vinyl alcohol) materials and its effect on shifting their properties to the reverse osmosis (RO) region. The morphology and ion rejection of the modified membranes will also be presented.

2. EXPERIMENTAL

2.1 Materials
Poly(vinyl alcohol) PVA with $M_w = 95000$ in the form of 95% hydrolyzed powder was supplied by Janssen Chemica and used as received. Polyamide PA6 and formic acid (98%) were supplied by Aldrich Chem. Co. and used as received. EDTA (0.1 M), Ca$^{2+}$, SO$_4^{2-}$, NO$_3^-$ and hardness indicators were received from Hach.

2.2 Membrane Preparation
Polymer solutions of PA6 and PVA were prepared separately at a concentration of 4 wt% at 40-50°C with continuous stirring. Formic acid (98%) was used as solvent. The two solutions were mixed in the desired proportions (PA6/PVA: 100/0, 80/20, 60/40, 50/50, 40/60 and 20/80 wt/wt) and stirred for 2h at ambient temperature. The membranes were prepared as thin films by casting the polymer solutions into shallow soda-glass dishes and allowing the solvent to evaporate relatively slowly. The resulting thin films of about 50 μm were dried at 60°C and placed under vacuum at 70-80°C for at least 3 days to constant weight and then thoroughly rinsed with deionized water.

2.3 Morphology
Morphology was studied by using a high-voltage Scanning Electron Microscopy (SEM, 1000 kV JOEL 6300). The samples were sputter coated with gold.

2.4 Filtration Experiments
The tests were conducted with a bench-scale system similar to that described by Qin et al.[8] and Meier-Haack et al.[9]. The water flux was measured at an average operating pressure of 0.5 MPa and at a temperature of 22.2±0.1°C.

2.5 Analysis Methods
The turbidity was measured by field turbidity meter (Turbo 550, Wissenschaftlisch-Technisch Co., German Parts, made in USA). The pH and electrical conductivity (EC) were measured by pH- and conductivity meters (Wilkens-Anderson Co., USA). The samples were analyzed for major components; Al$, Ca^{2+}$ and Mg$^{2+}$ and total hardness by titration with 0.1 N EDTA, and Cl$^-$ by titration with 0.1 N AgNO$_3$ with K$_2$Cr$_2$O$_7$ as indicator, SO$_4^{2-}$ and NO$_3^-$ (by DR/2000 Hach Spectrophotometer, USA) at λ = 450 nm for sulfate and 500 nm for nitrate. Total alkalinity was determined by titration with 0.1 N H$_2$SO$_4$ using methyl orange and phenolphthalein as indicators. A multiple tube test method was used to determine the presence of total coliform. 10 ml of water sample were added to ten test tubes containing Lauryl Tryptose Broth (LTB) media. The tubes were then incubated at 35°C for 24 hours. Gas bubbles were noticed inside the tubes indicating the presence of coliform bacteria (positive test). The tubes that showed negative results were incubated for an extra 24 hours. Total and faecal coliform were tested by inoculating the positive samples into two tubes containing Brilliant Green Lactose Bille Broth (BGLB) medium at 35°C and 45°C; the first to ascertain the positive results and the second to check for faecal coliform.

3. RESULTS AND DISCUSSIONS

3.1 Shifting Membranes Properties to Reverse Osmosis (RO) Region
Chemical and physical properties of polymeric materials are closely related to chemical and physical structures. Chemical properties describe how the chemical structure of the material changes under certain conditions. For example, aromatic polyamide is susceptible to chlorination in the presence of chlorine in water. On he other hand, physical properties include the degree of change in the physical structure in a given environment and also include physical parameters such as density, melting point, glass transition temperature, etc. Since membrane separation includes interfaces between the phase that involves the permeant mixture and the membrane phase, the interfacial properties are the most important properties of the membrane. The solubility parameter approach will be used to evaluate the interfacial interaction force working between molecules from the polymer-polymer mixing theory[5,6] and the chemical structure[10]. The solubility parameter can give a measure to the nature and magnitude of the interaction force working between the molecules that constitute the membrane material, and also the interaction force between the latter molecule and the permeant molecule which can be uniquely determined from the molecular formula. The mixing of polymeric materials occurs when the free energy of mixing is negative $\Delta G_m$ (J/mol) which can be written as

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

(1)

Where $\Delta H_m$ (J/mol), T (K) and $\Delta S_m$ (J/mol.K) are the heat of mixing, absolute temperature and, entropy of mixing, respectively. For high molar mass polymers the entropy term is small, therefore, the enthalpy contribution usually dominates in polymeric systems. Among the several methods proposed to evaluate $\Delta H_m$, Hildebrand equation[11] is the most popular:
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\[ \delta = \delta_d + \delta_p + \delta_h \]  

(3)

When only London dispersion force is present and the entropic contribution is considered to be negligible, the enthalpy of mixing is always positive or zero which leads to unfavorable contributions to \( \Delta G_m \) and mixing. The presence of specific interactions between the polymer blend components such as hydrogen bonding leads to negative \( \Delta H_m \) and favorable contribution to \( \Delta G_m \). The solubility parameters \( \delta_h \) and \( \delta_d \), which were chosen to represent hydrophobic and hydrophilic properties of the polymeric materials\(^{(10)}\), are plotted in Figure 1.

In Figure 1, the closed curve was drawn with respect to polymeric materials for which the preparation of RO membranes was attempted (50 different polymers) with sufficiently high sodium chloride rejection and permeation rates could be produced. Closed symbols represent the pure polymers while open symbols represent the blends of polymeric materials. For PA6/PVA blends of 80/20, 60/40, and 50/50, \( \delta_d - \delta_h \) were in a limited range. Clearly, by adding poly(methylmethacrylate), PMMA, and poly(vinyl acetal), PVAc, the compositions: 80/20, 60/40, 50/50 and 40/60 were all shifted more inside the RO region. These results indicate that the above solubility parameters can be employed to choose polymeric materials for the RO membranes.

\[ \Delta H_m = V_m \phi_d \left[ \delta_d \right]^2 \]  

(2)

where \( V_m \) is the total molar volume of the mixture \((\text{m}^3/\text{mol})\), \( \phi \) is the volume fraction, \( \delta \) is the solubility parameter, and subscripts 1 and 2 represent the first and second components of the polymeric mixture. The solubility parameter \( \delta \), is calculated from the summation of the London dispersion force, \( \delta_d \), the dipole force, \( \delta_p \) and the hydrogen bonding force, \( \delta_h \):

\[ \delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \]  

(3)

Figure 1. Solubility parameters \( \delta_h \) vs. \( \delta_d \). Notice shifting the PA6/PVA membranes to the RO region. The left-hand side figure was taken from Al-Rawajfeh\(^{(5)}\).

Figure 2. SEM of the low concentration cast solution of PA6/PVA membrane.
3.2 Morphology

SEM micrographs at μm and nm-scale of the air-side of the 80/20 PA6/PVA membrane are shown in Figure 2. The morphology of membranes is impressively complex, diverse, and irregular. It was found that all compositions that show nodular morphology are in the nm-scale and the size of the nodules increases with increasing PA6 content. Large void cavities (between 150 to 250 nm) are observed in the substructure for the low-concentration cast solution. While the PA6/PVA composite membrane exhibits large-scale surface roughness of ridge-and-valley structure, the PVA membrane surface is relatively smooth. The distinct roughness of composite membranes is an inherent property of PA composite membranes\[12,13\].

3.3 Feed Water Chemistry

The characteristics of the feed water, from two different sources in Amman, are shown in Table 1. The table presents the temperature, pH, turbidity, total hardness (TH), total alkalinity (TA), electrical conductance (EC), total dissolved solids (TDS), the major ionic composition (Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^{-}\), SO\(_4^{2-}\), NO\(_3^{-}\), HCO\(_3^{-}\), CO\(_2\) and CO\(_3^{2-}\)), total carbon dioxide (TC), CaCO\(_3\) saturation indexes for the feed water and the microbiological tests.

The water samples investigated in this study exhibit high concentration of Cl\(^{-}\) and HCO\(_3^{-}\) as the major anions and Ca\(^{2+}\) as the major cation. Calcium, bicarbonate and chloride are attributed to the dissolution of lime and halite in the investigated area. An Mg/Ca ratio of 0.86 to 0.93 indicates dolomite aquifer[14]. It is known that the solubility of carbonate and bicarbonate ions increases in the presence of excess chloride ions. Thus, the molar ratio of SO\(_4^{2-}\)/HCO\(_3^{-}\) is a predictive ratio to the type of the scale, if it is either SO\(_4\) or CO\(_3\) scale. A value less than 1 indicates high CO\(_3\) scale (i.e. > 80%) and low SO\(_4\) scale while a value between 1 and 10 indicates medium to high CO\(_3\) scale and medium SO\(_4\) scale[15].

3.4 Rejection of Ions

Mass transfer through RO membranes is usually described by the solution diffusion model[10]. The dependence of the solvent flow \(J_w\) on the operating pressure minus the osmotic pressure of the system \((\Delta P - \Delta \pi)\) which is the driving force for the process, should give a linear relationship. The slope of a plot \(J_w\) vs. \((\Delta P - \Delta \pi)\) should correspond to the water permeation coefficient \(A_w\):

\[
J_w = A_w \cdot (\Delta P - \Delta \pi) \quad [m / s]
\]  

(4)

The water permeation coefficient \(A_w\) can be estimated by varying feed pressures for various solutions. Bench and pilot studies with single and multicomponent solutions are required to estimate this empirical constant. The observed rejection of ions by the membranes (\(R_{obs,ion}\)) were investigated in two different feed waters.

\[
R_{obs, ion} = \frac{C_{ion, p}}{C_{ion, f}} \cdot 100\% ,
\]

where \(C_{ion, f}\) and \(C_{ion, p}\) are the concentrations of ions in the feed and permeate, respectively.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Feed Water I</th>
<th>Feed Water II</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.6</td>
<td>7.4</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>0.27</td>
<td>0.02</td>
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<tr>
<td>Total hardness, TH (mg/L)</td>
<td>405.0</td>
<td>340.0</td>
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<tr>
<td>Total alkalinity, TA (mg/L)</td>
<td>245.0</td>
<td>245.0</td>
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<tr>
<td>EC (μS/cm)</td>
<td>704.9</td>
<td>704.9</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>430.0</td>
<td>430.0</td>
</tr>
<tr>
<td>Ca(^{2+}) (mg/L)</td>
<td>176.0</td>
<td>57.6</td>
</tr>
<tr>
<td>Mg(^{2+}) (mg/L)</td>
<td>39.1</td>
<td>47.9</td>
</tr>
<tr>
<td>Cl(^{-}) (mg/L)</td>
<td>69.1</td>
<td>72.7</td>
</tr>
<tr>
<td>SO(_4^{2-}) (mg/L)</td>
<td>35.0</td>
<td>75.0</td>
</tr>
<tr>
<td>NO(_3^{-}) (mg/L)</td>
<td>57.8</td>
<td>6.4</td>
</tr>
<tr>
<td>HCO(_3^{-}) (mg/L)</td>
<td>57.2</td>
<td>19.2</td>
</tr>
<tr>
<td>CO(_3^{2-}) (mg/L)</td>
<td>1.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 1. Composition of the feed water.
The changes in the characteristics of the feed water which was purified using the two different filters and membranes and the observed rejection ($R_{obs,ion}$) of Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, Yeast & Mold and Total Coliform are show in Table 2.

4. CONCLUSION

Shifting to RO region, morphology and rejection of ions of modified membranes based on PA/PVA blends were studied. Solubility parameters $\delta_h$ and $\delta_d$ were employed to investigate if a polymeric material is suitable for the RO process or not. All compositions that show nodular morphology are in the nm-scale and the size of the nodules increases with increasing PA6 content. Large void cavities (between 150 to 250 nm) are observed in the substructure for the lower polymer concentrations in the casting solution. Cl$^-$ and HCO$_3^-$ were found to be the major anions with 100% rejection and Ca$^{2+}$ was the major cation with 69 to 80% rejection. In a future work, membrane surface properties will be investigated. Moreover, membrane's morphology will be studied by Atomic Force Microscopy (AFM).

Acknowledgement

This work was partially supported by the Ministry of Higher Education and Scientific Research, Jordan. Prof. Dr. J. Michler, Martin-Luther University of Halle-Wittenberg, is greatly acknowledged for SEM.

REFERENCES