Development of PEBAX Based Membrane for Gas Separation: A Review

M.S. Abdul Wahab and A.R. Sunarti

Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia Pahang, Gambang, Pahang, MALAYSIA

Abstract: Polymer is among the favorite materials used for membrane separation as they are cheap, easily cast, low maintenance cost and commercially easy to get even though the material needs to be altered to meet the separation industry specific needs. There are two common issues in membrane preparation which are the produced sheet are too brittle and has no strength to withstand pressure during separation process and the porosity of the sheet sometimes not suitable with the gas kinetic diameter for the separation to occur. PEBAX or Poly ether block amide is the answer for the issues as this elastomer provides good mechanical strength from the hard segment of the crystalline poly amide block while the soft polyether will drive the separation process. This unique material can be casted either by phase inversion of the PEBAX itself with other polymer or by coating them on the other polymer substrate.

Key words: PEBAX, Composite membrane, Substrate, Elastomer.

INTRODUCTION

Methane, a key component in natural gas composition has a wide availability. Contributing 75% of natural gas, these energy resources also can be obtained from biomass. The waste that can easily transformed into wealth have a bright future as a new way of creating energy. It is estimated that 25% of renewable energy in 2020 will be from biogas [1]. The decomposition of waste through anaerobic digestion of bacteria will produced biogas which contain methane in a natural way. The presence of 50-60 % methane is biogas composition are the major interest of the biomass [2-4]. Current method used for purification of methane from carbon dioxide are by water scrubbing[5], Polyethylene glycol scrubbing[6], carbon molecular sieves [7] and the popular membrane separation [8].

In natural gas processing membrane separation practically used as they offer low energy cost, high efficiency and low pollution [9]. It is usually employed to separate carbon dioxide, nitrogen, hydrogen sulfide and others from natural gas. Other technology in gas separation technology such cryogenic separation, absorption/adsorption separation, and supersonic separation. Despite all the high technology separation process, membrane separation has took a central stage in research arena as they are the alternative for a same purpose but with simple process [10].

Polymeric membrane offer an energy efficient with low capital cost, flexible process, ease of scale up and high efficient of raw material [11-14]. Various polymer has been used as based material, mixing and coating altogether to achieve desired need of gas separation. PES [15], PVDF [16], PVC [17], and PSF [18] are among the top polymer in this field of research. Every each of these polymers has their own ability to separate only limited kind of species.

This review paper will focus on preparation of dope solution and casting technique of PEBAX 1657 and PEBAX 2533 toward a perfect flat sheet membrane for gas separation. The modification of PEBAX membrane that leads to a perfect selective layer and method used to avoid gelation of PEBAX solution.

PEBAX A NEW ITERATION IN MEMBRANE DEVELOPMENT

PEBAX or poly (ether block amide) is a family of copolymers, consisting of polyamide hard segments and polyether soft segments in the long polymeric chains [19]. The hard amide block will put the material on the mechanical strength stability and the soft segment of polyether will primarily drive the separation process. These unique structures have made PEBAX a good chemical resistance towards acid, basic and organic solvents and high thermal and mechanical stabilities. In several studies, PEBAX has shown an excellent result for CO₂ separation due to their polar ether oxygen withCO₂ interaction with other non-polar gases [20].

There are two common type of PEBAX used in industry, PEBAX 1657 and PEBAX 2533. The PEBAX composition is tabulated in Table 1 [20, 21].
et al., 2012, found that PEBAX 1657 is less permeable and more selective compared to PEBAX 2533 correspond to their mechanical properties which 1657 has higher Young’s modulus than the samples with PEBAX 2533 [22]. The permeability properties of PEBAX strongly depend on the wt% of polyether contents as the armophous structure offer the excellent gas separation such the one in polyethylene oxide (PEO). Nevertheless, the permeability of each material can be enhance by altering the particles structure of the membrane.

PEBAX also can be turned into a composite membrane or mixed matrix membrane, MMM to improve the performance of the elastomers. In addition of another fillers commonly, zeolite, and silica nanoparticles will provide constant porosity with good diameter for CO₂ separation. R. Surya Murali et al., 2014, used nanosilica and H-Mordenite as a filler in PEBAX 1657 membrane to study the permeation of pure CO₂, H₂, O₂, and N₂ gases [23]. The addition of these material has enhanced the amorphous nature of the polymer and they founded that increasing the filler composition will improve the permeance significantly.

The composite PEBAX membrane could be produced by direct mixed of the two solution (PEBAX and other polymer) or by coating the PEBAX on the polymer substrate. The solvent used to dissolve PEBAX is a bit tricky as the combination of the solvent can be wrong and will affect the PEBAX itself. For PEBAX 1657, researcher suggested the solvent can be the combination of 70% ethanol and 30% water from the total solvent quantity [24, 25]. L. De Lorenzo et al., 2012, successfully used 50/50 of 2-propanol/n-butanol as a mixture to dilute the PEBAX 2533 for their nanocomposite PEBAX membrane [26].

To ensure that there is no effect of solvent used toward PEBAX, Table 2 summarized the common solvent with the effect range. The combination of the solvent with water or other chemical will reduce the effect and enhance the solvent properties.

<table>
<thead>
<tr>
<th>PEBAX Grade</th>
<th>Polyether Phase</th>
<th>Polyether Content (wt%)</th>
<th>Polyamide Phase</th>
<th>Polyamide Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1657</td>
<td>–(CH₂–CH₂–O)n-poly(ethylene oxide)</td>
<td>60</td>
<td>–(NH–(CH₂)5–CO)n-polyamide 6</td>
<td>40</td>
</tr>
<tr>
<td>2533</td>
<td>–(CH₂–CH₂–CH₂–CH₂–O)n-poly(tetramethylene oxide)</td>
<td>80</td>
<td>–(NH–(CH₂)11–CO)n-polyamide 12</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 1: Resistance of PEBAX® Grades to Common Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>PEBAX 1657</th>
<th>PEBAX 2533</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Propanol</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Butanol</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td>Boiling Water</td>
<td>A</td>
<td>A</td>
</tr>
</tbody>
</table>

A: Little/No Effect  B: Moderate Effect  C: Severe Effect

CASTING TECHNIQUE

Method 1: PEBAX 1657 or mixture of it with another polymers or filler can be straight away dissolve altogether in a mixture of ethanol/water (70/30 wt %) while PEBAX 2533 and its mixture can be dissolved in butanol under reflux at 80°C and 70°C respectively for 2h or until homogenous mixture is achieve. PEBAX concentration can be kept constant at 3 wt % while altering the other polymer/filler 10-50 wt % for developing of composite PEBAX membrane [27]. All polymers or filler can be dry for 24h at 80-100 °C to ensure that there is no water or moisture present, so that the dissolving of the contents will go easier. After the solution has been degassed for amount of time, casting can be done by using a Teflon petri dish. In Figure 1, Yi Li et al., 2010, showed the process diagram of PEBAX/POSS mixed matrix membrane for hydrogen purification via preferential CO₂ removal [28].

Method 2: This technique utilized the dense membrane by coating another material on top of the membrane to improve separation efficiency. The membrane can be prepared by phase inversion method either vapour-induced phase separation, VIPS [29], Thermally Induced Phase Separation, TIPS [30], Reaction Induced Phase Separation, RIPS [31], Solvent/Non Solvent Induced Phase Separation, SIPS [32], Dry/Wet Phase Inversion[33] and many other. Base membrane will be prepared first as a substrate in their suitable solvent by one of the method mention.
The produced substrate will undergo coating procedure by submerge the base membrane in the PEBAX solution for several time.

E. Ahmadpour et al., 2014, managed to produce PVC/PEBAX composite membrane for CO₂ separation by producing the PVC substrate and the coating procedure is as follows;

1. Produced the PVC substrate
2. 3 wt% of PEBAX was coated on the substrate for four times
3. Times interval for each coating was 30 minutes
4. The membrane was placed in an oven at 40°C for each coating
5. The obtained composite membrane was placed in an oven at 40°C for another 48h

The 30 minutes time for each interval is to make sure that the solvent vaporize before another coating is made. The obtained composite membrane undergoes the last drying process for 48h to ensure the complete vaporization of the solvent.

**METHOD TO AVOID GELATION IN PEBAX DOPE SOLUTION**

The tendency of gelation in PEBAX comprising solution is due to the incompatibility of the solvent. The solvent must give no effect toward the pellets. If PEBAX 1657 was used as a based membrane or coating solution, the solvent can be taken as formic acid, n-butanol and a mixture of 1-propanol/n-butanol [34, 35]. This four solvent will dissolve PEBAX 1657 evenly but the solution itself tend to gelation when cooled to room temperature. Only formic acid can avoid the gelation of the solution but the used of this solvent in large scale membrane preparation is inconvenient as they are expensive for a low cost polymeric membrane separation. M. Akhfash Ardestani et al., 2010, managed to prepare PEBAX by dissolving them in acid formic/1-propanol (3: 2 v/v) at 80 °C under vigorous mixing and reflux conditions [36]. In easy way the combination can always be used as 70/30 ethanol/water [37-41]. Slight changes in ratio may affect the incomplete dissolving of the PEBAX pellet. Table 3 show the dielectric constant for various PEBAX 1657 solvent. Differ to PEBAX 1657, PEBAX 2533 can be straight away dissolve in 1-butanol [42], ethanol [43] and ethanol/water 90/10 [44].

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric Constant</th>
</tr>
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<tbody>
<tr>
<td>58.5 Formic acid</td>
<td>58.5</td>
</tr>
<tr>
<td>17.6 n-Butanol</td>
<td>17.6</td>
</tr>
<tr>
<td>Mixture ethanol/water (30/70)</td>
<td>45</td>
</tr>
</tbody>
</table>

Continuous stir with uniform heat which around 80°C will help the homogenizing of the solution. The sudden stop of stirring aid will vaporize the solvent and change the ratio of the solution. The PEBAX pellet will stick at the bottom of the beaker and burnt the surface without dissolving the pellet.
PEBAX SURFACE MORPHOLOGY AND PERFORMANCE

Figure 2 showed the SEM image of surface (Figure 2a) and cross-section (Figure 2b) of PEBAX 1657 dense membrane. Surface of pure PEBAX is clear and homogenous with a smooth horizontal layered cross section morphology. R. Surya Murali et al., 2014, stated that the addition of inorganic filler such, Zeolite 4A will boost the performance of gas separation of the pure PEBAX 1657 [45]. Increased of filler in the polymeric matrix, the permeability of the gas also will rise significantly but the ideal selectivity can be achieved by manipulating the percentage of the filler itself [46-50]. Vajiheh Nafisi et al., 2014, has working on ZIF-8 (ZeoliticImidazolate Framework-8) filler into PEBAX 2533 matrix which lead to a very weak mechanical properties [43]. Figure 2c showed that there is a limit to the amount of loading ZIF-8 in Mixed Matrix Membrane, MMM. If ZIF-8 is loading up to 50% in PEBAX 2533, a porous layer with weak mechanical which can’t stand a high pressure feed will form.

If PEBAX is used as a layer to a polymer substrate, the selective layer must be as thin as possible. This is due to the gas permeance as it is inversely proportional to the thickness of selective layer coated on the substrate. However, if the membrane is too thin, there will be defects in the selective layer, which could dramatically reduce the gas selectivity. From the performance perspective, Pebax 1657. Md. Mushfequr Rahman et al., 2013, found that CO₂ permeability can be increased ranging from 73 to 152 barrer with increased of PEG-POSS contained [20]. It is 30% higher compared to the permeability of that gas in pure PEBAX 1657. The result proves that PEBAX layer or PEBAX membrane performance can be enhanced by adding nanoparticle altogether in the dope preparation.

CONCLUSION

The gelation of PEBAX solution is due to solvent effect which leads to the vaporization of the solvent before the solution is being casted. The polymeric particles inside the solution will solidify in room temperature. To avoid such condition, a proper solvent which gives severe or no effect should be used to dissolve PEBAX pellets. The combination of solvent which gives severe effect and no effect toward PEBAX can also be used by 70/30 ethanol/water. Researcher has been working on different kinds of materials to enhance PEBAX separation performance and modified their surface structure, POSS [51], SAPO-34 [52, 53] and many other inorganic nanoparticles materials. They found that the amount of materials added to PEBAX based membrane will significantly improve the separation performance but the composition of added material must be in control as there is a maximum concentration of the filler. If it exceeds the limit, it will give no improvement to the membrane morphology and could drop the performance itself.

![Figure 2: SEM image of PEBAX 1657(a and b) [45] and PEBAX 2533(c) [43].](image-url)
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