Amine-based vapor-phase crosslinking processes of polyimide-based membranes for energy efficient separations

Dave Mangindaan*
Professional Engineer Program Department, Faculty of Engineering, Bina Nusantara University, Jakarta, Indonesia 11480
dave.mangindaan@binus.ac.id

Abstract. Membrane processes are crucial in the industrial and engineering chemistry, for separation and purification of not only chemicals but also gases and wastewater treatment. In order to obtain high quality products from membrane processes, the membranes must be engineered to cater such performance, namely by chemical crosslinking process. One of the emerging crosslinking methods is the vapor phase crosslinking (VPC). The advantages of VPC for enhancing membranes are usage of fewer amounts of chemicals, with specific crosslinking of the top selective layer only (no unnecessary crosslinking of bulk layer). Therefore, membranes can boost their quality without sacrificing much of their productivity (quantity of flux). In this paper, several utilization of amine molecules for VPC of polyimide membranes for gas separations, pervaporation (gas-liquid separation), and organic solvent nanofiltration (OSN) are covered. The performance enhancements of the polymeric membranes for the aforementioned processes are summarized. Furthermore, the molecular mechanisms of the VPC of the amine-based vapors are reviewed, based on X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared characterizations. It was found that there are several possible scenarios of interaction between amines and polyimides, which are not only involving crosslinking (combination of several polymeric chains), but also grafting, and sometimes chain scissions. The investigation of molecular mechanism of the amine-based VPC process provides insights to the relationship between structural configurations towards the separation performance of various types of membrane processes, which paves way for the development of membranes of the future.

Keywords: Vapor phase crosslinking, amines, membranes polyimide, pervaporation, gas separation, organic solvent nanofiltration

1. Introduction
Membrane is a semi-permeable material that selectively separates a particular stream (permeate) from a mixture (feed), with several of driving forces such as differences of concentration, pressure, temperature, etc.[1] Nowadays, membrane processes are vital in the field of industrial and engineering chemistry, especially for separation and purification of not only chemicals but also food [2-5], gases [6, 7] and wastewater treatment [8-11]. Its performance is evaluated from the aspects of selectivity or rejection (representing quality) and flux or permeability (representing quantity). These two parameters in the field of membrane separations are quite opposing each other, and therefore research of membranes are conducted intensively in the world. Although both the aforementioned parameters can
be achieved, but there are several problems lurking to be solved, such as price, manufacturability, durability, thermal and/or mechanical resistance etc.[1] From materials point-of-view, there are 2 (two) major classes of membranes, i.e. (1) ceramic (inorganic) membranes, and (2) polymeric membranes [2, 12, 13]. Ceramic membranes exhibit high performance (both flux and selectivity), but expensive, and quite difficult to fabricate and also brittle (broken easily). Polymeric membranes are relatively easy to process and fabricate, much cheaper than ceramic membranes, however with low or moderate flux and/or selectivity. With proper treatment or modifications, polymeric membranes might be improved to be on par with ceramic membranes [14].

There are several polymeric materials for membranes [15], especially for that of glassy polymers such as polyvinylidene fluoride [16, 17], polybenzimidazole [18, 19], polyvinyl alcohol[20, 21], or polysulfone [22, 23], but the most common one is polyimide, with its widespread variations namely P84 [24-27] or Matrimid [7, 28], and some popular lab-made 6FDA-Durene materials [6, 29, 30]. These materials of glassy polymers are highly utilized for membranes because of the thermal resistance, mechanical properties, facile processing of using relatively safe solvents, etc. However, the separation quality of the polyimides is very moderate and therefore it is imperative to be improved.

To enhance the performance of membranes, there are several methods e.g. thermal annealing [31, 32], blending different polymers [18], or incorporation of nanoparticles [6, 33], etc. On the other hand those methods might have some drawbacks regarding the compatibility issues of polymer-polymer or polymer-nanoparticles interactions, which will hinder the true potential of membranes for the applications in the industrial and engineering chemistry. Another method that is common to be employed for improving polymeric membranes is crosslinking process [34, 35]. In this method, polymer chains are joined together to deliver more compact membrane structures, resulting not just in stronger and more durable membranes, but also in the increase of the selectivity (quality of a separation) of the membranes. However, it is also crippled with the loss of flux (quantity of a separation) [25], which is quite normal, considering the tighter pores of membranes brought by the crosslinking process.

| Membrane-based processes | Feed | Permeate | Amine crosslinker | Reference |
|--------------------------|------|----------|-------------------|-----------|
| Organic solvent nanofiltration (OSN) | Organic solvent (Rose Bengal dye in isopropanol) | Organic solvent (isopropanol) | Tris(aminopropyl) amine (TAPA) | [36] |
| Gas separation | Gas (H₂/CO₂) | Gas (H₂) | Tris(aminopropyl) amine (TAEA) | [29] |
| | Gas (H₂/CO₂) | Gas (H₂) | Diethylene triamine (DETA) | [30] |
| Pervaporation | Liquid (acetone/water) | Vapor (water) | Ethylenediamine (EDA) | [25] |
There are several conventional crosslinking methods, i.e. thermal, ultraviolet, and wet crosslinking processes [34]. Thermal crosslinking requires long time and also large input of energy, while ultraviolet crosslinking is more energy-efficient than the thermal crosslinking, but it suffers from unstable and random reaction and heavily equipment-dependent [37-39]. An emerging crosslinking process that deserves more exploration is vapor-phase crosslinking (VPC). It was first utilized by applying ethylenediamine vapor for modification of polyimide membranes for improved H₂ purification (gas-gas separation) [29, 30, 40, 41], and then extended for the pervaporation process (vapor-liquid separation) [25], and also for solvent-resistant nanofiltration (SRNF) or more recognized as organic solvent nanofiltration (OSN). It is quite interesting to review VPC as it is logically an economical process (crosslinker can be easily reused), perform crosslinking exclusively on top of the selective layer of membranes, and the use of mild conditions.

In this paper, the rising and unique procedure of VPC for selected various membrane processes (pervaporation, gas separation, and OSN, as shown in Table 1) is discussed and analyzed. The amines used are tris(aminopropyl)amine (TAPA) [36], tris(aminomethyl)amine (TAEA) [29], diethylene triamine (DETA) [30], and ethylenediamine (EDA) [25]. The molecular point-of-view of the crosslinking mechanism is also highlighted, as assisted by several chemical characterization methods, namely FTIR (Fourier transform infrared spectroscopy) and XPS (X-ray photoelectron spectroscopy).

2. Methodology
In this review, selected polyimide membranes (backbone shown in Figure 1) modified with amine-based VPC for various membrane separations are summarized in Table 2 (along with the functional groups of the related polyimide backbone in Figure 1).

| No. | Selected membrane processes | Polyimide | R1 | R2 | Amine crosslinker |
|-----|-----------------------------|-----------|----|----|------------------|
| 1   | OSN [36]                    | Matrimid 5218 | ![Image](image1.png) | TAPA |
| 2   | H₂ selective gas separation [29] | 6FDA-Durene | ![Image](image2.png) | TAEA |
| 3   | H₂ selective gas separation [30] | 6FDA-Durene | ![Image](image3.png) | DETA |
| 4   | Pervaporation [25] | P84 | ![Image](image4.png) | EDA |
Figure 1. Polyimide backbone for several selected membrane separations. The functional groups R1 and R2 are shown in Table 2.

The VPC was applied to the different membranes by using simple lab-made apparatuses shown in Figure 2. During VPC, there will be variations of operation conditions that are shown in Table 3.

![Figure 2. Apparatuses for amines VPC](image)

### Table 3. Operation conditions of several amine VPC processes

| No | Selected membrane processes | Amine crosslinker | Temperature (°C) | Time (min) | Volume of amines |
|----|-----------------------------|-------------------|-----------------|------------|-----------------|
| 1  | OSN [36]                    | TAPA              | 50-120          | 10-45      | 20 mL           |
| 2  | H₂ selective gas separation [29] | TAEA           | 40-80           | 10         | 15 mL           |
| 3  | H₂ selective gas separation [30] | DETA           | 80              | 10-60      | 25 mL           |
| 4  | Pervaporation [25]          | EDA               | 30-60           | 0.5-1.5    | 10 mL           |

The VPC modified membranes were tested at various separation processes, with feed and permeate are briefly mentioned in Table 1. In brief, the details of the experiments are as follows. In the OSN experiment, a dead-end permeation cell using membranes of 3.14 cm² was employed to separate Rose Bengal dye (50 ppm) in isopropanol. [36] The permeation cell was stirred by magnetic stirrer at 600 rpm. For the gas separation, a variable-pressure constant volume permeation system having upstream pressure of 3.5 atm was used to measure the permeability of standalone stream of pure H₂ and pure CO₂ gas (35 °C). To assess the separation performance with mixed gas as a mixture, the H₂ and CO₂ gas were mixed at 50/50 (v/v) as the feed, and measured with a variable-volume constant pressure permeation system with total pressure of 7 atm. [29, 30] For the pervaporation experiment, a lab-scale Sulzer pervaporation apparatus was used, using membranes of 15.2 cm², to capture water from acetone/water (85/15 w/w, 50 °C) feed [25]. The membranes modified by amines VPC were characterized in terms of morphology by using scanning electron microscopy (SEM) or field-emission SEM. The chemical functional groups were analyzed qualitatively by using Fourier transform infrared spectroscopy (FTIR) and quantitatively by using XPS (X-ray photoelectron spectroscopy).

3. Results and Discussion

The performance of the modified membranes via amines VPC process is shown in Table 4 (OSN and pervaporation) and Figure 3 (gas separations). Furthermore, in Table 4, there are also several data from other literatures cited in order to provide a good comparison between membranes modified with and without amines VPC. For H₂/CO₂ gas separation, the selectivity to H₂ is enhanced to pass the Robeson upper bond 2008, which is the benchmark of membrane-based gas separation processes before 2008. For the case of acetone/water pervaporation, the VPC modified polyimide membranes perform
acceptable separation factor (equals to rejection of 90%), balanced with the highest productivity of 1.8 kg m$^{-2}$ h$^{-1}$ of water in the permeate side of the pervaporation process.

Table 4. Separation performance of several OSN and acetone/water pervaporation modified by amines VPC

| Membranes               | Cross-linker/ modification | Rejection or separation factor | Flux                              |
|-------------------------|----------------------------|--------------------------------|----------------------------------|
| Matrimid 5218/UiO-66-NH$_2$ 0.1% [36] | TAPA VPC, 120 °C, 30 mins | Rejected Rose Bengal dye in isopropanol $\sim$95% | 4 L m$^{-2}$ h$^{-1}$ (stable at 10 bar, 12 days) |
| Deacetylated chitosan [42] | -                          | SF= 208                        | 0.240 kg m$^{-2}$ h$^{-1}$       |
| Chitosan [43]            | Glutaldehyde               | SF= 1276                       | 0.084 kg m$^{-2}$ h$^{-1}$       |
| PBI/P84 [18]             | p-xylene dichloride & heat treatment | SF= 1187                       | 0.284 kg m$^{-2}$ h$^{-1}$       |
| P84 [25]                 | EDA VPC, 50 °C, 1 min      | SF= 53.48                      | 1.825 kg m$^{-2}$ h$^{-1}$       |

Figure 3. H$_2$/CO$_2$ separation performance of membranes modified by DETA and TAEA

These successful enhancements of membrane processes by amines VPC are definitely related with the structural change of the membranes after the vapor crosslinking process. In general, the morphology (not shown here) of the membranes modified by amines VPC were quite distinctive, having increased dense selective on the top layer in the nanometric region, and up to 150 nm [25, 29, 30, 36], which is acceptable as the expected outcome of a crosslinking process.

The chemical characterization by FTIR (Figure 4) and XPS (Table 5) of representative EDA VPC-modified pervaporation membrane showed that the improvement of the membranes is highly related to the increased signal of amide groups at 1644 and 1520 cm$^{-1}$ (associated with C=O stretch and C-N stretch), at the cost of the disappearance of polyimide characteristic hands of imide groups at 1718 and 1352 cm$^{-1}$ (C=O symmetric stretch and C-N stretch), as a fruit of the attack on imide ring, causing the opening of the ring. The phenomenon captured by the FTIR results was recalculated by using XPS analysis, delivering the quantification of surface functional groups (via high-resolution deconvolution spectra, not shown here), led by the increasing of C-N bonds (285.5 eV [44, 45]. By observing Figure
4, it also can be seen that there is an optimized point of the temperature and time of amines VPC. Beyond that point, the membrane might be heavily damaged.

Table 5. High-resolution deconvolution spectra of EDA VPC-modified pervaporation membranes

| Name   | C-C/benzene 284.7 eV | C-N 285.5 eV | C=O 284.7 eV | R²  |
|--------|----------------------|--------------|--------------|-----|
| Control| 71.26                | 12.52        | 16.22        | 0.99|
| E30-60 | 64.77                | 20.07        | 15.16        | 0.99|
| E50-30 | 69.61                | 23.03        | 7.36         | 0.99|
| E50-60 | 60.91                | 31.14        | 7.95         | 0.99|
| E50-90 | 68.11                | 23.42        | 8.47         | 0.99|
| E60-60 | 75.97                | 11.94        | 12.09        | 0.99|

Figure 4. Typical FTIR results of polyimide membranes modified with amines VPC

Figure 5. Proposed molecular mechanism of amine-based vapor phase crosslinking (represented by TAEA)

Based on the result of FTIR and also XPS, it is clearly shown that the amine VPC process involves not only crosslinking (indicated by tighter pores, and slightly decreased flux, but higher selectivity),
but also attack of the imide groups that leads to opening of imide ring, and probable scission of polymeric chain. Moreover, grafting of amines (resulting from incomplete crosslink of polymeric chain by amines) is also possible. Therefore, the molecular mechanism of crosslinking of polyimide membranes by amines VPC is proposed in Figure 5, represented by TAEA VPC.

4. Conclusions
In this review, amine-based vapor crosslinkers (EDA, DETA, TAEA, TAPA) have been successfully applied for a wide array of membrane separations (OSN of Rose Bengal in isopropanol, acetone/water pervaporation, H₂/CO₂ gas separation) to improve the purification processes (selectivity, durability, productivity, etc.). Several advanced characterization techniques have aided to reveal the crosslinking mechanism (which deployed the opening of imide ring that permits not just crosslinking but also grafting that allows substantial incorporation of free amines) that is beneficial for designing membranes for the future.

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