

## Fabrication of Hybrid Membranes by Different Techniques

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Polyetherimide (PEI) flat-sheet nanohybrid membranes were fabricated through Dry-Thermal (DT) and Thermal-Treatment (TT) methods using nanoplatelet graphene oxide (GO) as nano-filler. The effects of GO incorporation and fabrication techniques were investigated on the membrane microstructures. The effects of GO embedment and fabrication method on the membrane physical properties were investigated through scanning electron microscopy (SEM) and contact angle. The impregnate membrane with GO exhibited significantly higher hydrophilicity. The SEM images revealed has a sponge-like structure for the membrane prepared via DT method while TT membrane possessed a dense structure.

### 1. Introduction

Pervaporation (PV) process is a process for liquid mixture separation in a liquid phase. This process is able to separate different components from mixtures such as water/organic, organic/water and organic/organic mixtures. Pervaporation process works by placing a liquid mixture to be separated (feed) in contact with one side of a membrane (Huang et al., 2010). Across the membrane, the chemical potential gradient works as the driving force for the mass transport of the materials. Also, using vacuum pump or an inert purge (normally air or steam) on the permeate side can help to maintain of a suitable permeate vapour pressure. Usually the kept pressure is lower than the partial pressure of the feed liquid. Finally, the permeated product (permeate) can be removed from the other side with low pressure vapour (Figure 1) (Kujawski, 2000). Most of the membrane materials used in PV techniques are usable in laboratory scale, but not in industrial applications. Thus, there is a need to survey more membrane materials possibilities which is important in order to overcome drawbacks in current membranes.

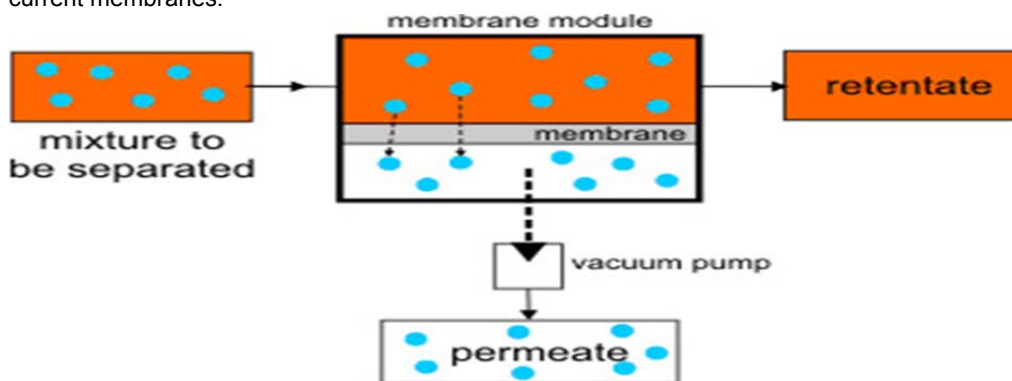


Figure 1: Schematic diagram of pervaporation process

In pervaporation, the membrane surface is in direct contact with the feed solution. The solution–diffusion model described separation in PV process in three steps i: dissolution onto the membrane, ii: diffusion through the membrane and iii: evaporation to the down-stream side which called permeate. Basically, hydrophilic and hydrophobic polymeric membranes are used to separate water or organic mixtures (Neel, 1995). Typically, hydrophilic membranes are considered to dehydrate n-butanol organic mixtures (Zhang et al., 2009). Potential of the industrial utility of this approach attracts for researchers to study the separation of azeotropic solution, pharmaceutical waste, isomeric and heat-sensitive liquid mixtures. Pervaporation survives the challenge of phase change by two aspects (Jin et al., 2010). First, pervaporation uses even with the minor components (usually less than 10 wt%) of the liquid solutions, and second, pervaporation applies the most selective membranes. An efficient membrane need to the suitable membrane materials and fabrication technique (Guo et al., 2004). To determine different procedures for fabricating membrane affects the morphological properties of the membrane. This research investigated novel fabricating techniques: of the Dry-Thermal (DT) and Thermal-Treatment (TT).

In addition, pervaporation also demonstrates incomparable advantages in separating heat sensitive, close-boiling, and azeotropic mixtures (Yoshida and Cohen, 2003) due to its mild operating conditions, no emission to the environment, and no involvement of additional species into the feed stream.

Most of the membrane materials used in PV techniques are usable in laboratory scale, but not in industrial applications. Thus, there is a need to survey more membrane materials possibilities which is important in order to overcome drawbacks in current membranes. Membranes used in the process of pervaporation possess porous or non-porous structures. Membranes with or without pores in their structure are called porous and non-porous membranes, respectively. The schematic of various types of the membranes are shown in Figure 2A and B. Difference of their pores size, shapes and distribution are the factors to determine pervaporation efficiency and selectivity of the membranes. In porous membranes, the permeation often carry out by size selection or exclusion. In permeating through the pores by diffusing process, such as separating water from organic solution using PV, a significant amount of water permeates across the membrane. Hence, a higher flux and lower selectivity are observed in the porous membranes.

The non-porous membranes function by first partitioning the molecule and then under a concentration gradient allowing it to diffuse through the solid material. So, in the non-porous membrane the partition coefficient and diffusivity effect on the separation of components, therefore, this type of membrane is used for PV processes whit high selectivity.

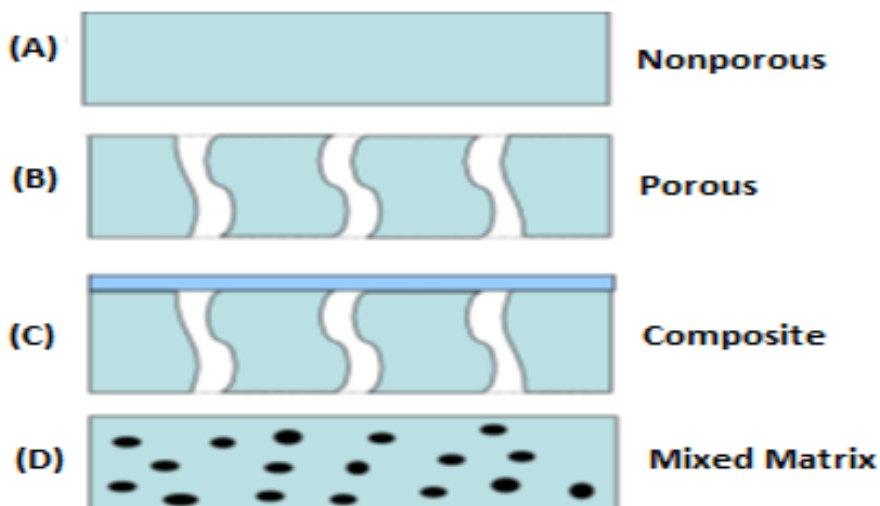


Figure 2: Schematic diagram of membrane morphology

Recently, graphene has attracted researchers for the derivative of graphene oxide (GO), which exhibits the different characteristics from graphene. Graphene has been used to prepare highly hydrophobic films and graphene structure is carbon based material. Since, nano-GO is a hydrophilic material with numerous active oxygenated groups it can be used for dehydration process. The polar groups of nano-GO can easily interact with water molecules and lead to the fast rate diffusion in the permeate side and high selectivity towards water molecules. Here, the hydrophilicity of membranes is increased and promotes the favorable properties of membranes for dehydration of the organic solvents (Jeon, 2012). Polyetherimide (PEI) was used in this study

as a matrix polymer for dehydration of n-butanol. This polymer has very attractive features for separation applications due to its specific properties such as excellent mechanical/chemical properties, less swelling characteristics, solvent resistance, good membrane-forming property, and high separation performance. However, permeation performance by PEI was not significant. Therefore, graphene oxide (GO) is applied as a modifier into PEI to enhance membrane properties like permeation/hydrophilicity (Mahmoudi, 2015).

Based on the materials of the membranes and morphology structure of the composite, the hydrophilic membranes classify to inorganic, polymeric and hybrid composite membranes. Hydrophilic membranes are mostly used by two main membrane structures including mixed matrix and composite membranes. Many researchers have focused on the efficiency of mixed matrix and composite membranes, as well as the type of materials which improve transfer rate and selectivity parameters. The polymeric membranes are extensively studied because of their low cost and high performance as compared to the inorganic membranes. On the other hand, the inorganic membranes are excellent in the thermal stability and mechanical integrity. The hybrid membranes are a combination of the polymeric and the inorganic membranes in order to enhance the performance of the polymeric membranes. Pervaporation dehydration membranes divide into two categories on the base of their hydrophilicity groups. The highly hydrophilic membranes are made by polyvinyl alcohol (PVA) or chitosan. These materials are usually cross-linked to enhance their stability and reduce their swelling in pervaporation feed conditions.

## 2. Methodology

The Graphene powder was synthesised to graphene oxide according to Hummers method (Hummers and Offeman, 1958). Graphene powder (2 g), sodium nitrate (1 g) and 46 mL of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$  98 %) were added into a reactor and stirred to control the temperature. In the next stage,  $\text{KMnO}_4$  (8 g) was added gradually to the mixture at temperature below  $10\text{ }^\circ\text{C}$  for 2 h, and then the temperature was increased to  $35\text{ }^\circ\text{C}$  and stirred for 1 h. Then the mixture was diluted with deionised water (96 mL) with the temperature below  $100\text{ }^\circ\text{C}$  and stirred for 1 h followed by further diluting with deionised water (100 mL). After that, 4 mL of 30 %  $\text{H}_2\text{O}_2$  was added to the mixture to reduce the residual  $\text{KMnO}_4$  and the mixture colour changed into a brilliant yellow. Finally, the mixture was centrifuged and washed with 5 % HCl aqueous solution. The wet powder was dried using a freeze dryer and a fine coffee colour powder was obtained at the end of this process (Manshad, 2016). The fine powder can observe in Figure 3. The chemical reactions of these three steps were shown in below Eq(1) - (3):



Figure 3: Digital photograph of graphene oxide powder

Graphene oxide was used as a filler in the membrane. Polyetherimide (PEI, Ultem, General Electric Company) utilised as a base polymeric material. Hybrid membranes prepared by 15 % polyetherimide (PEI) and 1 % graphene oxide and N-methyl-2-pyrrolidone (NMP) as solvent. Two techniques were employed for casting of the flat sheet hybrid membranes: Dry-Thermal (DT) and Thermal-Treatment (TT). Dry-Thermal membrane was prepared by three main steps: solvent preparation then solvent mixture was fabricated on the flat sheet. Third stage was drying of solvent mixture on the oven. The casting preparation was different for the DT and TT membranes. DT casting preparation required to drying at room temperature for 2 h then flat sheet transferred to the oven at 60 °C for 24 h. Thermal treatment membrane was fabricated in different conditions due to preparing the membranes with different physical and chemical properties. Thermal treated membrane was fabricated on the flat sheet. Then TT membrane kept in oven at 50 °C for 2 h and after that the temperature was increase to 70 °C for 12 h.

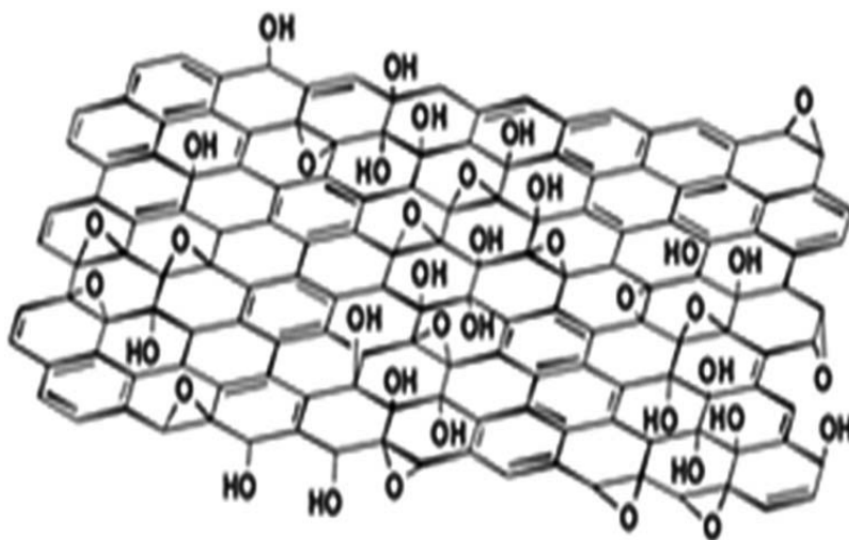


Figure 4: The chemical structure of graphene oxide

### 3. Result and Discussion

GO contains functional groups of hydroxyl, carboxyl and epoxide groups. These functional groups tend to react with the water molecule. Therefore, incorporating of the nano-graphene oxide into PEI increased hydrophilicity properties of the membranes. As Table 1 shows contact angle of neat polymeric membrane was reduced after adding graphene oxide into polymer. Contact angle of DT neat PEI was 66 but after GO incorporation contact angle of the DT membrane reduced to 53. Table 1 also illustrates effects of incorporation GO in Polymer improve hydrophilicity of both membranes (DT and TT). DT contact angle show higher hydrophilicity than TT membranes. Incorporation GO reduced contact angle degree of both membranes (thermal-treatment and dry-treatment). due to adding graphene oxide and fabrication techniques (drying time and temperature) (Hyder, 2008). Polyetherimide (PEI) was used in this study as a matrix polymer for dehydration of n-butanol. This polymer is very attractive features for separation applications due to its specific properties such as excellent mechanical/chemical properties, less swelling characteristics, solvent resistance, good membrane-forming property, and high separation performance.

Table 1: Contact angle

Membrane	Neat PEI (TT)	Neat PEI (DT)	Thermal-Treatment	Dry-Thermal
Contact angle (degree)	72	66	61	53

Figure 5 indicated scanning electron microscopy (SEM) A-surface and B-cross-section results of Thermal treatment and dry treated membranes respectively. SEM results show the effects of different fabrication techniques on the membrane morphology structure. In the figure A and B show dense and porous surface structure of Thermal and dry treated membranes. Different casting techniques provided different microstructure membranes as in SEM cross-section exhibited in Figure 4. Researchers apply modification process to enhance and change microstructure of the membranes which is not economical for industrial

application. This work was focused to modify physical and chemical structure of membranes by the most economical methods. The techniques impalement was effective for nanohybrid fabrication (Peng et al., 2010).

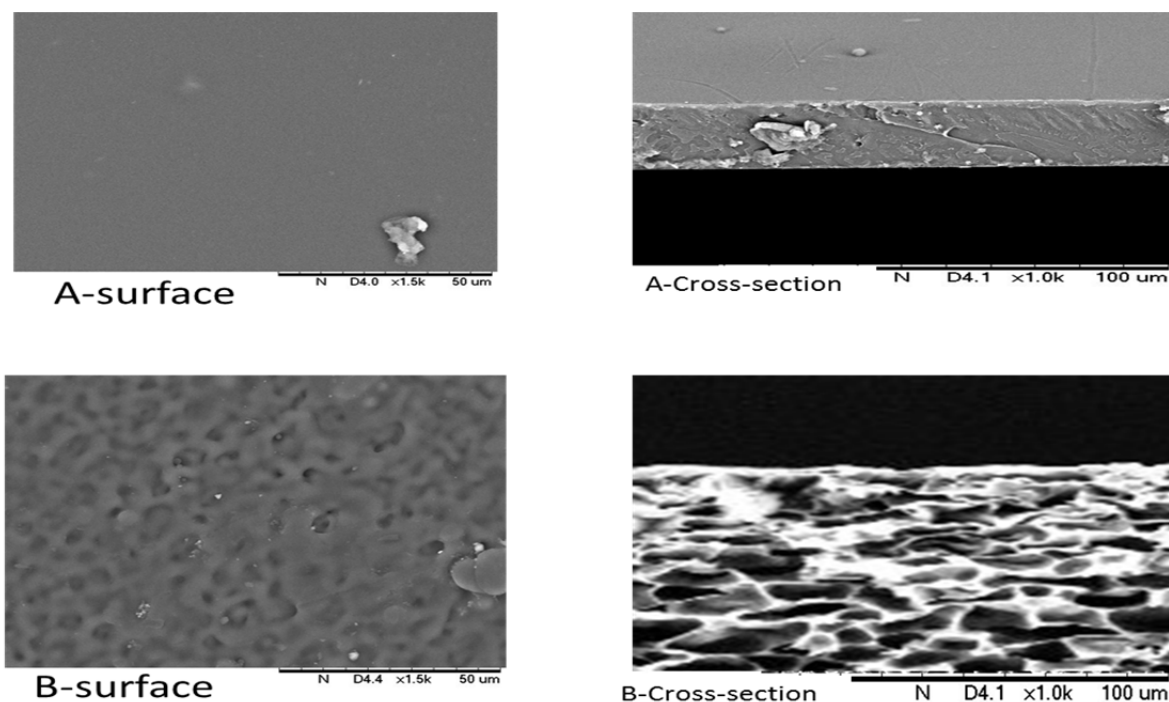


Figure 5: SEM of A and B-surface and cross section of TT and DT membranes

#### 4. Conclusion

The nanohybrid membranes were successfully fabricated by incorporation synthesised graphene oxide into Polyetherimide (PEI). Graphene oxide increased significantly hydrophilicity of dry-thermal (DT) and thermal treatment (TT) membranes. Dry-Thermal techniques provide sponge-like structure for the DT membrane. However, thermal treatment technique exhibited dense micro structure in SEM surface and cross-section morphology. Micro-structure of the TT and DT membranes were changed by temperature and drying time. Theoretically, sponge structure membrane utilised to improve permeation and dense structure membranes predicted with higher separation factor and lower permeation. Porous or sponge structure membranes are expected to show low separation factor and high permeation. Whereas, both fabricated membranes contain hydrophilic properties with different contact angle therefore both membrane can apply as hydrophilic membrane with different properties in separation factor and permeation performance. Contact angle results clearly exhibited different hydrophilicity degree between neat polyetherimide and incorporated graphene oxide.

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