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Basic Evaluation for Polyetherimide Membrane Using Spectroscopy Techniques

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***Abstract*—**Membrane performance depends on the kind of solvent used in preparation. A membrane made by Polyetherimide (PEI) was evaluated for gas separation using X-Ray Diffraction (XRD), Scanning electron microscope (SEM), and Energy Dispersive X-Ray Spectroscopy (EDS). The purity and the thickness are detected to evaluate the membrane in order to optimize PEI membrane preparation.

***Keywords*—**Energy Dispersive X-Ray Spectroscopy, EDS, membrane, Polyetherimide, PEI, Scanning electron microscope, SEM, Solvent, X-Ray Diffraction, XRD.

I. Introduction

IN the industry field, the use of membranes is a must. Experimentally, they are used to allow certain molecular to pass through it and prevent others. Membrane is a kind of special barrier that is widely used especially in refineries [Fig. 1]. The concept of the membrane separation is based on several mechanisms, molecular size, adsorption, partial pressure or chemical reaction.

Fig. 1 Membrane

In membrane market, there are a lot of different types of membranes. Beside their wide use in oil industry, they are also involved in medical field, food and beverages, and water waste field. Choosing the right membrane is based on the material used and the kind of required separation. Membranes are mainly divided into four types based on the manufactured material: polymeric, metallic, ceramic, and carbon. Polymeric membranes are heavily used in the market because of its low production cost and the competitive performance [1]. Generally, there are two categories of polymeric membranes. The first category is porous membranes are which used for liquid separation. The second category mainly used for gas separation is called dense membranes.

This paper will discuss a dense polymeric membrane (PEI) which is already manufactured in our lab. The chemical formula of PEI is $(C_{37}H_{24}O_6N_2)_n$. it has excellent thermal and mechanical properties. It is considered as one of the best membranes for gas separation [2]. The efficiency of this membrane will be examined through several tests using XRD, SEM, and EDS.

Fig, 2 XRD

II. XRD

XRD is widely used specially that determining the crystal structure and the composition of unknown crystalline material is a must in engineering and material science. In fact, XRD is a rapid and powerful instrument to reveal the unknown mineral especially that the used unite is widely available [Fig. 2]. It depends on generating and directing X-ray beams to the surface of the specimen. X-Rays are high energy electromagnetic radiation that have energy ranging from about 200 eV to 1 MeV[3].

In XRD instrument, the radiation is produced in an x-ray tube which contains a source of electrons and two metal electrodes. The principle of production is the rapid deceleration of electrically charged particles of sufficient kinetic energy. Using a Tungsten filament, electrons are produced and accelerated electrically through a voltage ranging from 30-60 kV. The electrons are brought to focus on a metal target which is usually copper. Consequently, a divergent beam of x-radiation is emitted. This beam has the same characteristics of the metal target. The target material must have a high atomic number to produce high intensity X-rays [4].

The energy of the X-ray photon and its wavelength are

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related by [5]:

$$E = \frac{hc}{\lambda}$$

A constructive interference and diffracted intensity is produced from the interaction of the incident rays with the sample. The diffracted x-ray intensity is continuously recorded at respective angles by a detector. Based on Bragg's Law the diffracted intensity is measured to identify sample's crystalline structure [Fig. 3] [6].

$$(n\lambda = 2d \sin\theta)$$

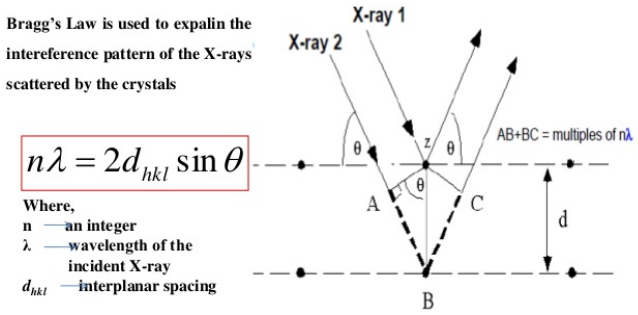

Fig. 3 Bragg's Law

This law relates the wavelength of electromagnetic radiation (λ) to the diffraction angle of the peak (θ) and the lattice spacing between atoms or layers (*d*) represented in the crystalline sample. The data acquired from the analysis are compared by the reference database existed in the instrument. Thereby, identification of crystalline phases is accomplished. Since, each mineral has its own fingerprint represented as peaks in a special pattern to identify it, the mineral and the chemical composition of the sample are revealed. Moreover, XRD is used for determining the unit cell dimensions and measuring the purity of the sample. In contrast, there are several limitations that prevent the ideal performance of XRD. It characterized by size limitations. The sample must be homogenous with clear and large crystalline structures otherwise the reflected intensity will be undetected by XRD readings. Also, for mixed material, the detection limit must be above 2% to provide unambiguous mineral determination [7]. Also, high angle reflections may cause peak overlay that affects the accuracy of the results.

After explaining the methodology of XRD, the information we got will be implemented to evaluate the membrane sample we have in labs. Fig. 4 represents the spectra of the membrane resulting from the test. It reveals two peaks which represents the fingerprint of PEI. The result shows that there are no additional peaks or peak overly detection, thus, the purity of the membrane is sufficiently acceptable.

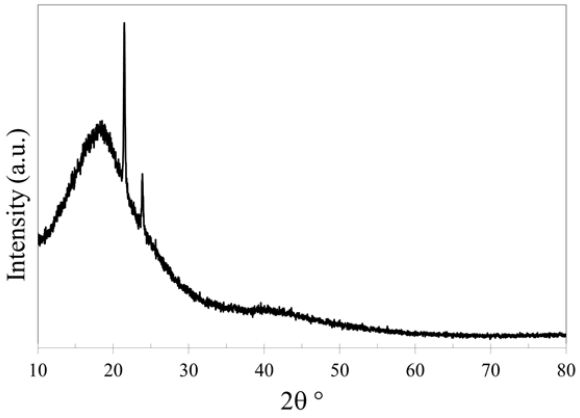

Fig. 4 XRD analysis of PEI membrane

III. SEM

SEM deals with electrons to identify the morphology of the solid specimens [Figs. 5, 6]. The concept of the instrument is generating and directing a focused beam of high-energy electrons at the surface of solid specimens. The generated electrons carry significant amounts of kinetic energy. The energy of the incidents electrons are dissipated as they interact with surface of the specimen. This electron-sample interactions produce variety of emissions and signals at the selected area of the specimen. These signals include secondary electrons, backscattered electrons, diffracted backscattered electrons, photons, visible light, and heat. In details, secondary electrons are responsible to produce the SEM images. It shows the morphology and the topography of the samples. The backscattered electrons and the diffracted backscattered electrons are used to determine crystal structures and orientations of minerals [8]. Furthermore, photons aid in analyzing the elements of the sample. By detecting and processing the reflected signals and emissions, a 2-dimensional image is formed, and the crystalline structure and the pore throats will be visible to be analyzed. In most applications, the dimensions of the image range from approximately 1 cm to 5 microns in width. Moreover, the magnification used in SEM range from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm [9].

Fig. 5 SEM

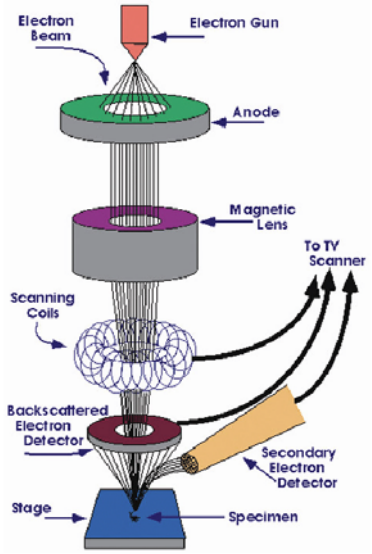

Fig. 6 Scheme of SEM

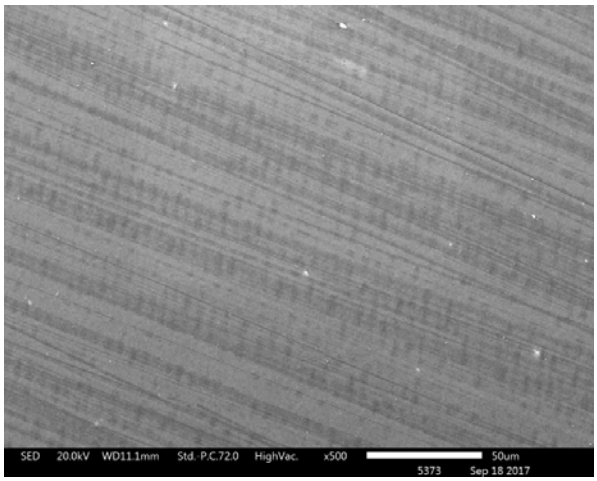

Fig. 7 Morphology of PEI membrane

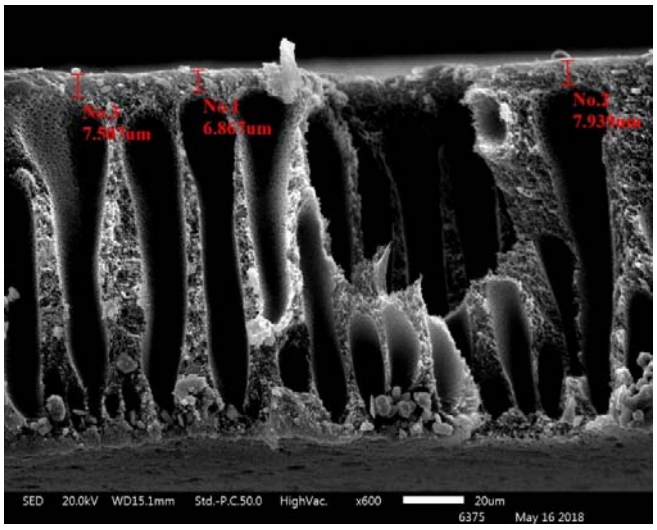

Fig. 8 Cross section SEM of PEI membrane for measuring the membrane thickness

To use the SEM, the sample needs to be conductive. In fact, most of the polymers are not. Therefore, coating the sample with a conductive material such as gold is needed. SEM was used to analyze PEI membrane to study the physical structure. Because the membrane is dense, the surface is expected to be free from holes [Fig. 7]. SEM was also used to measure the membrane thickness to calculate the membrane permeability [Fig. 8]. Actually, the membrane structure is a combination of porous and dense layers. This is due to using certain solvents during the membrane preparation for casting the membrane. After that, the solvent is removed by exchanging it with water and this will create an additional porous structure [10].

IV. EDS

EDS is considered as chemical microanalysis technique that provides an elemental composition map of the tested specimen. It is an additional instrument used in conjunction with the SEM. it is simple in components but effective in performance. It consists of a sensitive x-ray detector, liquid nitrogen Dewar, and software for analyzing.

During the electron-sample interaction that is performed by the SEM system, a variety of emissions are produced as mentioned before. X-rays are one of these different emissions that EDS is designed to detect. During the interaction, some electrons from the atoms at the sample surface are ejected and replaced with electrons from a higher state. Thus, x-ray is emitted to balance the energy difference between the two electrons' states. The EDS detector measures the relative abundance of emitted x-rays versus their energy to identify the elements composition of the specimen. The detector is mainly made of lithium-drifted silicon crystals. When an x-ray strikes the detector, a charge pulse is created. This charge is directly proportional to the x-ray energy. Using a charge-sensitive preamplifier, the charge pulse is converted to a voltage pulse. For each incident x-ray, the energy determined from the voltage measurement is sent to a computer for display and further data evaluation. In fact, the x-ray energy is characteristic of the element from which it was emitted. Consequently, the spectrum of x-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume [11].

Similar to any instrument, EDS has several limitations. It cannot detect the lightest elements that have an atomic number below 11. Also, several energy peak overlaps may occur and affect the certainty of the results. At high energies, individual peaks may relate to several different elements.

PEI membrane was analyzed by EDS to determine the elements. The chemical formula of PEI is $(C_{37}H_{24}O_6N_2)_n$. However, due to instrument limitation, only carbon and oxygen were detected as shown in Table I. Nevertheless EDS confirmed that the sample was pure due to not detecting any other elements.

TABLE I
EDS DATA FOR PEI MEMBRANE

Sample	PEI wt%	Carbon wt%	Oxygen wt%
PEI membrane	27	84.9	15.1

V. Conclusion

The characteristics of PEI qualify it to be one of the best gas membranes in the industry. The structure of the membrane is examined seeking for better performance of the membrane. The spectra with two peaks resulted from the XRD assure that the membrane is made of PEI and it is very pure. Moreover, only oxygen and carbon elements are detected through EDS due to its limitation. The thickness, porosity and permeability were inspected using SEM. It shows that the membrane is dense and has high thickness in which it affects the permeability of the membrane. In fact, all of these results determine the efficiency of the membrane. It aids in discovering the weak points of the membrane in order to optimize the membrane preparation methods for better membrane performance. To overcome the low permeability of the membrane, fillers are added during the membrane preparation to create voids for better gas transport.

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