Chapter

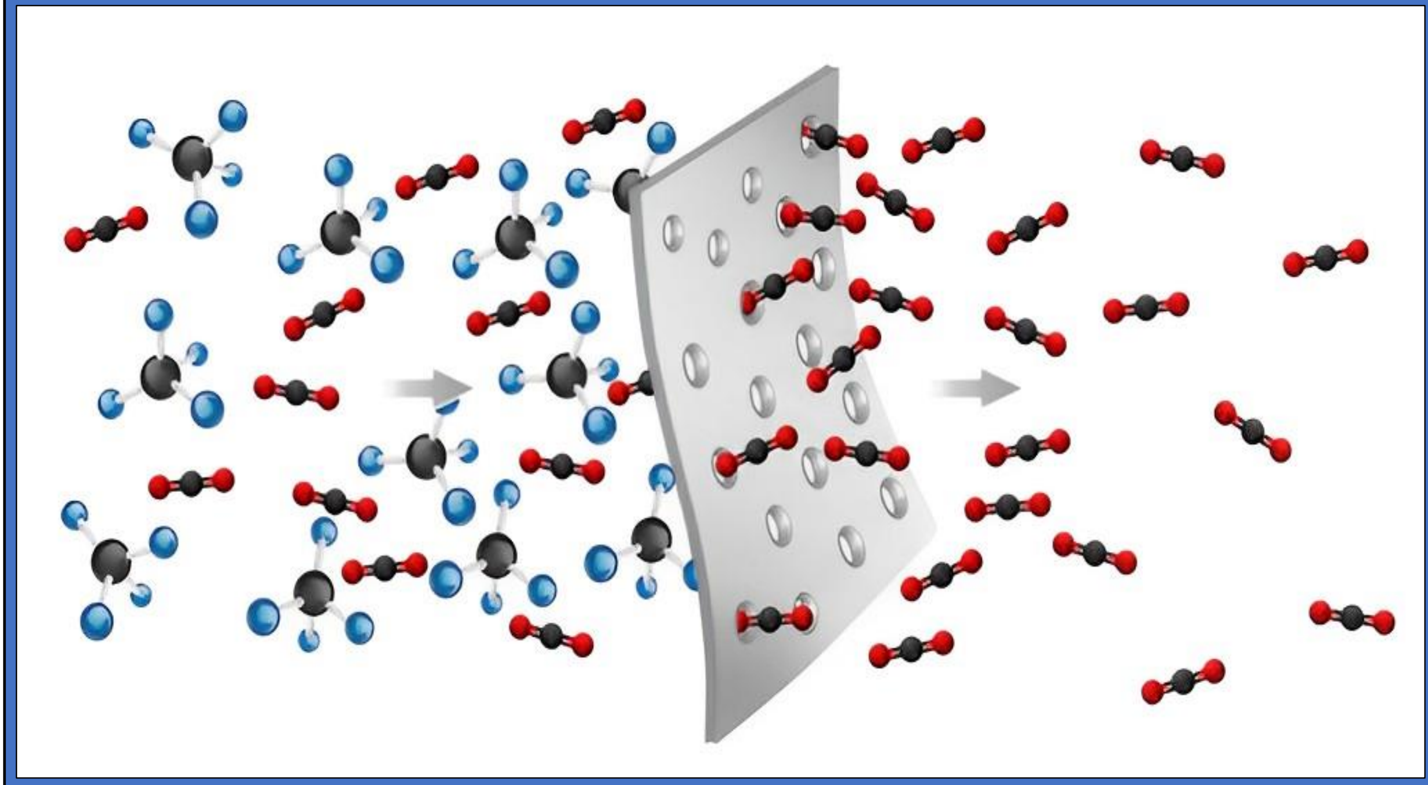
1

Introduction

Contents

Chapter - 1

Introduction



The reported thesis starts with an overview of the topic "Synthesis and Characterization of Glassy and Rubbery Polymer Nanocomposite Membranes." The word ‘membrane’ becomes the main center of the provided topic in this title. As a result, the description may begin with an understanding of the phrase. In common parlance, a membrane is a basic item such as a filter that bypasses one component while restricting another, however in scientific parlance, a membrane is a physically or chemically different two phase system that consists of a set of phases between them. Because of variations in the physical or chemical states of the two border phases, the membrane might control mass transport based on the applied force field. Moving on, ‘gas permeation’ refers to the transportation of gas molecules with regard to the applied force field. Membrane-based gas separation competes with other technologies in the chemical industry, such as adsorption, pressure swing adsorption, and cryogenic distillation. However, membrane technology is more relevant than other separation techniques in terms of total economics, safety, and environmental and technical issues. Several organic and inorganic materials can be used in membrane production. Polymeric materials, in general, are frequently used in important gas separation processes such as hydrogen recovery, natural gas purification, and air separation. Many new families of membrane material changes have been created to increase gas permeability and selectivity. As a result, selecting a membrane material for the gas permeation process is important. Because polymeric materials are used in this research, numerous alterations to membrane materials may be made to increase membrane efficiency in relation to the suggested application. This chapter includes theoretical background, objective of the work, literature survey and finally applications of the work.

1.1 Introduction

Over the last thirty years, membrane-based gas and vapour separation has evolved as a crucial unit activity in the chemical industry. The efficacy of this technique is highly dependent on the membrane materials used, their physicochemical qualities, and the process by which permeation occurs. The optimal material selection for ultrathin, dense gas separation membranes is far more demanding than for other membrane processes, such as ultrafiltration or microfiltration, where pore size and pore size distribution are critical concerns. The first practical achievements in membrane-based gas separation processes occurred between 1970 and 1980, and were based on a more or less random selection of well-known polymeric materials. However, these early advances had a significant influence on basic research of polymer transport characteristics for a broad range of chemical configurations.

One significant type of membrane materials for gas separation applications is glassy, rigid polyimides. More polyimides than any other chemical type of polymer have been studied for their gas-permeation characteristics. The major focus of the talk is on a diverse range of polyimides that have been synthesized in our laboratory. These scientists have come to the significant conclusion that polyimides outperform other polymers upper limit lines in a broad range of crucial applications, including the separation of CO_2/CH_4 and H_2/CH_4. Today, polymeric membranes are being challenged by inorganic membranes higher gas permeability capabilities and thermal stability. Only inorganic membranes weak mechanical qualities and present high cost keep them from meaningfully entering the membrane-based gas separation industry. Furthermore, inorganic membranes may be used effectively in pervaporation applications as well as gas separation and vapour permeation. Over one thousand glassy and rubbery polymers now have information on gas permeability characteristics. Permeation data for many structurally related polymers have been collected, and thus the qualitative and, to some extent, quantitative effects of polymer chemical structures on their gas and vapour permeation properties can be analyzed and predicted as a guideline for developing more advanced membrane materials. Furthermore, the apparent natural limitations of polymer permeability and selectivity for gas separation applications are well established.

The purpose of this work is to give a current overview of membrane-based gas, including both basic and practical issues. The introductory chapter is intended to provide background information for the subsequent chapters, including a brief historical overview and a detailed discussion of the fundamentals of the solution-diffusion mechanism, definitions of permeation, diffusion, and sorption parameters and units, and a brief discussion of the influence of gas and polymer properties, as well as operating conditions, on the observed transport parameters. The concept of solution-diffusion determines transport in non-porous polymeric membranes [1,2]. This 19th century model has based on the work of J. K. Mitchell [3],

T. Graham [4], and S. Von Wroblewski [5], who demonstrated that the presence of microscopic open pores or capillaries was not required for mass transfer through polymeric membranes such as natural rubber. First, Graham [4], and later Mitchell [3], observed that gases may permeate through non-porous rubbery polymeric membranes, and that this process was connected to gas dissolution and diffusion in polymeric materials.

1.2 Types of Polymers

Glassy and rubbery polymeric membranes have been widely used in the area of gas separation technology, but some of their drawbacks include degradation, poor chemical and thermal stability, limited permeability and selectivity, and poorer rejection of certain impurities.

Glassy polymers are a class of polymers that possess a rigid, glass-like structure at normal temperatures. These materials are characterized by their high glass transition temperatures (T_g) and have a more ordered, less flexible molecular arrangement compared to rubbery polymers. This structural rigidity often leads to increased strength and stability, making glassy polymers suitable for a variety of applications requiring mechanical integrity and dimensional stability. Some examples of glassy polymers include: polystyrene, polymethyl methacrylate (PMMA), polycarbonate (PC), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyethylene, polypropylene (PP). These polymers are widely used in industries such as packaging, automotive, construction, and electronics, where their mechanical and thermal properties play a crucial role in the performance of the final products.

Rubbery polymers, also known as elastomers, are characterized by their high elasticity and flexibility, as opposed to the more rigid structures of glassy polymers. This unique mechanical property allows rubbery polymers to deform significantly under stress and return to their original shape upon the release of that stress. These polymers typically exhibit a low glass transition temperature (T_g) and have a highly amorphous structure. Some examples of rubbery polymers include: polyisoprene (natural rubber), polybutadiene, polychloroprene (neoprene), polyisobutylene, polyacrylate, polyurethane (PU), poly(dimethylsiloxane) (PDMS).

Blended polymers, as the name suggests, are a combination of two or more different types of polymers that are mixed or blended together to create new materials with enhanced properties. The blending process allows for the modification of specific characteristics, such as mechanical strength, flexibility, or thermal stability, which may not be achievable with a single polymer. This approach is often used to improve the overall performance or to create specialized materials for specific applications [6]. Blended polymers find applications in a wide range of industries, including automotive, electronics, construction, and consumer goods, where their tailored properties can meet specific requirements for different products and components.

To increase gas permeability and selectivity, several novel families of membrane material modifications have been developed. As a result, selecting a membrane material for the gas permeation process is an important step. As polymeric materials have used in this research, several alterations may be made to the membrane materials to increase their performance with regard to the suggested application. Even the membrane-based separation and purification process uses less energy and is less expensive to run. A trade-off between the selectivity and permeability of gases dependent on a polymeric membrane and enhancing both the permeability and selectivity of parameters has generally limited polymeric membranes. The majority of research on polymeric gas separation membranes has improved gas permeability or selectivity. Typically, rather than the other way around, glassy polymers find it challenging to improve permeability without compromising their outstanding inherent selectivity. Thermally rearranged (TR) polymers and membranes for gas separation from precursor polyimides with ortho-positioned hydroxyl groups [4]. Due to their high-free volume topologies, TR polymers have a specific free-volume element architecture. These polymers excel at producing membranes with excellent permeability, selectivity, and resistance to harsh environments, which are required for a wide range of gas separation applications. Membrane technology may provide economic, environmental, and high-performance benefits as a low-cost, energy-efficient, and high-performance method of gas separation. The ability for chemically modifying nanofillers to interact better with polymer matrix has garnered a lot of interest recently [5].

1.3 Types of Membrane

Polymer materials form the foundation of the majority of membrane technologies, underscoring the critical role played by the selection of a suitable polymer material and the method of membrane preparation in the overall development of membranes. Membranes can be created using various processes such as sintering (commonly utilized for inorganic or ceramic membranes), solution casting, melt mixing and phase inversion.

1.3.1 Porous Membranes

These polymer membranes are characterized by a microporous structure, which leads to low barrier resistance for molecular transport. The membrane acts as a selective barrier, allowing smaller particles or molecules to pass through easily while excluding those larger than the pore size. Separation in these membranes primarily relies on the molecular size and the distribution of pore sizes within the membrane, essentially operating on the principle of size exclusion or a sieving mechanism. However, their application in gas separation is restricted due to the sub-nanometer size of gas molecules. To enable their use in gas separation processes, a dense layer of a polymer membrane must be coated onto the porous support.

1.3.2 Dense Membranes

Polymer membranes with a nonporous or dense microstructure have found widespread use in gas separation applications. In this context, the variation in applied pressures, with higher pressure on one side and lower pressure on the other side of the membrane, serves as the driving force for the diffusion of molecules. In a dense polymer membrane, the permeants are first solubilized in the polymer matrix, followed by their diffusion across the membrane. The selective transport of a permeant from a mixture is determined by the physical properties such as the solubility and diffusivity constants of the target molecule. Molecules of similar size can be separated based on their solubility and diffusivity through the membrane. Micro porous membranes typically have pore diameters ranging from 100 to 5000 nm and can be formed through various methods such as irradiation of nonporous polymeric membranes. Nonporous dense membranes rely on diffusion propelled by applied forces like pressure, concentration, or electric-field gradients for the transportation of permeates [14].

1.3.3 Organic Membranes

Organic membranes play a crucial role in various separation processes, finding applications in industries such as water treatment, gas separation, and biomedical fields.

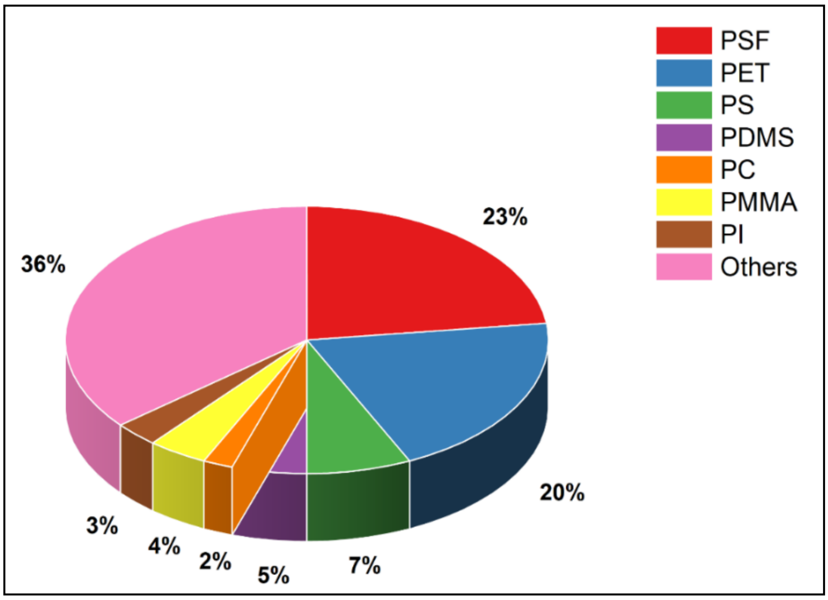


Figure 1.1: Polymer material used for gas separation in published literatures [15]

These membranes are typically made from organic materials, such as polymers, and are designed to selectively allow the passage of certain substances while blocking others. Polymeric Membranes, Most organic membranes are polymeric, meaning they are composed of long-chain molecules known as polymers. Polymeric membranes are widely used due to their flexibility, cost-effectiveness, and ease of fabrication. PSF, PET, PS and PDMS are one of the most promising candidates frequently used for air separation applications. Specially, PDMS is known for its high FFV, high gas permeability, and good thermal stability [15].

1.3.4 Inorganic Membranes

Inorganic membranes have been widely studied for air separation due to their high thermal and chemical stability, making them a preferred option over polymeric membranes. Zeolites, silica, graphene, and carbon molecular sieves membranes are capable of separating gas mixtures based on their molecular size and diameter [16].

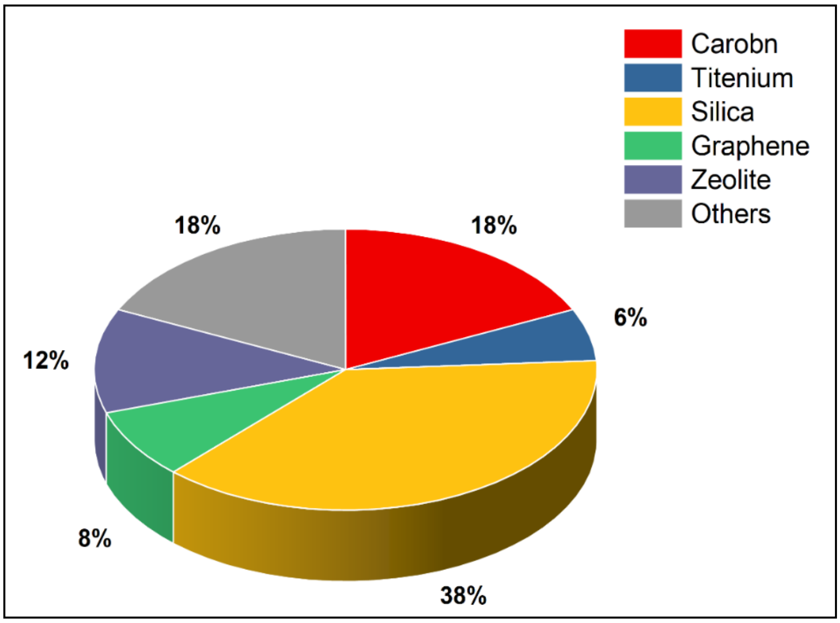


Figure 1.2: Inorganic materials used for air separation in published research papers [16]

Graphene, for example, has a pore size of 3.8 Å, which is close to the kinetic diameters of N_2 (3.64) and O_2 (3.46) gas molecules, and has demonstrated a high O_2/N_2 selectivity. The transport of gas molecules through inorganic membranes follows the sorption-diffusion mechanism. Inorganic membranes can be broadly classified into porous and nonporous types [17,18].

1.4 Types of Nanofillers

Nanofillers are nanoscale particles or fibers that are added to materials to enhance their properties, such as mechanical strength, thermal stability, electrical conductivity, and barrier properties. These additives are typically on the scale of 1-100 nanometers and are incorporated into various matrices, including polymers, ceramics, metals, and composites, to improve the overall performance of the resulting materials. Nanofillers have become essential in the development of advanced materials for a wide range of applications across industries [7].

Examples of nanofillers include: (a) Nanoparticles, these are nanoscale particles of various materials, such as metal oxides (e.g., titanium dioxide, zinc oxide), carbon-based materials (e.g., carbon black, carbon nanotubes, graphene), and other compounds (e.g., silica nanoparticles). They are commonly used in applications such as coatings, electronics, and biomedical devices. (b) Nanotubes: Carbon nanotubes are cylindrical carbon structures with nanoscale dimensions. (c) Nanocomposites: These materials combine polymers or other matrices with nanofillers to create hybrid materials with improved mechanical, electrical, and barrier properties. Nanocomposites are widely used in automotive components, packaging, and structural materials due to their enhanced performance and lightweight nature [8].

Blend composite polymers refer to materials that incorporate a combination of polymers and nanoscale fillers, such as nanoparticles, nanotubes, or nanofibers. These composite materials benefit from the enhanced properties resulting from the inclusion of the nanoscale additives, which can improve mechanical, thermal, electrical, and barrier properties. The use of nanofillers in polymer composites has enabled the development of materials with superior performance characteristics compared to traditional polymer blends [9]. Blend nanofiller composite polymers have revolutionized material science and engineering, enabling the development of high-performance materials for various applications. The nanofillers that used in this works are silica nanofillers, graphene oxide, carbon nanotube and titanium oxide.

Silica nanofillers find various applications in enhancing gas permeability and improving the performance of gas separation technologies. Some notable applications of silica nanofillers for gas permeability include:

(a) Gas Separation Membranes: Silica-based nanocomposite membranes are used for gas separation applications, offering improved selectivity and permeability. These membranes are designed to efficiently separate various gas mixtures, including carbon dioxide (CO_2)

removal from natural gas, hydrogen purification, and air separation for industrial and environmental applications [9].

(b) Catalysis: Silica-based nanofillers are utilized as catalyst supports in diverse catalytic processes for gas conversion and purification. The high surface area and thermal stability of silica enable efficient gas adsorption and catalytic activity, facilitating various gas conversion reactions, such as CO_2 conversion to valuable chemicals, contributing to the development of sustainable and eco-friendly processes [10].

The versatile applications of silica nanofillers in gas permeability underscore their significant role in advancing gas separation, storage, catalysis, and sensing technologies, offering promising solutions for addressing critical challenges in energy, environmental, and industrial sectors [10].

Graphene oxide (GO) nanofillers are a type of nanomaterial derived from graphite, which is a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice. Graphene oxide is synthesized from graphite and has oxygen-containing functional groups attached to its surface, which makes it hydrophilic and easily dispersible in water and other solvents. GO nanofillers are known for their exceptional mechanical, thermal, and electrical properties, as well as their high surface area and chemical reactivity. Graphene oxide (GO) nanofillers have gained significant attention in various fields due to their exceptional properties and diverse applications. In the realm of materials science, GO nanofillers are commonly used to enhance the mechanical, thermal, and electrical properties of composites and polymers. The incorporation of GO nanofillers into polymers can improve their strength, flexibility, and conductivity. In the area of water purification and desalination, GO nanofillers are used to fabricate advanced membranes with high water permeability, chemical stability, and excellent sieving properties. These membranes show promise in the efficient removal of contaminants and ions, enabling water purification and desalination processes [11].

Graphene oxide (GO) nanofillers have gained considerable attention in the field of gas permeability due to their exceptional properties and unique structural characteristics. Some notable applications of graphene oxide nanofillers for gas permeability include:

(a) Gas Separation Membranes: Graphene oxide-based composite membranes are used for gas separation processes, offering enhanced selectivity and permeability. These membranes are designed to selectively allow the passage of specific gas molecules, making them valuable in various industrial applications, including natural gas purification, carbon capture, and hydrogen recovery [11].

(b) Gas Storage: Graphene oxide-based materials are explored for their potential in gas storage applications, particularly in the storage and release of gases such as hydrogen and methane. The unique structure of graphene oxide allows for efficient gas adsorption and desorption, contributing to advancements in energy storage, transportation, and clean energy technologies [12].

Overall, the versatile nature of graphene oxide nanofillers continues to drive research and development across a wide spectrum of applications, demonstrating their potential for revolutionizing diverse technological and scientific domains.

Carbon nanotubes (CNTs) are one-dimensional nanomaterials with exceptional mechanical, electrical, and thermal properties, making them highly sought after for various applications. As nanofillers, CNTs are extensively used in composite materials to enhance mechanical strength, stiffness, and electrical conductivity. Their high aspect ratio and remarkable tensile strength make them ideal candidates for reinforcing polymer matrices, resulting in the development of lightweight and robust composite materials. In the field of electronics, CNT nanofillers find applications in the production of conductive inks, transparent conductive films, and flexible displays. Their superior electrical conductivity and transparency enable the creation of high-performance, flexible electronic devices. Overall, the diverse properties and multifaceted applications of CNT nanofillers underscore their potential to advance numerous technological domains, ranging from materials science and electronics to energy storage and biomedical engineering.

Carbon nanotube (CNT) nanofillers have been applied in various gas permeability-related fields, leveraging their exceptional properties to enhance gas separation and filtration processes. Some notable applications of CNT nanofillers for gas permeability include:

(a) Membrane Technology: CNT-based membranes have been developed for gas separation applications, such as the selective separation of gases or the removal of specific gas contaminants from mixtures. The incorporation of CNT nanofillers into polymeric membranes can significantly improve their gas permeability and selectivity, enabling more efficient and precise gas separation processes [11].

(b) Gas Sensors: CNT-based gas sensors are utilized for the detection and monitoring of specific gases in various environments. These sensors demonstrate high sensitivity, fast response times, and robust performance, enabling their deployment in diverse industrial, environmental, and biomedical settings for gas detection, monitoring, and control purposes [12].

The utilization of CNT nanofillers in gas permeability applications underscores their potential in enhancing gas separation, detection, storage, and transport processes, paving the way for the development of advanced technologies with improved efficiency and performance [12].

Titanium dioxide (TiO_2) nanofillers have found numerous applications in the field of gas permeability due to their unique properties and versatile characteristics. Some notable applications of TiO_2 nanofillers for gas permeability include:

(a) Membrane Technology: TiO_2 nanofillers are incorporated into polymeric membranes to enhance their gas separation capabilities. By improving the permeability and selectivity of the membranes, TiO_2 nanofillers contribute to the development of more efficient gas separation processes, such as the selective removal of specific gases from mixtures or the purification of industrial gas streams.

(b) Gas Permeable Coatings: TiO_2 nanofillers are used in the development of gas permeable coatings for various surfaces, facilitating gas transport or barrier properties in applications such as packaging, protective coatings, and gas separation modules. These coatings offer improved gas permeation control and selective barrier properties, ensuring the preservation and containment of specific gases in diverse industrial and commercial settings.

The diverse applications of TiO_2 nanofillers in gas permeability underscore their significant role in enhancing gas separation, detection, purification, and storage processes, offering promising solutions for addressing various industrial, environmental, and energy-related challenges [13].

1.5 Membrane Based Separations

Gas separation technology involves the separation of individual gases or gas mixtures from a combined stream, often for purification, recovery, or concentration purposes. Various methods and technologies are used, including membrane-based separation, adsorption, cryogenic distillation, and pressure swing adsorption, among others. These techniques play a crucial role in industries such as petrochemicals, natural gas processing, air separation, and environmental protection. Gas separation is essential for producing high-purity gases, minimizing environmental pollutants, and optimizing various industrial processes.

Examples of gas separation technologies include: membrane based separation, this process utilizes semipermeable membranes that allow certain gases to pass through while blocking others. Examples include polymer membranes, inorganic membranes, and mixed matrix membranes, used in applications such as air separation, carbon dioxide capture, and natural gas purification.

Membrane-based separation processes involve the use of thin films that selectively permit the passage of certain molecules or ions while restricting others. These processes can be classified based on the pore size and pore structure of the membranes. Nanofiltration membranes are instrumental in the separation of monovalent ions (such as Na^+, Cl^-, K^+) from divalent ions (e.g., Mg^{2+}, SO_4^{2-}). Typically, thin film composite membranes or polyamide membranes find widespread application in the nanofiltration process. Membranes featuring pores or channels smaller than 1 nm are predominantly used for atomic or ionic level separation processes like reverse osmosis, pervaporation, and gas separation. In the case of reverse osmosis, it is a pressure-driven process where the feed is subjected to higher applied pressures ranging from 15 to 60 bar. Electrodialysis and diffusion dialysis, on the other hand, represent charge-based membrane processes where cation or anion exchange membranes are used accordingly. For gas separation and pervaporation processes, dense membranes are utilized, allowing molecules to traverse the membrane via the voids or channels created by the thermal transitions of polymer chains. In these gas/pervaporation separation processes, molecule transport occurs through the solution diffusion mechanism [19].

1.6 Solution Diffusion Mechanism

The solution-diffusion mechanism is a vital process observed in various membrane-based separation techniques. It involves the dissolution of gas or liquid molecules into a dense membrane, followed by their diffusion through the membrane to achieve separation. This mechanism depends on the solubility and diffusivity of the target molecules within the membrane material. It has found extensive use in gas separation, liquid filtration, pervaporation, and other applications, making it a fundamental concept in the field of membrane technology. In dense membranes, the mode of gas transport varies depending on the nature of the polymer. In rubbery polymers, sorption is a prominent mechanism, where gas molecules are absorbed into the membrane material. In contrast, in glassy polymers diffusion plays a dominant role. Here, the permeation rate is typically higher for smaller gas molecules, as their kinetic diameter allows them to diffuse more readily through the polymer structure [20]. In this transport mechanism, the penetrants dissolve in the polymer, and the extent of solubility depends on their condensability as well as the nature of the interaction between the gas molecules and the polymer, as illustrated in Figure 1.3. Since the solution diffusion process involves a combination of mechanisms, the sorption of the gas molecules at the upstream end diffuses into the membrane and subsequently desorbs at the downstream side under the influence of the generated pressure gradient.

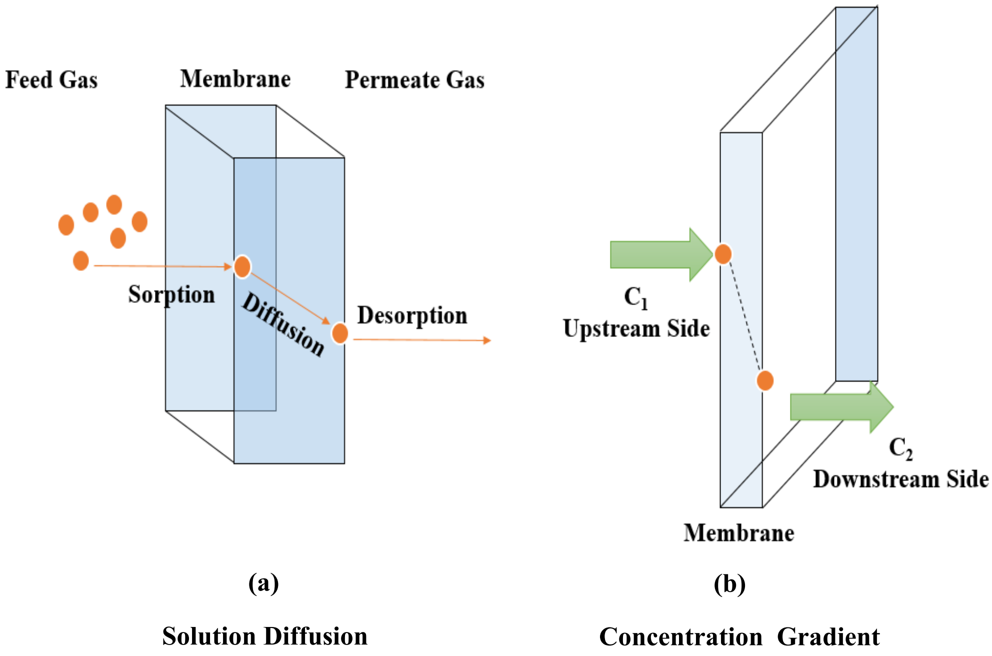


Figure 1.3: Schematic diagram of (a) Molecular transport in dense membrane through solution diffusion mechanism and (b) concentration gradient across the membrane $C_1 > C_2$

Thermodynamic partitioning activates transient gaps, generating free volume within the polymer chains, which facilitates the diffusion of gas molecules through the dense membrane. The transport of gas, as measured by the permeation rate, can be defined as the number of molecules transferred through per unit area per unit time. The flux or permeation rate can be described in terms of Fick's first law. Hence, the permeability of a membrane is determined by the interplay between solubility and diffusivity, which are controlled by thermodynamic and kinetic factors. According to the equation mentioned, the membranes permeability is intricately linked to its thickness. The permeability of the membrane is directly related to the membrane thickness [21]. The permeate of these membranes is determined by a thickness-dependent unit known as the Barrer, which can be defined as:

$$\textbf{Barrer} = 10^{-10}\,\frac{\mathbf{cm^3(STP).cm}}{\mathbf{cm^2.s.cmHg}} \qquad (1.1)$$

Where, cm^3 is the gas volume which diffuses in 's' time (s) from 'cm^2' area at 'cmHg' pressure through 'cm' thickness of the membrane. Since, in case of asymmetric membranes the active thickness of the membrane structure is not readily known, therefore the permeability of these membrane determines by the thickness independent formula i.e. Gas Permeation Unit (GPU) where the permeate is directly pressure normalized flux,

$$\textbf{GPU} = 10^{-6}\,\frac{\mathbf{cm^3(STP)}}{\mathbf{cm^2.s.cmHg}} \qquad (1.2)$$

The transportation process works gradually to equalize the concentration difference or the chemical potential of the penetrant in the phases separated by the membrane. This process can be effectively explained through Fick's first and second laws of diffusion. The product diffusivity (D) have unit of cm^2/s and solubility (S) have unit of (cm^3(STP)/cm Hg), is called the permeability coefficient, P,

So that,

$$\boldsymbol{P = D \times S} \qquad (1.3)$$

Gas transport within porous membranes is determined by the size of the pores in the membrane.

The selectivity, which is the separation factor of a gas mixture composed of gas A and B molecules, can be determined by dividing the permeability of the more permeable gas by the less permeable gas. It can be expressed as:

$$\boldsymbol{\alpha_{A,B} = {}^{P_A}/_{P_B}} \qquad (1.4)$$

The equation for the selectivity of component A over component B in a gas separation process. Here, $\alpha_{A,B}$ represents the selectivity, and P_A and P_B represent the partial pressures of components A and B, respectively. Selectivity in gas separation refers to the ability of a membrane or separation process to preferentially allow one gas to permeate through it over another. It is a crucial parameter in understanding the efficiency and effectiveness of gas separation technologies [22].

1.7 Mixed Matrix Membranes

The concept of mixed matrix membranes (MMMs) was initially introduced by Zimmerman et al. in the 1990s, aiming to overcome the limitations associated with polymeric and thin film composite membranes [23]. These membranes offer a combination of the easy fabrication process associated with organic polymeric membranes and the advantageous mechanical strength and functional properties of inorganic materials. Key features of mixed matrix membranes include high permeability, improved resistance to fouling, and increased hydrophilicity. MMMs provide the opportunity for tailored water treatment membranes due to their targeted functionalities, heightened selectivity, and superior mechanical, chemical, and thermal stability. They enhance the thermal and mechanical stability of polymeric membranes by mitigating the impacts of heating and membrane compaction, which often occur during the initial stages of membrane operation, leading to irreversible flux decline.

The addition of mechanically robust fillers to the bulk macro void region of asymmetric membranes serves to decrease structural losses, as the majority of compaction typically occurs in this specific region of the membranes. Mixed matrix membranes (MMMs) combine the properties of both organic and inorganic materials, thereby leveraging the advantages of each. They are composed of a polymer matrix integrated with inorganic fillers or particles, which often leads to enhanced gas separation performance.

By incorporating suitable additives, such as metal-organic frameworks (MOFs), zeolites, or carbon nanotubes, into the polymer matrix, these membranes can exhibit improved selectivity and permeability compared to traditional polymeric or inorganic membranes [23]. The synergy between the organic and inorganic components results in improved structural stability and gas separation efficiency, making MMMs a promising area of research in membrane technology. MMMs containing organic Metal Organic Framework (MOF) or inorganic fillers (graphene, carbon molecular sieves, carbon nanotubes etc.) have been incorporated in polymer membranes to achieve higher separation performance.

However, the compatibility of both polymer and inorganic phase in MMMs is essential for molecular level separation. To improve the polymer particle adhesion, nanofillers has been modified with different functionalities to create a defect free polymer matrix [24].

1.8 The Robeson's Upper Bound

The Robeson's upper bound, often referred to as the Robeson plot or Robeson's limit, is a graphical representation that establishes an upper limit on the trade-off between permeability and selectivity in polymeric membranes used for gas separation. This concept was introduced by Professor Lloyd M. Robeson in 1991 and later revised in 2008. The Robeson upper bound is typically presented as a plot with permeability (P) on the x-axis and selectivity on the y-axis. Permeability represents the ability of a membrane to allow a specific gas to pass through, while selectivity is the ratio of permeabilities of two different gases. The upper bound is essentially a performance limit that defines the best achievable combination of permeability and selectivity for a given type of membrane material.

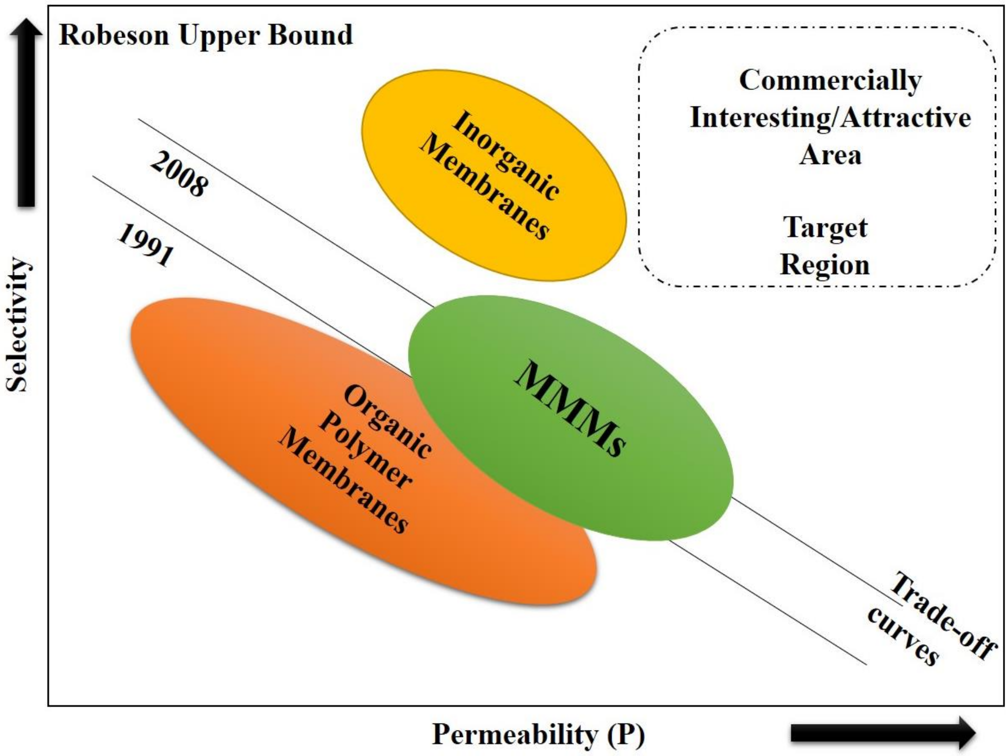


Figure 1.4: Schematic of Robeson upper bound showing Mixed Matrix Membranes

The plot provides a useful guideline for researchers and engineers working on membrane development. Membranes that fall below the Robeson upper bound are considered to be promising candidates for practical applications in gas separation processes. It is worth noting that the upper bound is not a fixed line but rather a region that membranes should ideally approach for optimal performance. Advances in membrane technology strive to push the boundaries of this upper bound to develop more efficient and effective membranes for various industrial applications, such as gas separation and purification. The Robeson upper bound is a valuable tool in the field of membrane research and development, particularly for gas separation applications. Here are some key applications and implications of the Robeson upper bound: membrane material valuation, researchers use the Robeson plot to assess the performance of different membrane materials. It helps in comparing the permeability and selectivity of various polymers, determining their suitability for specific gas separation processes [25].

The upper bound guides the optimization of membrane properties to achieve the best trade-off between permeability and selectivity. It serves as a benchmark for setting performance targets and improving membrane design. Membranes that fall below the Robeson upper bound are considered promising candidates for real-world applications. Researchers focus on developing membranes that approach or surpass this upper limit to enhance the efficiency of gas separation processes. In industrial implementation, the Robeson upper bound helps in selecting membrane materials for industrial-scale gas separation applications. Membranes that demonstrate high selectivity and permeability, while approaching the upper bound, are more likely to be viable for practical use. Researchers aim to push the performance limits of membranes beyond the upper bound by exploring new materials, fabrication techniques, and understanding the fundamental mechanisms governing gas transport in membranes. Membranes that approach the upper bound can have significant economic implications. They may lead to more energy-efficient and cost-effective gas separation processes compared to traditional methods like distillation or adsorption.

In summary, the Robeson upper bound is a critical tool for evaluating, optimizing, and guiding the development of polymeric membranes for gas separation. It plays a key role in advancing membrane technology and facilitating the transition from laboratory-scale research to industrial applications [26].

1.9 Applications of Gas Separation Membranes

Gas separation membranes find applications across various industries due to their ability to selectively separate gases based on their molecular size, shape, and affinity to the membrane material. Here are some common applications which in shows in Figure 1.5:

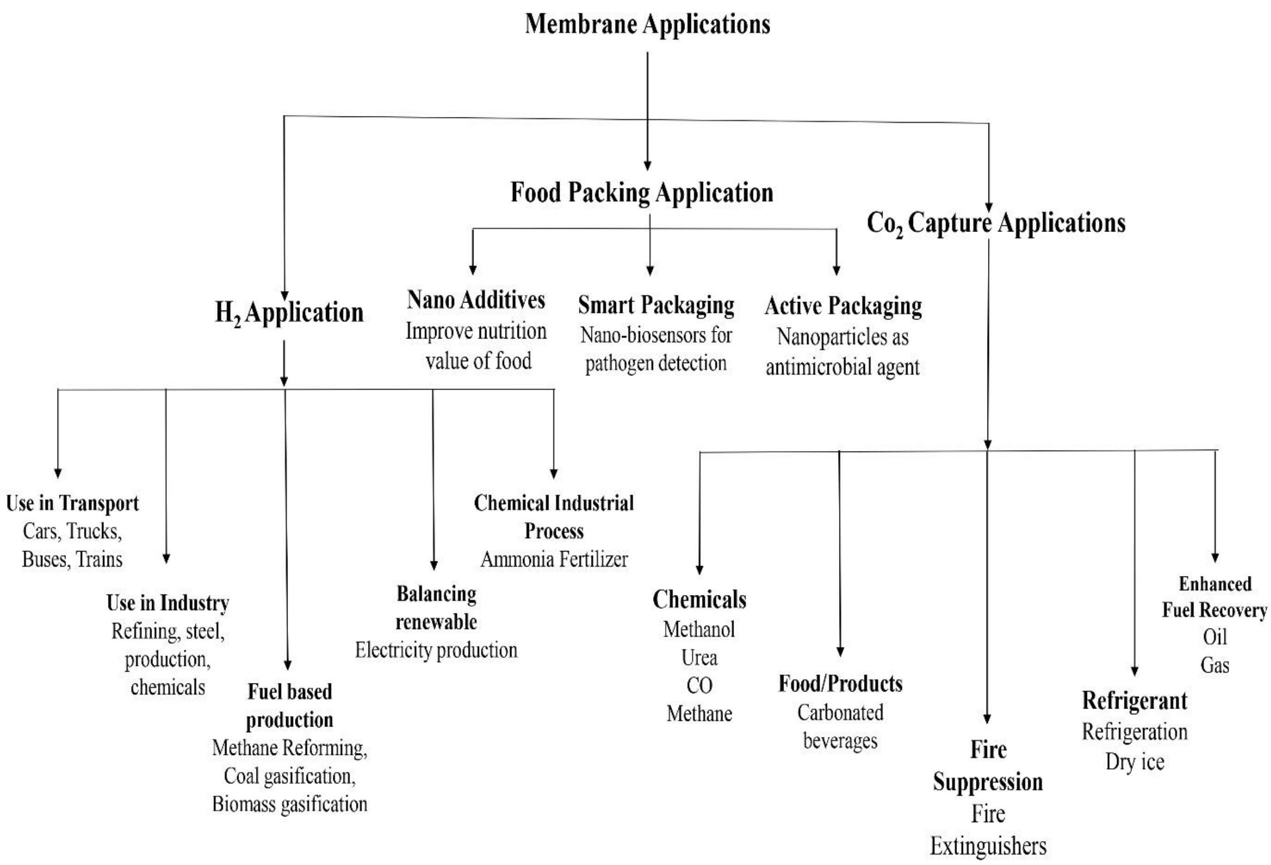


Figure 1.5: Polymer Membrane industrial applications

Ongoing research and development in this field aim to improve energy efficiency, reduce costs, and enhance the overall sustainability of gas separation processes. A multitude of polymers and processes were developed to facilitate various types of separations, including CO_2 separation, natural gas processing, H_2 recovery, volatile organics recovery from air streams, air separation, and paraffin-olefin separation, among others.

1.9.1 Air Separation

Air separation is one of the fastest growing separation technologies, as both major components of air, nitrogen (78%) and oxygen (around 21%), are elements of commercial interest for numerous applications. O_2/N_2 separation can be classified as oxygen-enriched air or nitrogen-enriched air based on the material properties. Oxygen-selective membranes can yield a product stream with higher oxygen content (purity 25-50%), while the retentive stream can contain nitrogen with relatively higher purity. Oxygen-enriched air is often used in combustion processes to increase fuel efficiency by reducing hydrocarbons, smoke, and carbon monoxide emissions. Nitrogen-enriched air produced by membranes can be utilized in food packaging for long-term storage, inerting aircraft fuel tanks, and other applications [27].

In India, the primary natural gas producers include the Oil and Natural Gas Corporation Ltd. (ONGC), Oil India Limited (OIL), and various private companies operating in Tapti, Panna-Mukta, and Rawa. Most of the gas production stems from the western offshore region, while the onshore fields in states such as Assam, Andhra Pradesh, and Gujarat contribute significantly to gas production as well [28,29]. In the natural gas industry, strict specifications and limits are enforced regarding the presence of impurities in hydrocarbon gas and condensates supplied to processing plants and downstream consumers. Researchers are increasingly embracing the use of small molecules as microstructural probes for studying polymers [30,31].

1.9.2 Hydrogen Separation

Hydrogen gas purification through polymer membranes is a critical application in the context of various industries. Polymer membranes are used for the selective separation and purification of hydrogen gas due to their ability to allow the passage of hydrogen molecules while blocking other gases [32]. Some specific applications include:

(a) *Hydrogen refining and recovery*: Polymer membranes facilitate the removal of impurities from hydrogen streams produced during various refining processes, including petroleum refining, ammonia synthesis, and coal gasification. This purification is essential to ensure the high purity of hydrogen used in various industrial processes [33].

(b) *Fuel Cell Technology*: Polymer membranes play a vital role in hydrogen fuel cell technology, where they are used for purifying hydrogen gas that powers fuel cells. These membranes help in eliminating impurities and moisture from the hydrogen stream, which is critical for the efficiency and longevity of fuel cells [34].

(c) *Hydrogen Production from Biogas and Biomass*: Polymer membranes are utilized in the purification of hydrogen gas produced from renewable sources such as biogas and biomass. This ensures the removal of contaminants and enables the generation of clean hydrogen for various energy applications [35].

Overall, the application of polymer membranes for hydrogen gas purification is instrumental in ensuring the efficient production, recovery, and utilization of hydrogen gas in a wide range of industrial and energy-related processes [36,37].

1.9.3 Carbon Capturing

Polymer membranes find important applications in the field of carbon capture and storage (CCS) due to their ability to selectively separate carbon dioxide (CO_2) from gas mixtures [38]. Some specific applications of polymer membranes in carbon capture include:

(a) *Industrial Emissions Control*: Polymer membranes are utilized in capturing CO_2 emissions from industrial processes such as power plants, cement production, and steel manufacturing. These membranes enable the separation of CO_2 from flue gas streams, reducing the release of greenhouse gases into the atmosphere [39].

(b) *Natural Gas Processing*: Polymer membranes are used in the purification of natural gas streams, aiding in the removal of CO_2 impurities to meet pipeline specifications. This ensures the production of clean natural gas for various industrial and commercial applications [40,41].

(c) *Carbon Capture from Ambient Air:* Polymer membranes are also explored for capturing CO_2 directly from ambient air. This technology offers the potential to mitigate CO_2 emissions from various sources, providing a promising pathway for carbon sequestration and environmental remediation [42,43].

Overall, the application of polymer membranes in carbon capture technology plays a significant role in reducing greenhouse gas emissions and addressing environmental concerns related to climate change and global warming [44,45].

1.9.4 Food Packing Application

Polymer membranes play a crucial role in the food packaging industry, providing various benefits such as extending the shelf life of perishable products, preserving food freshness, and preventing contamination [46]. Some specific applications of polymer membranes in food packaging include [47]:

(a) *Oxygen Barrier Packaging*: Polymer membranes with high oxygen barrier properties are used to create packaging materials that prevent oxygen from entering the packaged food. This helps to preserve the freshness and quality of the food, particularly for products that are sensitive to oxidation, such as meat, cheese, and certain fruits and vegetables [48].

(b) *Moisture Control*: Certain polymer membranes are used in food packaging to regulate moisture levels, preventing excessive moisture from entering or leaving the packaged products. Polymer membranes are utilized in the production of packaging materials that offer thermal insulation, enabling temperature control during the storage and transportation of perishable food items. This helps to preserve the products under optimal temperature conditions, thereby reducing the risk of spoilage and maintaining product quality [49].

(c) *Modified Atmosphere Packaging (MAP):* Polymer membranes are integrated into packaging systems that facilitate the control and modification of the gas composition surrounding the packaged food. This technology helps in prolonging the shelf life of food by controlling the levels of oxygen, carbon dioxide, and other gases within the packaging environment [50].

The use of polymer membranes in food packaging applications contributes significantly to the enhancement of food safety, quality, and overall consumer experience by ensuring the freshness and longevity of various food products [51].

1.10 Thesis overview

The proposed research delves into how modifying membranes affects transport parameters, offering a comprehensive analytical study through various characterization techniques. **Chapter 1** of the thesis elucidates the background and objectives related to this topic.

Chapter 2 encompasses the entirety of the experimental work, covering membrane fabrication, gas permeation experiments, and additional analytical characterizations. It details the various modifications implemented during the membrane synthesis process. Moreover, it discusses gas permeation tests conducted using both constant pressure/variable volume and constant volume/variable pressure systems. The chapter also elaborates on the mechanism and precision of the constant pressure/variable volume system devised in our laboratory during this research endeavour. Furthermore, it furnishes comprehensive information on system specifications and other characterization techniques.

In **Chapter 3**, discussed about detailed study of polyimides composites with silica nanoparticle and also thermal rearrangement process has been described. Additionally, this chapter investigates the impact of the kinetic diameter of various gases slated for testing. Gas separation analysis was also conducted through mathematical calculations.

In **Chapter 4.1**, focuses about hydrogen gas permeation application. It includes, study of dispersed graphene oxide (GO) in a polymer blend of polystyrene (PS) and poly(methyl methacrylate) (PMMA) nanocomposite membranes. The permeability measurements indicate that the GO nanofillers in blends of PS/PMMA have shown higher permeability for hydrogen gas than that of pure polymers.

Chapter 4.2 includes the study of polymer material that gives low permeability properties of material that will use as packaging material in the food industry. In chapter 4.2, study of gas permeability, thermal stability and mechanical properties of pure polyethylene terephthalate (PET), polyethylene glycol (PEG), their blends with weight percentage ratios of PET: PEG (50/50 w/w%) and blend of PET/PEG composite with different weight percent of DES/TiO_2 nanofillers included.

In **Chapter 5.1**, study of combination of glassy and rubbery composition for the gas transport process has been analysed by using blend of polystyrene (PS) and polydimethylsiloxane (PDMS) blend. However, to make further modification the blends has been composite with CNT nanofillers to fabricate blend-composite membranes and analyses in terms of solubility, diffusivity, permeability and selectivity. The composite membrane properties of PS/PDMS-CNT have been characterized by gas permeability measurement, and other standard characterization.

In **Chapter 5.2**, characterization of blend of polystyrene (PS) and polydimethylsiloxane (PDMS) blend composites with graphene oxide (GO) nanofillers as well as deep eutectic solvent (DES) based DES/GO nanofillers membranes are outlined along with a single gas permeation. The combination of glassy and rubbery polymers along with different wt% ratio of GO and DES/GO nanofillers has been analysed for gas permeability, structural property, mechanical property, thermal property and porosity of membrane.

Chapter 6 summarises of various studies in different chapters and describes the scope of upcoming studies on glassy and rubbery polymer with different nanocomposite membranes for various industrial applications. It also includes the whole resultant summary of the thesis concluding necessary comments.

References:

[1] D. R. Paul, The solution-diffusion model for swollen membranes, *Sep. and Puri. Methods*, **1976**, 5, 33–50.

[2] J. G. Wijmans and R. W. Baker, The solutiondiffusion model: a review, *J. of Membr. Sci.*, **1995**, 107, 1–21.

[3] J. K. Mitchell, On the penetrativeness of fluids, *J. of Membr. Sci.*, **1995**,100, 11–16.

[4] T. Graham, On the absorption and dialytic separation of gases by colloid septa. Action of a septum of caoutchouc, *Philosophical Magazine*, **1866**, 32, 401–420.

[5] S. von Wroblewski, 'Ueber die natur der absorption der gase durch flussigkeiten unter hohen drucken', Ann Physik u Chem, 8 (1879), 29–52.

[1] P. Y. Apel, Y. E. Korchev, Z. Siwy, R. Spohr, M. Yoshida, Diode-like single-ion track membrane prepared by electro-stopping, *Nuclear Instru. and Methods in Phy. Resea.*, **2001**, 184, 337-346.

[2] G. R. Guillen, Y. Pan, M. Li, E.M. Hoek, Preparation and characterization of membranes formed by nonsolvent induced phase separation: a review, *Indus. & Engin. Chem. Resea.*, **2011**, 50, 3798-3817.

[3] P. K. Prajapati, P. S. Singh, In-solution structure formation of poly (vinylidene fluoride) building units influencing on the final membrane characteristics, *J. of App. Poly. Sci*., **2020**, 15, 50-133.

[4] P. K. Prajapati, A. M. Kansara, P. S. Singh, Preparation and characterization of an oxygen permselective polydimethylsiloxane hollow fibre membrane, *RSC advances*, **2016**, 6, 88943-88953.

[5] A. Vijesh, P. A. Krishnan, A. M. Isloor, P. Shyma, Fabrication of PPSU/PANI hollow fiber membranes for humic acid removal, *Materials Today: Proceedings*, **2020**.

[6] J. P. Moore, K. Robling, C. Romero, K. Kiper, S. S. Dachavaram, P. A. Crooks, J.A. Hestekin, Oxone-Mediated TEMPO-Oxidized Cellulose Nanomaterial Ultrafiltration and Dialysis Mixed-Matrix Hollow Fiber Membranes, *Polymers*, **2020**, 12, 13-48.

[7] Y. Liu, Q. Han, T. Li, J. Hua, F. Liu, Q. Li, G. Deng, Heparin reduced dialysis through a facile anti-coagulant coating on flat and hollow fiber membranes, *J. of Memb. Sci*., **2020**, 595, 117-193.

[8] X. Zhang, M. Li, Z. Huang, H. Zhang, Fast surface crosslinking ceramic hollow fiber pervaporation composite membrane with outstanding separation performance for isopropanol dehydration, *Separation and Purification Tech.*, **2020**, 234, 116-130.

[9] M. Etxeberria, T. Johnson, S. Cao, B. Zornoza, J. Coronas, J. Sanchez, A. Sabetghadam, X. Liu, E. Andres-Garcia, F. Kapteijn, PBI mixed matrix hollow fiber membrane: Influence of ZIF-8 filler over H_2/CO_2 separation performance at high temperature and pressure, *Separation and Purification Tech.*, **2020**, 237, 116-147.

[10] S. Janakiram, J. Espejo, K. Hoiater, A. Lindbrathen, L. Ansaloni, L. Deng, Three-phase hybrid facilitated transport hollow fiber membranes for enhanced CO_2 separation, *App. Materials Today*, **2020**, 21, 100-115.

[11] A. Ghadimi, S. Norouzbahari, T. Mohammadi, Heat of sorption of gases in glassy polymers: prediction via applying physical properties of the penetrants and polymers, *J. of Chem. & Engin. Data*, **2017**, 62, 1433-1439.

[12] R. De Vos, H. Verweij, Improved performance of silica membranes for gas separation, *J. of Memb. Sci.*, **1998**, 143, 37-51.

[13] E. Gilliland, R. Baddour, G. Perkinson, K. Sladek, Diffusion on surfaces. I. Effect of concentration on the diffusivity of physically adsorbed gases, *Indus. & Engin. Chem. Funda.*, **1974**, 1, 95-100.

[14] S. Matteucci, Y. Yampolskii, B. Freeman, I. Pinnau, Transport of gases and vapors in glassy and rubbery polymers, *Materi. sci. of membranes for gas and vapor sep.*, **2006**, 1, 1-12.

[15] R. S. Murali, T. Sankarshana, S. Sridhar, Air separation by polymer-based membrane technology, *Sep. & Puri. Reviews*, **2013**, 42, 130-186.

[16] K. Fatyeyeva, A. Dahi, C. Chappey, D. Langevin, J Valleton, Effect of cold plasma treatment on surface properties and gas permeability of polyimide films, *Rsc Advances*, **2014**, 4, 31036-31046.

[17] D. Weibel, C. Vilani, A. Habert, C. Achete, Surface modification of polyurethane membranes using RF-plasma treatment with polymerizable and non-polymerizable gases, *Surface and Coatings Tech.*, **2006**, 201, 4190-4194.

[18] S. Konruang, S. Sirijarukul, P. Wanichapichart, L. Yu, T. Chittrakarn, Ultraviolet- ray treatment of polysulfone membranes on the O_2/N_2 and CO_2/CH_4 separation performance, *J. of App. Poly. Sci.*, **2015**, 132, 15451-15486.

[19] C. Jones, S. Gordeyev, S. Shilton, Poly (vinyl chloride)(PVC) hollow fibre membranes for gas separation, *Polymer*, **2011**, 52, 901-903.

[20] J. Jansen, M. Buonomenna, A. Figoli, E. Drioli, Ultra-thin asymmetric gas separation membranes of modified PEEK prepared by the dry–wet phase inversion technique, *Desalination*, **2006**, 193, 58-65.

[21] W. Yong, F. Li, Y. Xiao, T. Chung, Y. Tong, High performance PIM1/Matrimid hollow fiber membranes for CO_2/CH_4, O_2/N_2 and CO_2/N_2 separation, *J. of Memb. Sci*., **2013**, 443, 156-169.

[22] K. Nagai, T. Masuda, T. Nakagawa, B. D. Freeman, I. Pinnau, Poly [1- (trimethylsilyl)-1-propyne] and related polymers: synthesis, properties and functions, *Progress in Poly. Science*, **2001**, 26, 721-798.

[23] V. Shantarovich, I. Kevdina, Y. Yampolskii, A. Alentiev, Positron annihilation lifetime study of high and low free volume glassy polymers: effects of free volume sizes on the permeability and permselectivity, *Macromolecules*, **2000**, 33, 7453-7466.

[24] S. Kelman, B. W. Rowe, C. W. Bielawski, B. Freeman, Crosslinking poly [1-(trimethylsilyl)-1-propyne] and its effect on physical stability, *J. of Memb. Sci*., **2008**, 320, 123-134.

[25] J. Caro, M. Noack, P. Kolsch, R. Schafer, Zeolite membranes–state of their development and perspective, *Microporous and mesoporous materials*, **2000**, 38, 3-24.

[26] D. M. Ruthven, R. I. Derrah, Diffusion of monatomic and diatomic gases in 4A and 5A zeolites, Journal of the Chemical Society, *Physical Chem. in Condensed Phases*, **1975**, 71, 2031-2044.

[27] A. Singh, W. Koros, Significance of entropic selectivity for advanced gas separation membranes, *Indus. & engine.chem. resea.*, **1996**, 35, 1231-1234.

[28] P. Geffroy, J. Fouletier, N. Richet, T. Chartier, Rational selection of MIEC materials in energy production processes, *Chemical engine. sci*., **2013**, 87, 408- 433.

[29] C. Zhang, J. Sunarso, S. Liu, Designing CO_2-resistant oxygen-selective mixed ionic–electronic conducting membranes: guidelines, recent advances, and forward directions, *Chemical Soc. Reviews*, **2017**, 46, 2941-3005.

[30] Ş. Tantekin-Ersolmaz, C. Atalay-Oral, M. Tatlıer, A. Erdem-Şenatalar, B. Schoeman, J. Sterte, Effect of zeolite particle size on the performance of polymer–zeolite mixed matrix membranes, *J. of Memb. Sci*., **2000**, 175, 285-288.

[31] G. Dong, H. Li, V. Chen, Challenges and opportunities for mixed-matrix membranes for gas separation, *J. of Materi. Chem. A*, **2013**, 1, 4610-4630.

[32] R. Mahajan, R. Burns, M. Schaeffer, W.J. Koros, Challenges in forming successful mixed matrix membranes with rigid polymeric materials, *J. of App. Poly. Sci*., **2002**, 86, 881-890.

[33] R. Mahajan, W. J. Koros, Mixed matrix membrane materials with glassy polymers, *Poly. Engin. & Sci*., **2002**, 42, 1420-1431.

[34] S. Shu, S. Husain, W. J. Koros, A general strategy for adhesion enhancement in polymeric composites by formation of nanostructured particle surfaces, *J. of phy. Chem. C*, **2007**, 111, 652-657.

[35] J. Wall, B. Hu, J. Siddiqui, R. Ottenbrite, Monolayer grafting of organo-silica nanoparticles on poly (ethylene naphthalate) films, *Langmuir*, **2001**, 17, 6027-6029.

[36] H. Cong, X. Hu, M. Radosz, Y. Shen, Brominated poly (2, 6-diphenyl-1, 4-phenylene oxide) and its silica nanocomposite membranes for gas separation, *Ind. Eng. Chem. Res.*, **2007**, 46, 2567–2575.

[37] H. Cong, M. Radosz, B.F. Towler, Y. Shen, Polymer-inorganic nanocomposite membranes for gas separation, *Sep. Puri. Tech.*, **2007**, 55, 281–291.

[38] G. G. Kapantaidakis, S. P. Kaldis, Gas permeation through PSF-PI miscible blend membranes, *J. Memb. Sci.*, **1996**, 110, 239–247.

[39] W. F. Yong, F. Y. Li, et. al., Molecular interaction, gas transport properties and plasticization behavior of PIM-1/Torlon blend membranes, *J. Memb. Sci.*, **2014**, 462 119–130.

[40] H. Mannan, H. Mukhtar, M. Shima Shaharun, M. Roslee Othman, T. Murugesan, Polysulfone/poly(ether sulfone) blended membranes for CO_2 separation, *J. Appl. Polym. Sci.*, **2016**, 133, 1–9.

[41] S. S. Hosseini, M. M. Teoh, T. S. Chung, Hydrogen separation and purification in membranes of miscible polymer blends with interpenetration networks, *Polymer,* **2008**, 49, 1594–1603.

[42] N. K. Acharya, V. Kulshrestha, K. Awasthi, R. Kumar, A.K. Jain, M. Singh, D. K. Avasthi, Y. K. Vijay, Gas permeation study of Ti-coated, track-etched polymeric membranes, *Vacuum*, **2006**, 81, 389–393.

[43] A. K. Patel, N. K. Acharya, Study of gas transport phenomenon in 23 layered polymer nanocomposite membranes, *Trends Appl. Adv. Polym. Mater.*, **2017,** 191–206.

[44] Z. Dai, L. Ansaloni, L. Deng, Recent advances in multi-layer composite polymeric membranes for CO_2 separation: A review, *Green Ener. Environ.*, **2016**, 1, 102–128.

[45] H. Xu, J. Xiao, B. Liu, S. Griveau, F. Bedioui, Enhanced electrochemical sensing of thiols based on cobalt phthalocyanine immobilized on nitrogen-doped graphene, *Biosensors and Bioelectronics*, **2015**, 66, 438-444.

[46] G. Camino, S. Lomakin, M. Lazzari, Polydimethylsiloxane thermal degradation, *Polymer*, **2001**, 42, 2395-2402.

[47] I. Pinnau, Z. He, Pure-and mixed-gas permeation properties of polydimethylsiloxane for hydrocarbon/methane and hydrocarbon/hydrogen separation, *J. of memb. sci.,* **2004**, 244, 227-233.

[48] J. Caro, M. Noack, Zeolite membranes–recent developments and progress, *Microporous and Mesoporous Materials*, **2008**, 115, 215-233.

[49] A. Singh, W. Koros, Significance of entropic selectivity for advanced gas separation membranes, *Industrial & engine. Chem. research*, **1996**, 35, 1231-1234.

[50] M. Rezakazemi, K. Shahidi, T. Mohammadi, Sorption properties of hydrogen selective PDMS/Zeolite 4A mixed matrix membrane, *Intern. J. of Hydro. Ener.*, **2012**, 37, 14576-14589.

[51] G. Lin, M. Abar, L. M. Vane, Mixedmatrix silicon andfluorosilicon/zeolite 4A membranes for ethanol dehydration by pervaporation, *Separation Sci. and Techno.*, **2013**, 48, 523-536.