Characterizing carbon molecular sieve and polymeric nanocomposite membrane materials

Chen, Jiahui

2011

Chen, J. (2011). Characterizing carbon molecular sieve and polymeric nanocomposite membrane materials. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/53761>

<https://doi.org/10.32657/10356/53761>

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**CHARACTERIZING CARBON MOLECULAR SIEVE AND
POLYMERIC NANOCOMPOSITE MEMBRANE
MATERIALS**

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2011

Acknowledgements

This thesis presents the research work I did for the past four years in School of Chemical and Biomedical Engineering, Nanyang Technological University. I would like to thank many people who have helped me and accompanied with me in those days.

I am deeply indebted to my supervisor Professor Wang Kean and Professor Loo Sun Sun, Leslie for their supervision, instruction, encouragement and support during the whole course of my Ph.D. research. They not only helped me in the research work, also let me feel their patient guidance and kindness in many aspects of my life.

I would like to acknowledge my colleagues in our group: San Hein, Guan Cong, Li Cunben, Xu Dan, Zhang Xingui, Zhou Qi, Hu Enping and Song Xianghua for their valuable discussion and friendship. We have a harmonistic and comfortable working atmosphere.

I also want to thank School of Chemical and Biomedical Engineering for offering me permission to commence my research work and to do the necessary experiments.

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List of abbreviations

AC	activated carbons
ARE	average relative error
CMS	carbon molecular sieve
CNT	carbon nanotubes
CS	chitosan
CTMSS	carbonized template molecular sieve silica
DS	degree of swelling
GC	gas chromatography
L1	lignin 1
L2	lignin 2
MW	molecular weight
MWNT	multi-walled carbon nanotubes
OA	octa-ammonium
OA-	octaanion
OAPS	octaaminophenylsilsesquioxane
ONPS	octa nitro phenyl silsesquioxane
PA6	polyamide 6
PANi	polyaniline
PBAT	polybutyleneadipate-co-terephthalate
PI	polyimide
PNC	polymer-nanocomposite
POSS	polyhedral oligomeric silsesquioxane
PP	polypropylene
PSD	pore size distribution
RH	relative humidity
SEM	scanning electron microscope
SWNT	single-walled carbon nanotubes
TGA	thermal gravimetric analysis
XRD	X-ray diffraction

Nomenclature

A	area of membranes (m^2)
b	sorption affinity (kPa^{-1})
C_μ	adsorbed phase concentration (mmol/g)
$C_{\mu s}$	sorption capacity (mmol/g)
D_μ	diffusion coefficient for adsorbed phase (cm^2/s)
D_μ^0	diffusion coefficient at zero loading (cm^2/s)
D_k	diffusion coefficient
$D_{\mu\infty}^0$	surface diffusivity at infinite temperature (cm^2/g)
E_{pore}	potential energy of a molecule confined in a pore (J/mol)
E_{pore}^g	potential energy of gas phase molecules confined in the pore (J/mol)
E_s	the adsorption heat of graphite surface (J/mol)
J	permeation flux ($\text{g/m}^2 \text{ s}$)
J_μ	diffusion flux ($\text{g/m}^2 \text{ s}$)
j	flux fraction of species
L	permeation time lag (s)
L_B	time lag in blind pore (s)
L_T	time lag in through pores (s)
l	thickness of membrane (m)
M	molecular weight (g/mol)
P_i	permeability of i component
P	bulk phase pressure (kPa)
P_0	permeation pressure (kPa)
P_M	at steady state, the permeance (mole/s)
ΔP	the pressure difference (kPa)
r	pore size ($\text{\AA}$)
T	temperature (K)
t	time (s)
V	volume (L)

z diffusion coordinate (cm)

Greek letters

β a parameter characterizing the solid surface

ε porosity

ε_{sk} the cross Lenard-Jones parameters calculated using a geometric mean

θ surface loading

ρ_s number density of carbon molecule per unit volume

σ kinetic diameter (Å)

σ_{sk} the cross Lenard-Jones parameters calculated using an arithmetic mean

Subscripts

ads adsorption

B blind pore, bottle

bulk the property in bulk phase

exp experiment

i component i

pore pore phase

T through pore, throat

0 initial

Superscripts

T through pore, throat

B blind pore, bottle

0 initial

Abstract

Carbon molecular sieve (CMS) and polymer-nanocomposite (PNC) membranes are getting increasingly more applications in practical processes. We have developed new theories, experimental techniques, and mathematical models for the characterization of the microstructure and the gas permeation properties of CMS and PNC membranes in this project. Polymer-nanocomposite fibers were also synthesized and characterized for their mechanical and structural properties. The specific scopes of this project are:

1. PNC fiber

Chitosan (CS) was embedded with three types of nanofillers [i.e. i) lignin, ii) polyhedral oligomeric silsesquioxane (POSS), and iii) single-walled carbon nanotubes (SWNT)] to synthesize CS-nanocomposite fibers via wet-spinning technique. The effect of filler composition on the morphology and tensile properties of the fibers was investigated. Compared to the pure (or native) CS, the composite fibers exhibited superior overall mechanical performance (strain at break, tensile stress, Young's modulus, toughness) at the optimal filler loadings. Deviation from the optimal loadings would result in fibers with poorer performance.

2. PNC membrane

Chitosan-POSS membranes (CS-OA- and CS-OAPS) were synthesized and their permeation properties of water vapor were investigated. It was found that the permeability and flux of the PNC membranes increase with the weight

content of POSS in general. The OA- fillers were found mainly to increase the hydrophilicity of the membrane while the OAPS aggregates to provide more diffusion channels for the water molecules to pass through the membrane.

An improved time lag method was proposed to experimentally measure the permeation properties of gas-vapor mixtures on PNC and CMS membranes, which is capable of simultaneously measuring the transport properties for the mixture as well as for part components. The humidity-assisted permeation of CO₂ was conducted in a CS-OA- composite membrane to demonstrate the feasibility of this new methodology.

3. CMS membrane

CO₂ adsorption equilibrium was measured on a microporous CMS (KP1000) membrane over a wide pressure range and at various temperatures. The isotherm data were well fitted by the Toth equation, suggesting a heterogeneous surface. Micropore hysteresis was observed at 77 K but was not found at an ambient temperature. Ar adsorption isotherms were measured on another CMS membrane (KP800) at various temperatures and over a range of pressures, which were employed to calculate the overall pore size distribution (PSD) of the KP800 CMS. The transient permeation time lag was employed to further discriminate the PSD into through pores, blind pores, and ink-bottled pores. The majority of the pore volumes were found to be contributed by the blind pores.

The pore irregularity (connectivity) of CMS membrane was studied by analyzing the steady state permeation data. A 3-section structural pore model was proposed and applied to develop a mathematical model for gas permeation. It was found that, by assuming different pore sizes in different section (the ‘throat’ and ‘bottle’ pores), the model was capable of simulating adsorption equilibrium and permeance data of CO₂ and Ar on different CMS membranes over a range of pressures and temperatures. It must be pointed out that, the single section model would fail to cope with the diffusional anomalies observed on the CMS samples.

Chapter 1. Introduction

1.1 Carbon molecular sieve (CMS) membrane

The inorganic membranes made of zeolite, silica or carbon molecular sieve, etc., have attracted increasingly more research attention because of their high permeability, selectivity, thermal and chemical stabilities [1, 2]. Carbon molecular sieve or CMS membranes are prepared from a controlled pyrolysis of polymeric precursors (e.g., polyimide, phenolic and cellulosic resins, polyfurfuryl alcohol, or mixed matrix polymers, etc.) [1, 3, 4]. The microporous network of a CMS is known to be ‘turbostratic’ [5], i.e. the graphitic microdomains are randomly embedded in amorphous carbons to form slit-shaped micropores that provide the ‘sieving’ effect at the molecular level [6, 7]. The CMS materials comprising of micropores of relatively uniform size enable the discrimination of gas molecules of similar dimensions [1, 3, 8]. CMS membranes exhibit excellent permeability and selectivity for a number of industrially important gas mixtures such as: He/N₂, H₂/CH₄, O₂/N₂, CO₂/N₂, CO₂/CH₄, and etc. [9].

In comparison with polymeric membranes, CMS membranes are refractory in porous structures with good mechanical and chemical stabilities [4]. In addition, their microstructure is largely determined by the thermal-treatment process, rather than the precursors used in the synthesis of the materials [10].

The gas permeation in CMS membranes has been known to follow the ‘sorption-diffusion’ mechanism, in which the penetrating molecules are always

under the potential fields of the walls of micropores. Although the micropores are slit-shaped in nature, their real structures are very complicated, comprising of through pores, hedged pores, blind pores, corner/void, and etc. Because of their structural complexity, a number of adsorption/diffusion anomalies have been reported for gas permeation in CMS membranes [10-12]. Therefore, a detailed characterization of their microstructure is of critical importance for designing/optimizing gas separation/permeation processes in such porous media.

1.2 Chitosan

Chitosan (CS) is the derivative of chitin, (1-4)-linked 2-amino-2-deoxy-β-Dglucan, which is the main structural component of crab and shrimp shells and is the 2nd most popular biopolymers in the nature. The structure of CS is shown in Figure 1-1.

Figure 1-1 Chemical structure of chitosan

As a linear natural polysaccharide, CS has broad chemical and biomedical applications, given its biocompatibility, biodegradability, low toxicity, and its abundance [13]. For example, CS has been used in bandages to quickly clot bleeding. Its hypoallergenic and natural anti-bacterial properties make it appealing to be used in field bandages [14]. It is also used as artificial skin and

bone substitutes. In water treatment, CS has been used as flocculants and adsorbents for dye molecules, metals ions, and oil spills etc. [15-17]. CS is used in food industry for purifying wine, mead, beer, and used as the food packaging materials [18].

CS is also used in chemical industry in the forms of membranes, beads, micro- and nanoparticles, gels, etc. Because of the good film forming property, specific affinity, and hydrophilicity, CS-based membrane materials are widely used in pervaporation and filtration processes for the separation of azeotropic mixtures and biomolecules [19]. The CS based membranes were also reported to have a number of applications in gas separations [20-22]. However, native CS suffers from some disadvantages. For example, it will lose mechanical strength and selectivity under wet conditions. To overcome this defect, CS has been used to form composites with nanofillers or crosslinking agents to improve its chemical and mechanical properties.

1.3 Gas permeation and time lag analysis

Time lag method is widely used in studying the permeation of pure gas as well as gas mixtures in polymeric/inorganic membranes. The permeation properties (at both transient and steady state) of the system can be derived from the pressure-time response curves (at the downstream or upstream), as shown in Figure 1-2. In general, the transient mass transfer property (diffusion coefficient) is related to the time lag intercept while the steady state permeation flux can be derived from the slope [23]. Subject to different assumptions and boundary conditions, the time lag analysis also represents an excellent example

of mathematical interpretation of a real physical process and is a powerful tool for characterizing membrane structure.

Figure 1-2 Pressure-time response (at downstream) of a time lag experiments. The time lag intercept and steady state slope are related to diffusion coefficient and steady state flux, respectively.

1.4 Objectives

This project has three main objectives: 1) synthesizing CS-based nanocomposite fibers and characterizing their mechanical properties, 2) fabricating CS-based nanocomposite membranes for the permeation of pure gas and gas mixtures, and 3) synthesizing CMS membrane and characterizing the porous structure of CMS membrane for gas permeation. The specific topics are:

- 1). Synthesizing CS-based nanocomposite fibers, including, CS-lignin, CS-POSS, CS-CNT and characterizing their mechanical and chemical properties;

- 2). Characterizing gas/vapor permeation properties on the native CS and CS-POSS nanocomposite membranes;
- 3). Synthesizing CMS membrane and activated carbons (AC) and determining their adsorption properties;
- 4). Modeling the gas adsorption and permeation processes in CMS membranes and characterizing the microstructures.

1.5 Outline of thesis

This thesis consists of eight chapters.

Chapter 1 briefly introduces the background, motivation, and objectives of the research project.

Chapter 2 reviews the research areas closely related to this project, which include: i) CS-based nanocomposite membranes, ii) CS-based nanocomposite fibers, iii) gas permeation in CS-based polymeric membranes, and iv) gas permeation in CMS membranes.

Chapter 3 introduces the experimental methodology of the project, which includes: sample preparation, measurement of permeation, adsorption and mechanical properties of the fibers/membranes, as well as the common instruments and techniques used in structural characterization.

Chapter 4 presents the characterization of three types of CS-based nanocomposite fiber (CS-lignin, CS-POSS, and CS-CNT).

Chapter 5 presents characterization of the permeation properties on CS-based nanocomposite membranes. A novel method was developed and verified to measure permeation properties of gas mixtures.

Chapter 6 investigates the gas adsorption (CO_2) and permeation (Ar) properties of CMS membranes. An integral approach was employed to model the diffusion anomalies observed in both the transient and steady state permeation processes.

In Chapter 7, the microstructure of a CMS membrane is characterized based on the adsorption equilibrium and further discriminated to blind pores and through pores via the transient permeation kinetics. A new structural model is proposed and based on which the mathematical model is developed to describe the diffusion anomalies observed at steady state permeation processes.

Chapter 8 gives the conclusions of this project and outlines the recommendations for future studies.

Chapter 2. Literature review

2.1 CS and CS-based nanocomposite membranes

A membrane is a selective barrier between two adjacent phases, regulating the transport of different substances. It functions mainly based on the adsorption and transport selectivities [24]. Membrane separations do not need additives and can be performed at low or high temperatures, which means they are low in energy consumption compared to other traditional thermal separation processes.

Polymer membranes are commonly used for separating various gas mixtures due to their good perm-selectivity and processability [25]. However, they suffer from the solvent resistance, low strength and easy fouling [26]. The mixed matrix membranes (also termed as nano-composite or hybrid membranes), which are composed of an organic polymer and inorganic filler phases, are able to overcome some of those hurdles and give an improved performance [27]. This type of membranes combined the advantages of the two elements: the high separation capabilities of the inorganic fillers and the desirable mechanical properties and economical processing capabilities of the polymers.

Inorganic nano-particles such as zeolite [28, 29], silica [30, 31], clay [32, 33], and carbon nanotubes [34], etc., have often been used as the fillers. For example, researchers found that CS-based membrane embedded with surface modified HZSM-5 zeolite showed a better selectivity and permeation flux for pervaporation of alcohol solutions compared to those embedded with

unmodified zeolite [35]. This is attributed to the interfacial morphology resulting from the electrostatic interactions between the modified zeolite and the CS. Therefore, choosing suitable inorganic fillers and polymer matrix is of crucial importance for such membranes. The silicalite zeolite embedded into CS matrix was found to improve the pervaporation separation of toluene/methanol and toluene/ethanol mixtures [36]. Yang et al. synthesized nano-sized TiO_2 particles and dispersed them homogeneously into CS matrix. It was found that the nanocomposite membrane containing 6 wt% TiO_2 exhibited the best pervaporation performance for ethanol-water solution [37]. However, so far there are very few studies on the gas separation/permeation in such membranes [38].

Many studies have attempted to improve the interaction between the polymer and the fillers in order to enhance the separation performance of the membrane. For example, researchers tried to chemically modify the surface of molecular sieve with silage coupling agents, such as (3-aminopropyl)-triethoxy silane, N- β -(aminoethyl)- γ -aminopropyltrimethoxy silane, (γ -glycidylloxypropyl)-trimethoxy silane and (3-aminopropyl)-dimethylethoxy silane [39-41]. The results shows that both permeability and selectivity of mixed matrix membrane made from (3-aminopropyl)-diethoxymethyl silane modified zeolite are higher than those membranes made from unmodified zeolite at 20 wt% zeolite loading because of decrease in the degree of partial pore blockage of zeolites [42].

As a relatively new silane agent, polyhedral oligomeric silsesquioxanes (POSS) is a type of promising nano-fillers for mixed matrix membranes. POSS are

organic-inorganic hybrid materials that have received extensive attentions because of their processability, cage-like framework, and compatibility with other polymers, as shown in figure 2-1. POSS is considered as a new generation of nano-filler [43]. Its formula is usually presented as $(\text{RSiO}_{1.5})_{2n}$ ($n = 2, 3, 4$). POSS is produced by the hydrolysis of trifunctional RSiY_3 molecules [44-46] and can be modified by a number of substitution reactions. Thus, functionalized silsesquioxanes are very interesting precursors for organolithic macromolecular materials [47-49] or hybrid inorganic–organic membrane materials [50-53]. Other than silsesquioxanes with silicon–oxygen frameworks, different hetero- and metalla-siloxanes [54] were reported, such as alumino-, titana-, and gallium silsesquioxanes where one [55-61] or several silicon atoms are replaced [62].

Figure 2-1 The basic structure of POSS

Hybrid polymer membranes incorporated with organosiloxane compounds have been recently studied [31]. A typical hybrid material will contain a cross-linked inorganic phase bound (often covalently) with an organic phase [63]. This polymer-POSS compatibility is formed by the formation of covalent and non-covalent bonds between tethers and polymer chains [64]. Due to the rigidity of the cage like structure of Si_8O_{12} and the flexibility of the tethers, POSS

molecules are well dispersed, affecting the morphology and mechanical stability of POSS-reinforced polymer matrices.

POSS was incorporated into CS to form inorganic-organic nanocomposite membrane for pervaporation dehydration of ethanol aqueous solutions [65]. It was found that the morphology and pervaporation performance of the hybrid membranes were influenced by the type and content of POSS and the interactions between POSS and CS. An addition of 3-5 wt% of POSS was found to promote both the selectivity and permeability, but overloading the POSS will cause a reduction in selectivity. For the hydrophobic POSS, if the particles are homogeneously dispersed in the polymer matrix, they may restrain the polymer segmental mobility and reduce the size of free volume, thereby enhancing the selectivity of the hybrid membranes. However, overloading of POSS will cause a reduction in selectivity due to the nonselective voids resulting from the serious agglomeration of POSS and phase separation. For the hydrophilic POSS, the selectivity of the membrane is also enhanced which is attributed to the increase in hydrophilicity of the hybrid membranes. However, because of the small molecular sizes of POSS (1-3 nm in diameter), they may be embedded in the polymer network as a barrier to the diffusant, therefore, overloading the POSS would cause the reduction of flux [65]. The CS-POSS composite membrane prepared with sol gel method was used to permeate amino acids [66]. Membrane permeability was found to be indirectly affected by the POSS tethers due to the changes in the morphology of the hybrid membrane at the nanoscale level. A longer tether resulted in a higher packing density of CS

chains in the membrane and lowered its diffusion permeability to amino acids [66].

In this project, POSS derivatives with 2 types of tethers were used to modify the morphology of the CS membrane. POSS will be incorporated into the CS matrix via blending and phase inversion. The mechanical properties of the resulted composite fiber and the permeation properties of the composite membrane will be investigated.

2.2 CS and nanocomposite fiber

CS is widely used in the textile and biomedical industry in the form of fibers or composite fibers, due to its allergenic, antimicrobial and deodorizing properties [67]. CS-transition metal ion complex fibers were used as a shielding material for radiations and electromagnetic waves [68]. CS-cellulose (Rayon) blend fibers (“Crabyon”) have been commercialized as a functional textile material for underwear, sportswear, towels, socks and non-woven fabrics [69]. CS-collagen fibers were used to improve the CS biocompatibility in the tissues [70]. Three important CS-nanofiller composite fibers that will be studied in this project are CS-POSS, CS-lignin and CS-CNT fibers.

2.2.1 CS-POSS fiber

POSS molecules can be incorporated into polymer systems via blending, grafting or copolymerization. Blending POSS with polycarbonate (PC) has been reported to give a composite with better mechanical and thermal

properties [71]. Here POSS is expected to act as a nanoscale filler to modify the PC matrix with new or improved properties. Compared with traditional fillers, POSS is known, in some cases, to exhibit enhanced compatibility resulting from a match between its organic substituent and matrix polymer. It is generally believed that nanoscale POSS domains with ordered and self-assembled features in a polymer matrix are highly desirable and lead to the observed improvement in material properties. POSS/poly (ethylene terephthalate) nanocomposites fiber was reported to have better tensile strength and modulus [73]. Moreover, the melt blending of POSS and polypropylene [74] also gave better mechanical performance, with higher elastic modulus as well as higher elongation at break [75]. Furthermore, POSS blended with poly (2,6-dimethyl-1,4-phenylene oxide)/polyamide 6 has improved the mechanical properties and thermal properties [42].

POSS was reported to modify the morphology of CS membranes and consequently change their permeability [66]. Bleha et al. studied the effect of POSS functionality on morphology of thin CS film [76]. The preparation and diffusion permeability of CS-amino-POSS and CS-epoxy-POSS membranes were introduced as well [77]. However, so far there are very few reports on the CS-POSS fiber and their mechanical properties.

2.2.2 CS-CNT fiber

Carbon nanotubes (CNT) possess excellent mechanical properties [78], as well as electrical [79] and thermal conductivity [80]. They are classified into single-walled carbon nanotubes (SWNT) and multi-walled carbon nanotubes

(MWNT). SWNT consist of a single layer of graphite sheet wrapped around in a cylindrical shape while MWNT consist of multi-layers of graphite wrapped on top of each layer to form a tubular structure. A SWNT can exhibit a tensile strength of up to 45×10^9 Pa whereas the highest grade steel alloy used in the construction of mega structures can only withstand up to 2×10^9 Pa. The current carrying capacity of CNT is estimated to be around 1×10^9 A/cm² while the most expensive copper wire will burn out at a much smaller capacity of 1×10^6 A/cm².

Calvert reported that CNT has a very high aspect ratio (length to diameter ratio). The aspect ratio of the carbon fiber is only 100 while CNT can have aspect ratios of 1000 or more, giving it excellent mechanical properties [81]. As shown in Figures 2-2, the longer the reinforcing material in the matrix, the stronger the material. The material shown in Figure 2-2a would definitely have better resistance to load bearing as compared to the composite material shown in Figure 2-2b.

Figure 2-2 Filler materials with a) Longer aspect ratio, and b) shorter aspect ratio.

Table 2-1 shows the comparison between some common materials and CNT. CNT has the highest Young’s modulus and tensile strength. Its density is 3

times lower than that of steel, making it an extremely light and strong material. Researches on polymer composites have seen the dramatic effect of CNT fillers on polymers [82].

Table 2-1 The superior qualities of CNT and the comparison with other materials.

Material	Young's modulus (GPa)	Tensile strength (GPa)	Density (g/cm ³)
MWNT	1200	150	2.6
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

CNT composites are composed of a polymer/ceramic or a biomolecules matrix that is reinforced by CNT dispersed within the matrix [82]. These composites to some extent exhibit many of the mechanical and electrical properties of pure CNT [83]. CNTs have been considered as ideal reinforcing fillers for polymer matrixes to achieve high performance, because of their nanometer size, high aspect ratios, and more importantly, their extraordinary mechanical strength and high electrical and thermal conductivity.

It is reported that adding CNT as reinforcement into polymer can result in super-tough fibers [84]. By using the “coagulation spinning” method, several hundred meters of composite fibers of 60 wt % SWNT/poly-(vinyl alcohol) could be spun, such fibers had a tensile strength of 1.8 GPa, comparable to that of spider silk. Gao et al reported a chemical processing technology that allowed a continuous spinning of SWNT-polyamide 6 (PA6) fibers by an in-situ

polymerization of caprolactam in the presence of SWNT, which simultaneously optimizes the morphology of the composite [85]. A 153% increase in Young's modulus and 103% increase in tensile strength with 1 wt% carboxylated SWNT were obtained.

CS-CNT composites have been reported in a number of studies. Tang et al. investigated the effects of MWNTs content on water transport behavior and tensile properties of CS membranes [86]. They found that the water flux of CS-SWNT composite membrane (10 wt% MWNTs) is 4.6 times that of the pure CS membrane. Furthermore, improved tensile strength of porous CS membranes has been achieved by adding MWNTs. CS-CNT films also have applications in electronics. Cu nanoparticles/CNTs/CS (Cu/CNTs/CS) films fabricated by Yang et al. were used as sensors to detect nitrite [87]. Fibers composed of CS, polyaniline (PANI), and SWNTs have been fabricated using wet spinning by Spinks et al. [88]. The SWNTs were effective in improving the conductivity and mechanical strength of the composite fibers. In this thesis, the mechanical properties (maximum stress, strain at break, Young's modulus, and toughness) of CS-CNT composite fibers will be studied.

2.2.3 CS-lignin fiber

Lignin is a heterogeneous, aromatic biopolymer present in large amounts in the cell wall of plants, especially in woody tissues. Together with cellulose, lignin is one of the most abundantly occurring renewable resources [89]. Lignin is a matrix polymer that is the product of the dehydrogenative radical polymerization of monolignols such as p-coumaryl, coniferyl and sinapyl

alcohols, which are connected via carbon-carbon bonds and ether linkages [90].

The chemical structures of three primary precursors are shown in Figure 2-3.

Figure 2-3 Primary precursors of lignin: (a) p-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohol [91].

The amount of monolignol units varies from plant to plant. In softwood, the coniferyl moieties comprises of about 95% and the rest is made up by other units, while in hardwood and dicoryl crops such as flax and hemp, the mixture of coniferyl/sinapyl ratio can vary considerably [92].

Lignin is a versatile molecule that possesses multiple properties such as UV-absorption, anti-fungal and antibiotic activity. Besides its traditional use as an energy source and in leather tanning, lignin is also used in polymer reinforcement, or as pesticides dispersants, or sequestrants (i.e. antioxidants). It has been suggested that lignin can be used for stabilization of food and feed because of their antioxidant and antifungal properties. It was also reported that lignin have anti-carcinogenic and antibiotic activities [93]. When depolymerized, lignin can be used to produce valuable chemicals such as vanillin.

Furthermore, lignin is used as a reinforcing agent for synthetic rubber to augment the supplies of carbon black and other fillers [94]. Lignin can also be used as stabilizer for rubbers [95], and as a base for polymeric products such as lignin graft polymer, lignin-thermosetting polymer systems and lignin-elastomer systems [96]. Due to its complex structure, this amorphous and heterogeneous polymer behaves either like filler or like a reactive macromonomer. For instance, non-modified lignin or chemically modified lignin have been used with silicate clays and natural fibers [97], polyesters [98], polyurethane [99], poly(ethylene terephthalate) [100], polypropylene [101], or polyfurfuryl alcohol resin [102]. Furthermore, Rozman et al. [103] in their study showed that lignin played a positive role in improving the tensile strength of rubberwood-PP composites. Lignin as a filler or compatibilizer reinforced the mechanical and thermal properties of the composites. Despite the large amount of studies on lignin/polymer composites, there have been no studies on CS-lignin composites. Hence, in this project, lignin was added into CS to synthesize composite fiber for the first time with the aim of synthesizing a CS-nanocomposite that has low cost and possesses improved mechanical properties.

2.3 Gas permeation in CS based polymeric membrane

In membrane separation, CS membranes were mainly applied in pervaporation and extraction of metallic ions from water. The literature on gas permeation in CS membranes is limited [104]. CO₂/N₂ permeating through dry and a wet CS membrane at 20°C and 30 °C was reported [105]. The perm-selectivities for CO₂ and O₂ in CS membrane were also investigated [106]. It was shown that, at low relative humidity (RH), the CS film presented very low O₂ and CO₂

permeabilities of 1.24 and 7.4 amol/(Pa m s) respectively at 25 °C, 1 atm and on a CS membrane with a thickness of ~ 20 µm. For relative humidity higher than 60%, O₂ and CO₂ permeabilities increase exponentially to 1290 and 36700 amol/(Pa m s), respectively, at 95% RH. The selectivity ratio (CO₂/O₂ permeability) of all films tested at a high RH was very high ranging from 10 to 28 as compared to conventional synthetic films (4 to 6) [107]. El-Azzami and Grulke [104] found that dry CS is a good candidate for facilitated transport membranes, which can be used in industrial applications including fuel cell operations and other purification processes. They studied the effect of temperature on the transport properties of CO₂, N₂ and H₂ in a gas mixture [104] and found that the material is feasible for such applications.

Moreover, CS-based polymer membranes were also reported in literature. CS membrane modified with amino acid salts (arginine-sodium) can be used as a fixed-facilitated transport membrane for the separations of CO₂ from H₂ and N₂ [108]. The addition of arginine salts increased the number of amino groups for facilitated transport of CO₂ and increased the membrane water content in the arginine CS-salt membranes compared to swollen CS membranes at the same humidification conditions. These membranes achieved high CO₂ transport properties at the operating temperatures and pressures suitable for industrial applications such as fuel cell process and flue gas purification. These CS-based membranes had the CO₂ flux about three times more favorable than those for swollen CS membrane.

Furthermore, carbon nanotubes (CNT) have been proposed as a type of potential fillers for gas separation applications due to their superior gas separation and mechanical properties. Polyimide (PI)/CS-functionalized multi-walled carbon nanotubes (C-f-MWNT) mixed matrix membranes were fabricated by phase inversion method [109]. Gas permeation results showed that addition of 1 wt% C-f-MWNT into casting dope could increase CO₂ and CH₄ permeabilities by 20.48 and 0.71 Barrer, respectively. The increase in permeabilities of CO₂, CH₄ and He in the study can be attributed to the presence of high diffusivity tunnels in the MWNT within the polyimide matrix. It is interesting that the CO₂/CH₄ selectivity was also increased by 51.4% (from 10.9 to 16.5) by the addition of C-f-MWNT.

2.4 Gas permeation in CMS membrane

The separation of industrial gas mixtures such as landfill gas recovery, natural gas processing, olefin/paraffin separation, air separation, etc. continue to require robust membrane materials with higher selectivity and permeability. Currently polymer membranes seem to have reached a limit in productivity-selectivity tradeoff despite concentrated efforts to tailor polymer structures to enhance separation properties [110]. Porous CMS and ceramic microporous membranes possess high permeability, high selectivity and are chemically and thermally stable. Therefore, they are attractive for applications in gas separation and gas production reactions [111]. For example, Da Costa's group synthesized carbonized template molecular sieve silica (CTMSS) that shows good flux and selectivity towards H₂/CO mixtures [112].

CMS membranes are another attractive alternatives due to their high selectivity, permeability, and stability at harsh operation conditions (high-temperature, high-pressure, presence of contaminants, etc.) [113]. Similar to CMS adsorbents, CMS membranes have been used successfully in adsorption/separation processes for separating molecules of similar dimensions as the pore structure [114].

Early works revealed that polymer-derived CMS membranes have high selectivities for O₂/N₂ separation [113, 115]. Subsequently, various researchers found that a range of CMS membrane morphologies and permeation properties depend on the properties of the starting polymer precursors such as polyimide, polypyrrolone, poly (furfuryl alcohol) and polyetherimide, together with other important parameters in the pyrolysis process [116, 117].

Geiszler and Koros studied the effects of polyimide pyrolysis conditions on CMS membrane properties, and used gas mixtures such as O₂/N₂ and H₂/N₂ to evaluate membrane performance [118]. The results showed that increasing the pyrolysis temperature from 500°C to 800°C caused a significant decrease on the permeate flux and a significant increase in the selectivity for CMS membranes produced by both vacuum and inert purge pyrolysis techniques. Moreover, CMS hollow fiber membranes have been investigated for CO₂/CH₄ separation [9]. In their experiment, the mixed gas feeds of 10% CO₂ and 90% CH₄ on the shell side were investigated at three different temperatures (24°C, 35°C and 50°C) under high-pressure (up to 1000 psi). The CMS hollow fibers presented attractive permeation properties for CO₂/CH₄ separation. In particular, the

mechanical stability and selectivity stability of the CMS membranes at high pressure (up to 1000 psi) are particularly desirable. Rao and Sircar studied CMS membranes for refinery gas separation and hydrogen recovery [119]. They found that the CMS membrane could efficiently separate H_2 from refinery gas. This technology has been employed by Air Products and Chemical Inc. for hydrogen enrichment to 56-60% prior to PSA purification in order to produce 99.99% H_2 [120].

Many researchers investigated the structures of CMS membranes. The microstructure of a CMS membrane was characterized using supercritical adsorption equilibrium by Nguyen et al. [121]. Adsorption isotherms of N_2 and CH_4 on a polyimide-based CMS membrane were measured at high temperatures and under a wide range of pressures (0.1-50 bar). The pore size distribution was found to be predominantly in the upper-ultra-micropore range, without significant contribution of mesopores [122]. Wang developed analytical mathematical expressions for permeation time lag and permeability to characterize the CO_2 permeation in a CMS membrane. By comparing the theoretical models with the permeation time lag data of CO_2 measured on the CMS membrane, it was found that under their experimental conditions, the apparent surface diffusivity of CO_2 had a functional concentration dependence stronger than the traditional HIO model. This abnormality was observed at both transient and steady state and was attributed to the complicated micro-structure of the CMS membrane [10]. Later, a structural model of CMS membrane was proposed by Wang, which assumed the CMS membrane consisted of through pores (which function as the adsorption/diffusing channels at both transient and

steady states) and dead-end pores (which function only at the transient state as “concentration sinks”) in the overall porous network. The overall (observed) time lag (L) is the contribution from the blind pores (L_B) and through pores (L_T), i.e.:

$$L = L_T + L_B \quad (2-1)$$

where

$$L_T = \frac{l^2}{D_\mu^0} \left\{ \frac{1}{\ln(1 + b_T P_0)} \left[\frac{1}{2} - \frac{1}{(1 + b_T P_0) \ln^2(1 + b_T P_0)} - \frac{\ln(1 + b_T P_0) - 1}{\ln^2(1 + b_T P_0)} \right] \right\} \quad (2-2)$$

and

$$L_B = \frac{l^2}{D_\mu^0} \times \frac{C_{\mu s}^B}{C_{\mu s}^T} \left[\frac{2di \log\left(\frac{k}{k-1}\right) - 2di \log\left(\frac{k w}{k-1}\right) - 2 \ln(1 - k + k w) \ln\left(\frac{k w}{k-1}\right) + k \ln^2 w}{2(k-1) \ln^3 w} \right] \quad (2-3)$$

$$(\text{with } k = b_B / b_T > 1, w = (1 + b_T P_0), di \log(x) = \int_0^x \frac{\ln(t)}{1-t} dt)$$

Where l is the membrane thickness, r is the pore size, p is pressure, b is sorption affinity, C_μ is adsorbed phase concentration, and $C_{\mu s}$ is the sorption capacity. The superscripts ‘ T ’ and ‘ B ’ represent the through pore and blind pore, respectively. D_μ is diffusion coefficient following the Darken type concentration dependence, $D_\mu = D_\mu^0 (\partial \ln P / \partial \ln C_\mu)_T$, D_μ^0 is diffusion coefficient at zero surface loading.

The model successfully interpreted the diffusion anomalies at transient state for CO_2 and N_2 gases in a CMS membrane [123]. However, the diffusion anomalies at steady state permeation remain unsolved.

In this work, we will investigate the adsorption and permeation properties of CMS membrane. Special attention will be devoted to the diffusion anomalies at steady state.

Chapter 3. Experimental methodology

3.1 Introduction

This chapter describes the experimental procedure conducted in this research, which includes the preparation of nanocomposite membranes and composite fibers, the measurement of adsorption, permeation, as well as mechanical properties, and the structural characterization of the nanocomposite fibers and membranes.

3.2 Experimental

3.2.1 Materials

Chitosan (CS) was obtained from Bannawach Bioline Company, Thailand. It was synthesized by the deacetylation of chitin from crab shells. The measured molecular weight (MW) of the CS sample is 187,260. Four kinds of POSS selected for this experiment were Octaanion (OA-) (MW: 1378g/mol), Octaaminophenylsilsesquioxane (OAPS) (MW: 1153g/mol), octa nitro phenyl silsesquioxane (ONPS) (MW: 1393 g/mol), and octa ammonium (OA) (1173 g/mol). The first three samples were purchased from Mayaterials Inc., USA, while OA was supplied by Hybrid Plastics, Inc., USA. The structures of the four POSS are shown in Figure 3-1. Acetic acid and methanol were supplied by Sigma Aldrich and used as received. NaOH was purchased from AikMoh

Paints & Chemical Pte. Ltd., Singapore. All the chemicals were of chemical reagent grade unless otherwise specified.

Figure 3-1 The structure of four types of POSS

The other nanofiller, SWNT, were obtained from Cheap Tube Inc., USA. Its properties are listed in Table 3-1.

Table 3-1 The basic properties of SWNT used in the experiment.

	Outer diameter nm	Length μm	Purity
SWNT	<2	5-15	>90wt%

Lignin 1 (which is lignin, alkali, typical MW: 28,000) and lignin 2 (which is lignin, alkali, low sulfonate content, typical MW: 60,000) were purchased from Sigma-Aldrich Pte Ltd. The two lignin samples will be abbreviated as L1 and

L2, respectively in the subsequent discussions. The structures of the two lignin samples are show in Figure 3-2.

Figure 3-2 The structures of (a) lignin 1 (L1) and (b) lignin 2 (L2).

3.2.2 Preparation of CS-based nanocomposite fibers

1) Preparation of CS solution

0.15 g CS was dissolved in a 25 ml conical flask containing 10 ml of 1% acetic acid solution and was stirred at a constant rate of 700 rpm at a room temperature for 4 hours. After the CS was fully dissolved, appropriate amounts of the filler (lignin, POSS or SWNT) were added into the solution and stirred at a constant rate of 700 rpm at a room temperature for 24 hours. This ensured that the filler powder was blended homogeneously in the solution before subjected to wet spinning. Care was taken to remove all air bubbles in the solution. Different concentrations (w/w%) of CS-nanofiller were prepared. The above mentioned steps were repeated to prepare all the CS-filler solutions shown in Table 3-2.

Table 3-2 Composition of fillers in CS based composite fiber components.

Composition (w/w%)	1%	3%	5%	7%	9%
L1	0.0015 g	0.0045 g	0.0075 g	0.0105 g	0.0135 g
L2	0.0015 g	0.0045 g	0.0075 g	0.0105 g	0.0135 g
OA	0.0015 g	0.0045 g	0.0075 g	0.0105 g	0.0135 g
ONPS	0.0015 g	0.0045 g	0.0075 g	0.0105 g	0.0135 g
SWNT	0.0015 g	0.0045 g	0.0075 g	0.0105 g	0.0135 g

2) Fiber fabrication by wet spinning

The nanocomposite fibers were fabricated by wet spinning due to the high viscosity of the mixture solution. Melt spinning is not suitable since CS will degrade at high temperatures. 1 M NaOH was flowed from a beaker through an epoxy-cured silicone tube into the coagulation bath using a spinner. Each sample, which is known as the dope, was loaded into a 10 ml syringe. The dope was also pumped through the silicone tube at a rate of 5 ml/min into the coagulation bath. In the bath, the polymer precipitated into fibers. The fibers were left in the bath for about 15 minutes. The NaOH solution was then drained away from the fibers before soaking them in deionized water twice, for a duration of 15 minutes each. Next, the fibers were removed from the deionized water and soaked in methanol for 20 minutes at room temperature. Methanol

acts as a drying agent to expedite the process of drying the fibers. Finally, the fibers were air dried and stored in a petri dish for analysis. Figure 3-3 shows the schematic diagram of fiber fabrication process.

Figure 3-3 Schematic diagram of wet-spinning apparatus.

3.2.3 Preparation of CS-POSS nanocomposite membranes

The preparation of CS-POSS composite membrane (via solution casting) was as follows: 1g of CS was dissolved in 100 ml of 1% (v/v) acetic acid in flask and stirred for 4 hours. After the CS was fully dissolved, 1%, 3%, 5%, 7%, 9% of POSS was added into the CS solution, respectively, and stirred for 24 hours. The undissolved materials were then filtered out. 20g of each solution was put in petri-dish and heated at 40°C in an oven. During the drying process, air bubbles in the solution were removed. The dried membrane was washed with sodium hydroxide (1 mol/L) and DI-water. The washed membranes were then dried at room temperature, and peeled off from the dishes. The resulting membranes had a thickness of 20 to 25 μm. Figure 3-4 shows the schematic diagram of casting composite membrane.

Figure 3-4 The schematic diagram of casting membrane.

3.2.4 Preparation of CMS membranes

The CMS membrane was prepared via the controlled pyrolysis of a polyimide thin film under vacuum. The polymer film was first cut into circular shapes and put between graphite blocks, which were then placed in a quartz tube reactor (tube furnace). The ramping rate of the treatment temperature was set as 10°C/min. The soaking temperature was selected at 1000°C and 800°C, respectively. The soaking time was fixed at 2 hours. After thermal soaking, the system was cooled down to ambient temperature via natural cooling. Molecular probe experiments (adsorption and permeation experiments using adsorbates with different molecular dimensions) were conducted at ambient conditions (25°C) to examine the pore size and selectivity of the membrane. The membrane samples were confirmed to be pinhole free, symmetric in structure, and with good perm-selectivities at ambient conditions. The performance of the CMS membrane treated at 1000 °C (termed as KP1000) had a thickness of 23

μm with the properties shown in Table 3-3. There are some conflicting values from different sources in the kinetic diameter of the gases. The values used in this thesis are mostly taken from the book: *Zeolite Molecular Sieves: Structure, Chemistry, and Use* [124]. The density of the CMS membrane was measured by the pycnometer (helium expansion). The perm-selectivity was measured by gas permeation using time-lag rig.

Table 3-3 Gas permeation-selectivity of KP1000 at ambient conditions^a

gas	H ₂	He	N ₂	O ₂	CF ₄	CO ₂
Kinetic diameter σ (Å)	2.89	2.60	3.64	3.46	4.70	3.30
Perm-selectivity, (<i>P</i> _{helium} / <i>P</i> _i)	0.47	1	680	29	∞	6.73

^a Note: perm-selectivity (A/B) = permeability of A/permeability of B

The CMS membrane thermally treated at 800°C (termed as KP800) had a thickness of 125 μm. The general properties of the membrane are listed in Table 3-4.

Table 3-4 The properties of the KP800 membrane

Pyrolysis Temp. (°C)	Ramp (°C/min)	Density (g/cc)	Perm-selectivity (<i>P</i> _{Helium} / <i>P</i> _i)			
			<i>P</i> _{He} / <i>P</i> _{CO2}	<i>P</i> _{He} / <i>P</i> _{N2}	<i>P</i> _{He} / <i>P</i> _{Ar}	<i>P</i> _{He} / <i>P</i> _{H2}
800	10	~1.99	0.67	22.28	22.30	0.31

3.2.5 Testing of the mechanical properties

CS-Lignin, CS-OA and CS-ONPS fibers were subjected to tensile tests at room temperature. Tensile tests were performed using a Tensile Testing Device made

by Sensorcraft Technology. A data acquisition unit with DC 104R software was used to record the stress and strain of each sample. An elongation rate of 0.06 mm/s was used in most of the experiments. The properties of at least 6 samples were measured and averaged for the reported value. A phase microscope (Olympus BX51) was used to determine the thickness and to provide images of the fiber samples. Figure 3-5 shows the tensile test unit of the experiment.

Figure 3-5 The tensile test unit.

3.2.6 Testing of the adsorption properties

1). Adsorption measurements

The high pressure adsorption isotherms (up to 50 atm) were measured using a standard commercial gravimetric rig (A Cahn 2000 microbalance). The low pressure adsorption isotherms (up to 1 atm) were measured on a standard commercial pore and surface analyzer (BEL, Japan) which uses the volumetric method. Prior to the isotherm measurement, the samples were degassed under vacuum overnight at 200°C. The dosing processes were pre-set by computer program and the measurements proceeded automatically. The dosing gases for

volumetric rig on KP950 and KP1000 was CO₂, And the gravimetric method on KP800 were Ar, N₂, CO₂, etc.

2) Permeation measurements

The transient state permeation time lag and the steady state permeation flux of pure gases on the membrane samples were measured on a conventional time lag rig, which is shown schematically in Figure 3-6.

Figure 3-6 Schematic diagram of the gas permeation rig.

The permeation system consists of a membrane cell, upstream and downstream gas cylinders and a membrane holder. The volume of the two upstream cylinders was 500 cc each (2 cylinders can make a total volume of 1100 cc, with the tubing), and downstream cylinder volume was ~150 cc. The area of membrane holder was 4.906 cm². The pressure transducers were fixed on the upstream and downstream cylinders, respectively. When the pressure changed, the pressure transducers converted the pressure signal into voltage. A data

logger (Agilent 34790A) is used to convert the voltage into digital signal. The upstream pressure can be controlled in range of 0 to 250 psi, while the downstream pressure transducer (MKS 750B11TCD2GG) has a range of 10^{-6} to 10 torr. A turbo molecular drag pump is used to evacuate the system and can achieve a pressure of less than 1×10^{-4} torr.

The membrane is fixed in a membrane holder and then the system was degassed at an ultra vacuum. The membrane was isolated after the cleaning. During the experiments, the upstream gas cylinder was charged with the gas permeate at the designated pressure while the downstream cylinder was kept at vacuum. At time zero, the valve was opened and the membrane was subjected to the upstream pressure and the permeation began. A photo of the setup is shown in Figure 3-7.

Figure 3-7 The permeation rig in the Lab

It is easy to see from Figure 1-2 that the slope of the pressure-time response is:

$$\text{slope} = \frac{dP}{dt} \quad (3-1)$$

where t is time and P is the pressure at the downstream cylinder (with the volume V). Applying the Clapeyron ideal gas law $PV=nRT$, we have:

$$\frac{dn}{dt} = \frac{dP}{dt} \times \frac{V}{RT} \quad (3-2)$$

where n is the number of molecules. The steady state flux is calculated by

$$J_{\infty} = \frac{1}{A} \frac{dn}{dt} \left[\frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right] \quad (3-3)$$

where A is the membrane area. The permeability is the normalized flux, defined as:

$$P_e = \frac{J_{\infty}}{\Delta P / L} \quad (3-4)$$

$$\text{So } P_e = \frac{LV}{APT\Delta P} \frac{dP}{dt}$$

where ΔP is the pressure difference between the upstream and downstream vessels. L is the membrane thickness.

$$\text{Therefore, } P_e = \frac{LV}{APT\Delta P} \frac{dP}{dt} \quad (3-5)$$

3.3 Structural characterization

Scanning electron microscope (SEM) is a microscope that uses electrons instead of light to form an image. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface morphology. In this research, JEOL JSM-6390 LA Analytical

Scanning Electron Microscope (SEM) was used to observe the morphology of the cross-section of the fibers.

Chapter 4. Characterizing CS-based nanocomposite fibers

CS-lignin, CS-POSS, and CS-CNT nanocomposite fibers were fabricated using the phase inversion techniques. The method of preparation and their compositions were discussed in Chapters 2 and 3. The structures and properties of these three types of fibers will be discussed in this chapter.

4.1 CS-lignin composite fibers

Figure 4-1 shows the maximum stress of the CS-lignin composites as a function of loading force and cross-section area of the fiber. The maximum stress of the fiber increases from 87.4 MPa in pure CS to a maximum value 156 MPa in 3% L1/CS composite. This is an increase of 78%. The maximum stress declines at higher contents of L1. However, the strengths of all CS-L1 composite fibers are higher than that of pure CS. A similar trend is observed in CS-L2 composites. The mean value increases by 58% from pure CS to 3% CS-L2 composite. The maximum stress also decreases as L2 concentration increases further.

Figure 4-2 shows the strain at break data for the CS-lignin composites. The strain data exhibits a similar trend as the maximum stress. The strain increases at low lignin concentration and reaches a maximum at 3% lignin. Then the strain drops at higher levels of lignin. The CS-lignin composite fibers are generally more ductile than pure CS.

Figure 4-1 Maximum stress data for CS-lignin composites

Figure 4-2 Strain data of CS-lignin composites.

Figure 4-3 shows the Young’s modulus of the composite fibers. All the composite fibers have higher Young’s modulus than pure CS except 1% CS-L1 fiber, which has a lower Young’s modulus. The highest Young’s modulus is

observed in 3% CS-lignin composites, which shows a 39% increase in CS-L1 and a 27% increase in CS-L2 in Young’s modulus compared to pure CS.

Figure 4-4 shows the toughness of the composite fibers. The highest toughness is observed in 3% CS-L1 composite, which shows a 305% increase in toughness compared to pure CS, while CS-L2 composite shows a 162% increase. The toughness then decreases with increasing concentration of lignin. The increase in toughness is in tandem with the results from the maximum stress and maximum strain data, which also exhibits a peak value at 3% lignin content.

Figure 4-3 Young’s modulus data of CS-lignin composites.

Figure 4-4 Toughness (MPa) data of CS-lignin composites.

From the above results, it is clear that 3% CS-L1 and 3% CS-L2 composites exhibit superior mechanical properties than that of pure CS and CS-lignin composites with other lignin content. The reason for the improvement of the overall mechanical properties at 3% lignin is attributed to the enhanced interactions resulting from a relatively good match between the lignin and the CS matrix through strong bonds. The methoxyl, carboxyl, carbonyl and hydroxyl (phenolic or alcoholic) groups in lignin may be the reason for the present of noncovalent bonds such as hydrogen bonds and hydrophobic interactions which may contribute to the strong interactions between the lignin molecules and the CS matrix.

Figures 4-5a and 4-5b shows the SEM micrographs of the fracture surface of pure CS and 3% CS-L1 composite respectively. The fracture surface of pure CS is relatively smoother than the fracture surface of the 3% CS-L1 composite. The

random scattering of protrusions on the fracture surface of CS-lignin composite demonstrates the presence of lignin molecules in the individual fibers. This also shows that the lignin molecules are well integrated and adhere strongly onto the CS matrix. Proper interfacial interaction is an important factor when the particles are to be used as toughening agents. The strong adhesion also prevents matrix debonding at moderate levels of stress, which results in matrix deformation [125].

Figure 4-5 SEM micrographs of fractured surface of (a) pure CS and (b) 3% CS-L1 fibers.

The lack of improvement in mechanical properties at higher lignin contents may be attributed to the poor dispersion and phase separation of lignin molecules in the composites, thereby resulting in poor interactions or interface adhesion between the matrix and the dispersed phase [126]. Figures 4-6a and 4-6b show the SEM micrographs of the fracture surface of 3% CS-L2 and 9% CS-L2 respectively. The lignin particles can be seen in both graphs. It can be seen that the lignin particles are more homogeneously dispersed in 3% CS-L2

while some aggregation owned in 9% CS-L2 composites. Hence 3% L2 in CS is the optimal composition.

Figure 4-6 SEM micrographs of fractured surface of (a) 3% CS-L2 and (b) 9% CS-L2 fibers.

It is reported that the stiffness of polybutylenedipate-co-terephthalate (PBAT)/lignin biocomposite containing 14% lignin was 5.5 times that of neat PBAT (40 MPa). However, as lignin content increased to 30%, the modulus of composite dropped to 4 times the value of the neat PBAT [127]. The trend is similar to our results. Klason et al. [128] has observed that the presence of lignin in the filler influenced the adhesion to the matrix.

In carbon nanotube (CNT) enforced CS composite fibers, Spinks et al. [129] reported that the Young's modulus of the CS-CNT fiber more than doubled that of the cross-linked neat CS. However, that the elongation at break for CNT-reinforced CS (10%-14%) was worse than for neat CS (24%). In our work, the strain at break of 3% lignin is 18%-20% higher than the neat CS. For the modulus, there is a 39% increase in CS-L1 and a 27% increase in CS-L2 compared to pure CS. Hence, adding lignin into CS matrix results in an increase of the maximum stress, strain at break, modulus of elasticity and toughness, and

consequently an overall enhancement in mechanical performance of the composite.

The experimental results show that 3% CS-L1 composite and 3% CS-L2 composite are the optimum concentration for superior mechanical properties (tensile strength, strain at break, Young's modulus and toughness) when compared to the pure CS. Any further increase in the concentration of L1 or L2 will result in a declining trend. The optimum distribution of the reinforcement lignin particles in the CS matrix, coupled with the various bonds interactions between lignin molecules and CS matrix are responsible for the improvement of the mechanical properties of the composites. Hence this work demonstrates the feasibility of forming high performance fibers from cheap resources.

4.2 CS-POSS composite fibers

4.2.1 CS-OA composite fibers

Figure 4-7a to 4-7d show the maximum stress, strain at fracture, Young's modulus and toughness respectively of CS-OA nanocomposites at various filler loadings. The amount of stress that the samples can handle generally increased as the loading of OA increased, until it reached a maximum at 7 wt%, beyond which it decreased. A similar trend was seen in the bar charts for strain, Young's modulus and toughness. The loading at 7 wt% also resulted in the highest strain at fracture, Young's modulus and toughness.

Figure 4-7 The mechanical properties of CS-OA composites as a function of OA concentration: (a) maximum stress, (b) strain at break, (c) Young’s modulus, (d) toughness.

4.2.2 CS-ONPS composite fibers

Fig. 4-8a to 4-8d shows the stress at fracture, strain at fracture, Young’s modulus and toughness respectively of CS-ONPS composites for different ONPS loadings. Similar to CS-OA data, the stress at fracture data generally showed an increasing trend with increasing amounts of ONPS up to a 50%, after which it decreased. The trend is generally similar for the other properties. It is seen that 5 wt% loading of ONPS in CS resulted in best mechanical performance.

Figure 4-8 The mechanical properties of CS-ONPS composites as a function of ONPS concentration: (a) maximum stress, (b) strain at break, (c) Young’s modulus, (d) toughness.

Figures 4-9a to 4-9b show the images of the fractured samples obtained from SEM for 7 wt% OA and 5 wt% ONPS respectively. From the images, it could be seen that the cross-sectional area of the fibers were approximately circular and hence, the fibers could be approximated to be cylindrical and the fiber was porous in nature. Since the size of POSS particles are very small, ranging from 1 to 3 nm, the pores within the structure could be indication of POSS particles integrated within the CS matrix which detached during fracture, described as particle-matrix debonding during deformation by Kopesky et al [125]. The even

distribution of pores throughout the cross-section could imply that the POSS domains were evenly distributed through the fracture surface.

Figure 4-9 SEM images of fiber cross-section: (a) OA 7 wt%; (b) ONPS 5 wt%.

4.3 CS-SWNT composite fibers

Figs 4-10a to 4-10d show the stress at fracture, strain at fracture, Young’s modulus and toughness of CS-SWNT composites. It is seen that 1 wt% loading of SWNT in CS resulted in the highest stress at fracture among all the samples, an increase of 17% over pure CS. The increase in strain for 1 wt% SWNT was calculated to be 27%. Further increase in SWNT loading beyond 1 wt% resulted in a decrease in stress at fracture of the fibers.

Figure 4-10 The mechanical properties of CS-SWNT composites as a function of SWNT concentration: (a) maximum stress, (b) strain at break, (c) Young’s modulus, (d) toughness.

In generally, the fibers’ stress at fracture is also the ultimate stress. Upon reaching the point of ultimate stress, there was no sign of any further elongation before fracture. This could be attributed to the small dimensions of the fibers that caused instability during the initial stage of neck formation and hence, fracture to take place easily.

The stress at fracture and toughness of the composites increase with increasing amount of loading for both POSS and SWNT. This is in accordance to the fact that the addition of POSS or SWNT results in nanocomposites which are

mechanically stronger as noted recorded by Song et al [130]. However, a maximum amount of stress attained by the fibers is achieved with a certain amount of filler, beyond which the stress would decrease as more filler is added. For the CS-POSS nanocomposites, this could be due to the interference of POSS molecules with the CS matrix as more POSS is added, hence disrupting the structure and causing the fibers to fracture at a smaller load amount. As reported by Kopesky et al. [125]. Larger POSS crystallites weakened the material. Since the size of ONPS is larger than OA due to the presence of side phenyl groups, lesser amount of ONPS is required to attain the maximum amount of stress as compared to OA.

Song et al. [130] also reported that an increase in strain could be due to a better stress transfer mechanism between the two components in the nano-composite as it is stretched. They also reported that the effect of the amount of POSS added on the Young modulus of the nano-composites was not significant. These results could be observed in CS-POSS samples in our work.

For SWNT, the addition of 1 wt% saw an increase in the stress, Young modulus and toughness. However, the fibers fractured at low loadings for low additions of SWNT. This could be due to the fact that as more CNT were added, the chances of non-alignment of the CNT increase, hence weakening the composite structure instead of strengthening it. Spinks et al. also reported that large CNT aggregates were also not effective in reinforcing the material [129]. This could explain the decrease in stress, Young's modulus and toughness at higher level.

Spinks et al. [129] noted that the elongation at break for the neat CS (24%) is almost double that of CNT-reinforced CS (10%-14%). However, the Young's modulus for the cross-linked neat CS was 4.25 GPa, in contrast, the CNT dispersed by sonication and then centrifuged to remove aggregates produced a composite with a more than doubled modulus (10.25 GPa). In our work, maximum stress of 1% CNT increases 17% over neat CS. The strain at break was 27% higher than that of pure CS. While there is a 15% increase and a 120% increase respectively for the modulus and toughness compared to pure CS. Hence, adding SWNT into CS matrix may improve the maximum stress, strain at break, modulus of elasticity and toughness, consequently all-round improvement the mechanical properties of the composite.

4.4 Summary

CS-lignin, CS-POSS and CS-SWNT nanocomposite fibers with improved mechanical properties have been successfully fabricated by the wet-spinning method. Fibers fabricated were stiff and rigid as observed by the minimal amount of necking before fracture. The amount of loading resulting in the greatest tensile stress that could be handled was determined to be 3 wt% for L1, 3 wt% for L2, 7 wt% for OA, 5 wt% for ONPS and 1 wt% for SWNT. An increase in loading resulted in a decrease in tensile strength, which could be due to the disruption of the structure as more filler was introduced. The random alignment of SWNT could be a cause for the weakening of the nano-composite structure. Nonetheless, the improved mechanical properties for CS will serve as a framework for the future development in its application to different fields such as medical and membrane separations.

Chapter 5 Characterizing the permeation properties of CS-based nanocomposite membranes

5.1 Introduction

Permeation time lag is an important tool to study mass transfer in membranes/porous media because it enables one to obtain the system properties of both the transient state (diffusion coefficient) and the steady state (permeability) [131]. Since Frisch proposed the simplified mathematical method for time lag analysis (i.e. the method of Frisch) [131], a number of research progress has been made on such aspects as: the concentration dependent diffusion coefficient [132], the spatial/time dependent diffusion coefficients [72], isotherm and membrane geometry [23, 133], structural heterogeneity [123] and blind pore characteristics [134], etc.

This chapter will report gas/vapor permeation properties on CS-POSS composite membrane. In addition, a novel experimental method will be proposed for measuring the permeation properties of a gas-vapor mixture. It requires minimal modification of the traditional time lag rig and is capable of measuring both the transient and steady state properties of gas/vapor mixtures.

5.2 OA- membrane permeation of water vapor

Figure 5-1 shows the effects of the type and loading amount of POSS on the degree of swelling (DS%) of the CS membrane and CS-POSS composite membranes in de-ionized water. The DS% of CS-POSS membranes is lower than that of CS membrane. For CS-OAPS and CS-ONPS membranes, the DS% gradually decreases with increasing POSS content. For the CS-OA and CS-OA-, the DS% first decrease, then increase with increasing POSS loading. However, even for the composite membranes with the highest composite loadings, their DS% was still lower than the CS membrane. It is known that the swelling of a membrane in water depends on the chemical composition, microstructure, and the incorporated moiety.

Figure 5-1 DS% of the CS membrane and CS-POSS composite membrane in de-ionized water.

As OA- and OA are hydrophilic with the same swelling ratio, while OAPS and ONPS are hydrophobic with a similar swelling ratio. We choose one

hydrophilic OA- and hydrophobic OAPS to study the CS-composite membrane permeability in this thesis.

CS-OA- membranes are fabricated with the methods described in Chapter 3. The OA- content (wt%) was 3%, 5%, 7% and 9%, respectively. Their structural and permeation properties are studied.

Figure 5-2 shows the SEM images of native CS membrane of its (a) surface, and (b) its cross-section. From the SEM image, it is observed that the membrane is dense and no defects are found in surface or cross-section of the membrane.

Figure 5-2 SEM images of CS membrane: (a) surface and (b) cross-section.

Figure 5-3 shows the SEM images of the CS-OA- composite membranes. It is observed that 1 to 9 wt% loading of OA- membranes have smooth surfaces and cross-sections, which is similar to that of the CS membrane. It seems that OA- can be well dispersed in the CS matrix because OA- is relatively hydrophilic and has good compatibility with the polymer.

Figure 5-3 SEM images of CS-OA- composite membranes: (a) surface of 1 wt% loading; (b) cross-section of 1 wt% loading; (c) surface of 5 wt% loading; (d) cross-section of 5 wt% loading; (e) surface of 9 wt% loading; (f) cross-section of 9 wt% loading.

Figure 5-4 shows the permeation results of water vapor on the CS-OA- membrane at room temperature ($\sim 23^{\circ}\text{C}$) and at a permeation vapor pressure of ~ 20 Torr. It is observed that, with the increased concentration of OA-, the time lag decreases while the permeation flux (related to the slope) increases. Using a

value of $L = 25\text{ }\mu\text{m}$ for the thickness of the dry membrane, the diffusion coefficient was found to increase with the content of the POSS, which suggests that the OA- increases the hydrophilicity of the CS and facilitate the transport of water molecules.

Figure 5-4 Pressure-time plot for the permeation of water vapor on CS-OA-membranes

Figure 5-5 shows the relationship between the pressure response and the time on 3% OA-. It is seen that the time lag is derived from the trendline and the D_K is calculated as $5.511 \times 10^{-8}\text{ cm}^2/\text{s}$.

Figure 5-5 3% POSS (OA-) Pressure-Time plot and the determination of time lag

Table 5-1 presents the time lag and D_K value for CS membrane with different OA- concentration. We see that, as the OA- content increases from 3% to 9%, the diffusivity increases by about 6 times. This may be caused by two factors, 1) the POSS content increases the hydrophilicity of the membrane so that the water solubility is higher, and 2) the POSS cage may provide extra channels (Figure 2-1) for water molecules (~0.26 nm) to pass through. Therefore, the water molecules penetrate the composite membrane more quickly than on the neat CS membranes.

Table 5-1 The diffusion coefficients on different CS-OA- membrane

Concentration	Pure CS	3%	5%	7%	9%
Slope	0.0021	0.0024	0.0042	0.004	0.0082
Time lag (s)	1984.43	1915.25	1559.02	1168.28	303.51
$D_K \times 10^{-8}$ (cm ² /s)	5.25	5.51	6.68	8.92	34.32
Flux $\times 10^{-4}$ (mol/ m ² /s)	1.20	1.37	2.39	2.28	4.68
Permeability $\times 10^{-12}$ (mol/Pa/m/s)	0.98	1.12	1.95	1.86	3.81

Table 5-1 also shows the water flux and permeability of membranes for each concentration of OA-. With the increasing in OA- concentration, both the flux and permeability increase. The permeability at 9% POSS is about 3.5 time that of the native CS. But it is noticed that both the flux and permeability of POSS 5% POSS is a bit little higher than (or comparable to) the one with 7% POSS. The exact reason is unclear but it is likely due to the fact that 5% CS-OA- membrane contains some small bubbles due to the uneven thickness of the membrane. So 5% CS-OA- membrane flux and permeability is higher than that of 7% CS-OA- membrane.

5.3 OAPS membrane permeation of water vapor

Figure 5-6 shows the morphology of the CS-OAPS composite membranes. It is observed that, in the CS-OAPS membranes, particles with the sizes less than 1 μm are still present, which may due to the agglomeration of OAPS. With the increasing concentration of OAPS up to 9%, the number of particles also increases. The formation of aggregations of hydrophobic OAPS in membranes

are possibly due to their poor compatibility of this type of POSS with the hydrophilic CS matrix.

Figure 5-6 SEM images of the CS-OAPS composite membranes (a) surface of 1 wt% loading; (b) cross-section of 1 wt% loading; (c) surface of 5 wt% loading; (d) cross-section of 5 wt% loading; (e) surface of 9 wt% loading; (f) cross-section of 9 wt% loading.

Figure 5-7 presents the water vapor permeation in CS-OAPS membrane at room temperature and saturated vapor permeation pressure. It is seen that, increasing the concentration of OAPS, the permeation time lag generally decreases, except that the 3% membrane has a shorter time lag than the 5%

membrane. It is possible that the POSS had not totally dissolved in CS solution. After filtration, the 5% membrane actually contains slightly less than 5% POSS. So the 5% line shows a little abnormality in Figure 5-7.

Figure 5-7 Pressure-time response at the downstream

The water vapor permeability of the CS-OAPS composite membranes is listed in Table 5-2. It is observed that with the increasing OAPS concentration, the slope, D_K , flux and permeability increase simultaneously as well, while the time lag decreases. However, the results for 3% and 5% are a little abnormal. As explained earlier, it is likely due to the fact that not all OAPS have totally dissolved in CS solution. So the actual content of the POSS in the fabricated membrane may be different from the original composition of the solutions.

Table 5-2 The permeation results of CS-OAPS membrane

Concentration	1%	3%	5%	7%	9%
Slope	0.0038	0.0042	0.0041	0.0046	0.0148
Time lag (s)	1207.95	1103.00	1237.66	833.20	686.01
$D_K \times 10^{-8}$ (cm ² /s)	8.623	9.444	8.416	12.502	15.184
Flux $\times 10^{-4}$ (mol/ m ² /s)	2.166	2.394	2.337	2.622	8.437
Permeability $\times 10^{-12}$ (mol/Pa/m/s)	1.766	1.952	1.906	2.138	6.879

Comparing the permeation properties of the two types of the POSS fillers, it is seen that the CS-OAPS membranes have higher flux and permeability than CS-OA- membranes, possibly due to the pore/matrix structure of the two kinds of composite membranes. OA- is hydrophilic, it was well dispersed in CS matrix and resulted in a more homogeneous composite structure. OAPS is hydrophobic, the compatibility with CS is not as good as the CS-OA- membrane. The less well-dispersed POSS particles may possibly result in bigger pore channel (the void between the POSS particle and the core of a POSS molecule is permeable to water molecules) inside the composite membrane, so as to increase the flux and permeability. It was also noted that the water diffusivity of OA- composite membrane increases quickly as the POSS content increases from 3% to 9% (an increase of ~ 6.5 times). This value is ~ 3.5 times that of the OAPS composite. This may suggest that, for OA- content higher than 7%, the hydrophilicity will play a dominant role in the sorption-diffusion process. The more hydrophilic CS-OA- composite will reach the steady state more quickly than the hydrophobic counterpart.

5.4 Permeation study of binary vapor-gas mixtures with the improved time lag method

A conventional time lag rig is capable of measuring the permeation properties of a pure gas. To measure the permeation properties of a binary or multicomponent gas mixture, however, a diffusion cell technology is preferred (e.g. a Wicke-Kallenbach cell) [135], in which an inert gas (e.g. helium) is used as the “sweeping gas” at the downstream to carry the permeates to a GC or MS for the composition analysis. Such a device, however, has a number of problems. Firstly, helium is a highly permeable gas. The chemical potential gradient may drive helium to diffuse back to the upstream vessel and, according to the Maxwell-Stefan theory; the helium flux will exert a strong interaction with the other diffusing components. Secondly, using GC/MS for composition analysis is time consuming and expensive. Thirdly, such a device is more suitable for measuring the permeation properties at steady state.

To measure both the transient and steady state permeation properties of a binary gas/vapor mixture, the traditional permeation time lag rig is modified by adding a cold trap around the downstream vessel. By controlling the temperature of the cold trap, one species (the vapor) can be condensed to liquid or solid phase while the other species (the gas) still remains in the gas phase. In this way, the transient and steady state permeation properties can be determined for the mixture and for its components, respectively. The schematic diagram of the modified system is shown in Figure 5-8. Compared to the traditional diffusion cell, this method requires little extra resources and does not disturb the membrane cell. In our experimental rig, the upstream and downstream vessels

are Teflon-lined with the volumes of ~1,120 cc and ~170 cc, respectively. The temperature of the cold trap can be manipulated via a commercial Thermoset (with a temperature range of -40°C to 100°C). The cold trap can also be conveniently maintained at the dry ice (-78°C) or liquid nitrogen (-196°C) temperature.

Figure 5-8 Schematic diagram of the improved permeation rig.

To demonstrate the feasibility of this technology, the permeations of binary mixtures of water vapor-CO₂ were investigated on a CS-OA- (9 wt%) nanocomposite membrane. The membrane, which was obtained from the solution casting, was in the shape of a thin film with a diameter of 2.54 cm and a thickness of 20 μm. This system is the so-called ‘humidity-assisted’ permeation process because the hydrophilic CS membrane will swell under humid/wet conditions and become permeable to such gases as N₂, O₂ or CO₂ [21, 136]. The purpose of adding OA- is to increase the mechanical strength and selectivity of the membrane. The effects of the nanofiller/cross-linker on CS membrane properties have been discussed in other papers [65, 137].

The permeation of gas-vapor mixtures was conducted at room temperature (25°C). The system was first evacuated by a turbo molecular pump to a high vacuum of $\sim 10^{-4}$ torr. Meanwhile, the temperature of downstream vessel was stabilized at the desired value. The membrane, upstream and downstream vessels were then isolated by turning off the related valves as shown in Figure 5-8. Next, water vapor was charged to vessel 1 (volume of 500 cc) to the desired pressure and was then isolated. CO₂ gas was charged into the upstream vessel 2 (volume of 500 cc) to the designated pressure. Care was taken to prevent the condensation of water vapor when the two components were mixed (i.e. the partial pressure of water vapor should be below its saturation pressure at that temperature. A heating source was used to mildly heat up the two vessels to assist the mixing). Three binary mixtures of water-CO₂ were premixed in upstream vessels and tested in the subsequent permeation experiments. Table 5-3 lists the charged pressures of each component before mixing and the composition of the binary mixture after mixing.

Table 5-3 Compositions of the binary water-CO₂ mixtures.

Mixture No	Vessel pressure (torr)		Total pressure (torr)	Partial pressures (torr)		Percentage humidity (%)
	Water	CO ₂		Water	CO ₂	
1	20	7	12.1	8.9	3.2	37.5%
2	22	30	23.2	9.8	13.4	41%
3	21	180	89.7	9.4	80.3	39%

Note: Percentage humidity = partial pressure of water vapor/saturated vapor pressure of water

In Table 5-3, the total pressure and the partial pressure of each component were calculated based on ideal gas assumption. During the experiments, the pressures in upstream and downstream vessels were monitored continuously by pressure transducers and an Agilent® data logger. The steady-state permeation flux, J_{∞} , can be calculated from the gradient of pressure-time response, dP/dt , at the downstream vessel [10]. The steady state overall permeation flux (J) and the flux of CO_2 (J_I) can be derived directly with this technology.

The permeation of pure water vapor in the CS nanocomposite membrane is shown in Figure 5-9. The upstream pressure was charged to 23.8 torr (i.e. the saturated water vapor pressure at 25°C). The cold trap was kept at -14.5°C. It is observed that even though the CS nanocomposite membrane was highly hydrophilic, it took the water molecules ~600 s to penetrate the membrane before reaching quasi-steady state. This slow permeation process is attributed to the fact that the polymeric membrane is swelling constantly before the final quasi-steady state is reached. The swelling degree of the composite membrane can be up to ~180% in water solution [65]. Because the actual membrane thickness at steady state is a function of feed humidity, the permeation flux rather than permeability is used for comparison purposes in this study.

The hump in Figure 5-9 is due to water vapor at the downstream vessel being over-saturated to ~1.6 torr before condensation took place and stabilized at a pressure of 1.3 torr, the saturated vapor pressure of ice at the cold trap temperature [138].

Figure 5-9 Permeation of pure water vapor.

The membrane was found to be impermeable to pure CO₂ gas at dry conditions. However, CS-based membrane has been known to lose this gas barrier property at high humidity. To investigate this phenomenon, Mixture 1 (water (8.9 torr)-CO₂ (3.2 torr)) was charged into the upstream vessel for the testing. The pressure response at the downstream vessel is shown in Figure 5-10. It is seen that the overall permeation time lag increased to ~ 1400 s, which is about twice that of the pure water vapor. Furthermore, no appreciable amount of CO₂ has penetrated the membrane at this humidity (a percentage humidity of 37.5%), because there is no perceivable pressure increase after the system reached steady state (condensation stage) after 6,800 s. This suggests that, at this water vapor pressure (or humidity), the degree of swelling in the membrane is low so that water molecules penetrate slowly while CO₂ molecules cannot penetrate the composite membrane. This is consistent with the swelling experimental results. The degree of swelling of 9% CS-OA- membrane is about 145% in deionized

water. However, in the humidity of 37.5% water vapor environment, the degree of swelling in the membrane is correspondingly low.

Despond et al. [136] investigated the adsorption and permeation of water vapor in native CS film and found that, when the relative water vapor pressure (P/P_0 , where P_0 is the saturated vapor pressure of water at the temperature) is below 0.4, the sorption capacity and permeability of the membrane were generally low. When P/P_0 exceeded 0.4, however, they were significantly increased due to the plasticization effect. These results are in general agreement with our experimental observations, although our membrane is a composite one with lower degree of swelling and higher selectivity [65].

Figure 5-10 Permeation of Mixture 1 of water (8.9 torr) - CO₂ (3.2 torr)

Figure 5-11 shows the permeation of Mixture 2 (water (9.8 torr)-CO₂ (13.4 torr)). It is observed that the system reached its first quasi-steady state (in

Section I) in $\sim 1,300$ s (with a time lag of ~ 1000 s). After condensation had taken place, the pressure in the downstream vessel continued to increase at a slow but constant rate. Assuming that the permeated water vapor is frozen instantly to ice in the vessel, the system can be regarded to have reached its second quasi-steady state (in Section II). The pressure increase is due to the permeation of CO_2 gas only.

Figure 5-11 Permeation of Mixture 2 of water (9.8 torr) - CO_2 (13.4 torr)

Finally, the partial pressure of CO_2 gas was further increased in the feed of Mixture 3 (water vapor (9.4 torr) – CO_2 (80.3 torr)). The permeation results are shown in Figure 5-12. It is noted that CO_2 permeation flux is more significant at this feed condition, because the downstream pressure kept on rising significantly.

As the percentage humidities are close to each other in Mixture 2 and 3 (41%, vs. 39%), the increase in CO₂ permeation flux is then attributed to the high solubility of CO₂ in the swollen membrane because of its higher partial pressure in the feed. This explains the experimental observations in Figure 5-11 and 5-12. However, due to a significant drop in the absolute humidity (or the mass fraction of water vapor), it took a much longer time (~ 6,000 s) for the permeation of Mixture 3 to reach the quasi-steady state. With Mixture 1, the membrane is impermeable to CO₂ because of the lower partial pressure of CO₂ and lower humidity of the feed.

Figure 5-12 Permeation of Mixture 3 of water (9.4 torr) - CO₂ (80.3 torr)

The steady state permeation fluxes were calculated for each species and listed in Table 5-4. It is seen that pure water has the highest permeance and the shortest time lag. When the partial pressure of CO₂ increases, the flux drops

quickly while the overall time lag increases significantly. Meanwhile, the perm-selectivity of water decreases significantly from infinity to 2.5.

The overall permeation time lag of the mixture, L , was determined by the steady state time gradient of dP/dt in Section I, as shown in Figure 5-9 to Figure 5-12. The *apparent* time lags for CO_2 , L_2 , was determined by parallel up-lifting the straight line of pressure-time response in Section II to the condensation point then intercepting with the time axis. In doing so, we assume that the steady state permeation time gradient of CO_2 (dP/dt , P_i is the partial pressure of CO_2 in downstream vessel) is the same before and after the condensation point. The negative time lag value of CO_2 is possible as indicated by Ash [139], since that the time lag of a binary system is a complicated issue. In Table 5-4, the time lag of water, L_2 , is calculated using the equation:

$$L = j_1 L_1 + j_2 L_2$$

Where $j_1 = J_1/(J_1+J_2)$ is the flux fraction of species 1 [139]. It is seen in Figure 5-11 that, even CO_2 presents a very large negative time lag, its contribution in overall time lag is small due to low flux ratio.

Table 5-4 Permeation property of CS-OA- nanocomposite membrane

	H ₂ O (24 torr)	Mixture 1	Mixture 2			Mixture 3		
			Overall	H ₂ O	CO ₂	Overall	H ₂ O	CO ₂
Time lag (s)	630.0	1,375.0	990.0	~990.0	< 0	3,270.0	1,900	-12,000
Steady flux ×10 ⁵ (mol/m ² /s)	3.80	0.60	3.24	3.22	0.019	0.35	0.25	0.10
Perm- selectivity ($J_{\text{H}_2\text{O}}/J_{\text{CO}_2}$)	-	∞	165.0			2.50		

With this technology, two important issues may need to be taken into account in computing the permeation properties: a) the vapor-gas system is not an ideal gas mixture, and b) the gaseous CO₂ may adsorb onto the tiny ice crystals formed in the downstream vessel. The first issue can be solved by invoking the use of the equation of state for real gases, e.g. Peng-Robinson or Virial equations, in calculating the exact feed composition and the permeation fluxes. For the second issue, Adamson and Jone have demonstrated that CO₂ adsorbs very marginally on ice crystals at a much lower temperature ($< -70^{\circ}\text{C}$) while the formation of clathrate requires a considerably high pressure [140]. Because the setup turns the vapor into solid, it can handle a high flux of condensable vapor. If the permeation flux is high and contains large fraction of non-condensable gas, the volume capacities of upstream and downstream vessels should be further increased to approximate the constant boundary conditions needed in time lag analysis.

With a careful selection of temperature for the cold trap, this technology may be conveniently extended to study permeation/separation properties of a number of important real systems and used for such applications as: dehydration of nature gas and separation of binary mixtures of CO₂/N₂, CO₂/CH₄, H₂O/hydrocarbon, etc. It can significantly reduce the experimental efforts while providing valuable permeation information of the mixture and its components.

5.5 Summary

The permeation properties of water vapor on CS-OA- and CS-OAPS composite membranes were studied. With the increased loading of the composite particles, the flux and permeability were found to increase in general, confirming that the POSS nanofillers can effectively improve the flux/permeability/diffusivity of native CS membranes. It is suggested that OA- can disperse homogeneously into the CS matrix which functions more like a polymer and improve the hydrophilicity of the composite. The hydrophobic OAPS, on the other hand, functions mainly like the organic fillers which provide more diffusion channels within the particles. At the low filler content (or loading), OAPS is more effective in improving the water permeability.

The permeation properties of gas-vapor mixtures were conveniently measured by the proposed novel experimental method. It was demonstrated that, by adding a cold trap onto the traditional permeation time lag rig, this versatile technology can measure the permeation properties of a binary mixture, and more importantly, it can identify the contribution of each component. This technology can be adapted to study the permeation of a number of important gas mixtures in the future.

Chapter 6. Characterizing gas adsorption and permeation in CMS membranes

6.1 Introduction

An interesting phenomenon of “diffusion anomaly” is commonly observed in gas permeation in CMS membrane, that is, the diffusion coefficient presents stronger functional dependence on loading than the traditional Darken relation. Such phenomena were observed in different CMS membranes and were reported by a number of researchers such as: Koresh and Soffer [4], Ash, Barrer and Pope [11], Lagorsse, Magalh and Mendes [12], Galiatsator, Kanellopoulos and Petropoulos [141], and Wang, Suda, Loo and Haraya [10, 142]. In their analysis, this diffusion anomaly (also referred to as non-Fickian diffusion) has been attributed to a number of factors such as: surface heterogeneity, multilayer sorption and interaction of the adsorbed species, local isotherms, time or spatial dependence of the diffusion coefficient, or the existence of blind pores, etc.

It is generally agreed that the structural heterogeneity of the microporous network of the membrane plays a dominant role in dictating this diffusion anomaly. It also results in the discrepancy between the gas permeation properties at the transient and steady states. Therefore, the modeling of gas permeation in a CMS membrane may require a proper understanding of the structural characteristics of the microporous network and the difference in the

diffusion paths at the transient and steady states [134]. There are very few studies on the comparison of gas permeation at the transient and the steady states. As molecules with different configuration and dimension may present different accessibility in the porous network of a membrane, the comparison of diffusion behaviors of various gas molecules are also important for the characterization of a CMS membrane.

In this chapter, we will investigate 1) CO₂ adsorption equilibrium on a CMS membrane (KP1000) at ambient temperature and in a wide pressure range, and 2) Ar adsorption and permeation in a CMS membrane (KP800). The adsorption properties will be discussed while the diffusional anomalies will be modeled for the transient as well as steady state permeation processes in an integral approach and compared with other permeation gas species.

6.2 CO₂ adsorption on KP1000

6.2.1 Isotherm models

The adsorption of gas molecules on microporous CMS materials generally follows the type I isotherm (IUPAC), which is described by the Langmuir equation:

$$C_{\mu} = C_{\mu s} \frac{bP}{1 + bP} \quad (6-1)$$

where b is sorption affinity, P is the bulk phase pressure, C_{μ} is the adsorbed phase concentration, and $C_{\mu s}$ is the sorption capacity. Eq. 6-1 is generally applicable for a homogeneous surface. For an adsorbent with structural heterogeneity, the Toth isotherm is a better choice:

$$C_{\mu} = C_{\mu s} \frac{b_t P}{[1 + (b_t P)^t]^{\frac{1}{t}}}$$

(6-2)

where t is the heterogeneity parameter for the sorption system. Eqs. 6-1 and 6-2 will be used to compare with the experimental data.

6.2.2 Results and discussion

The high pressure CO₂ adsorption experimental data are plotted in Figure 6-1 with the adsorption data (shown as solid symbols) and desorption data (shown as hollow symbols). Slow sorption rates were noted (especially for the first pressure point); however, the adsorption and desorption data virtually overlap with each other, and no evidence of micropore hysteresis was observed in this system. Also shown in Figure 6-1 are the fits using the Langmuir isotherm (solid lines) and the Toth isotherm. It is observed that the Toth isotherm gives a slightly better fit. Table 6-1 shows the optimal model parameters and the goodness of fit (in terms of the average relative error, or ARE) of the two models.

Table 6-1 Optimal isotherm parameters

T	Langmuir isotherm			Toth isotherm			
K	$C_{\mu s}$	b	ARE	$C_{\mu s}$	b_t	t	ARE
	(mmol/g)	(kPa ⁻¹)		(mmol/g)	(kPa ⁻¹)		
298	3.32	1.19×10 ⁻²	10.7	3.65	2.46×10 ⁻²	0.63	8.99
333	3.07	6.44×10 ⁻³	4.57	3.31	9.69×10 ⁻³	0.725	2.65
353	2.86	4.36×10 ⁻³	2.91	3.21	6.36×10 ⁻³	0.70	1.31

Note: The average relative error (ARE) is defined as: $ARE = \frac{100}{N} \sum_{k=1}^N \frac{|Y_{model} - Y_{exp}|}{Y_{exp}}$

Figure 6-1 CO₂ isotherm on KP1000 CMS membrane measured with microbalance. — Langmuir; ---- Toth; ● ■ ▲ Adsorption; ○ □ △ Desorption.

The heterogeneity parameter of the Toth isotherm ($t \approx 0.7$) suggests that KP1000 has a relatively homogeneous surface compared to commercial activated carbon (in which t generally ranges from 0.2 to 0.5) [143]. This is in agreement with the molecular probe experiments, which show that the pore sizes of KP1000 are below 7 Å (effective pore size, wall to wall).

The surface barrier effect (i.e., slow sorption rate when molecules penetrate the narrow necks of micropores) generally occurs for gas sorption on CMS materials, and this effect is significant for the KP1000 sample. Figure 6-2 shows CO₂ isotherms measured with a standard pore and surface analyzer. The pore and surface analyzer uses a different measuring methodology (volumetric) compared to the microbalance (gravimetric) and is capable of measuring

sorption at pressures as low as 0.133 Pa. The criteria used for the pore and surface analyzer to decide the *EQUILIBRIUM* for a dosing is set so that the pressure variation must be less than 0.133 Pa in 5 min. with such a criterion, it is seen in Figure 6-2a that the desorption data (hollow symbols) significantly deviate from the adsorption data (solid symbols) at all experimental temperatures. These hysteresis are indications of surface barriers at low sorption pressure, confirming the existence of a portion of small micropores in KP1000 which are difficult for CO₂ molecules to penetrate. This surface barrier becomes much stronger in the case of N₂ sorption at 77 K so that the equilibrium criteria ($\Delta P < 0.133$ Pa in 5 min) cannot be met for the first isotherm point within days, making it impractical for the standard N₂ sorption measurement.

Figure 6-2b combines the adsorption isotherms of CO₂ measured by the two methods at 333 K (on the logarithmic scale). It is seen that, considering the experimental error and different techniques, the two isotherms (methods) agree well with each other at a similar pressure range.

Figure 6-2 (a). CO₂ isotherm measured by the pore and surface analyzer (volumetric technology). Solid symbol = adsorption; hollow symbol = desorption; (b). The combined adsorption isotherm of CO₂ on the CMS at 333K.

6.3 Adsorption and permeation of Argon on KP800

6.3.1 Theory

The adsorption isotherm of Ar on KP800 membrane is assumed to follow the Langmuir isotherm described in Eq. 6-1. The diffusion flux, J_μ , of the gaseous species in the microporous network of the membrane is expressed in terms of the gradient of the adsorbed phase concentration, C_μ , as:

$$J_\mu = -D_\mu \frac{\partial C_\mu}{\partial r} \quad (6-4)$$

where r is the diffusion path and D_μ is the apparent diffusion coefficient which relates to the diffusion coefficient at zero loading, D_μ^0 , via the local isotherm:

$$\frac{D_\mu}{D_\mu^0} = \left(\frac{\partial \ln P}{\partial \ln C_\mu} \right)_T \quad (6-5)$$

where P is the hypothetical bulk phase pressure in equilibrium with the adsorbed phase, and T is the temperature. D_μ^0 is specific to the sorption system and independent of the surface loading. Eq. 6-5 is the popular Darken relation. With the Langmuir isotherm $C_\mu = C_{\mu s} bP / (1 + bP)$, Eq. 6-5 will reduce to:

$$D_\mu = \frac{D_\mu^0}{1 - C_\mu / C_{\mu s}} = \frac{D_\mu^0}{1 - \theta} \quad (6-6)$$

Where θ is the surface loading. Eq. 6-6 is the HIO model (the model is named after the initials of the authors: Higashi, K; Ito, H.; Oishi, J.) for a homogenous surface [144]. To cope with experimental observations, a modified HIO model was used [142], which allows D_μ to take a flexible dependence on loading:

$$D_\mu = \frac{D_\mu^0}{(1 - C_\mu / C_{\mu s})^n} = \frac{D_\mu^0}{(1 - \theta)^n} \quad (6-7)$$

where 'n' represents the heterogeneity for diffusion. Eq. 6-7 reduces to the Darken relation with the Langmuir isotherm and $n = 1$. The overall mass balance on a slab membrane with the thickness of l is:

$$\frac{\partial C_\mu}{\partial t} = \frac{\partial}{\partial r} \left(D_\mu \frac{\partial C_\mu}{\partial r} \right) \quad (6-8)$$

Eq. 6-8 is subject to the boundary conditions of the system, that is:

$$@ r = 0, P = P_0; @ r = l, P = 0; @ t = 0, C_\mu = 0,$$

The time lag expression can be derived from Eq. 6-8 and the boundary conditions using the method of Frisch [131] as:

$$L = \frac{l^2(n-1)}{D_\mu^0(w-1)} \times \left[\frac{1}{2} + \frac{(n-1)^2 w^{2+1/(1-n)} - (n-1)(n-2+3w-2nw)}{(2-n)(2n-3)(w-1)^2} \right] \quad (6-9)$$

where $w = (1 + bP_0)^{(n-1)}$. If the diffusion is Darken type (Eq. 6-6), the expression of time lag will become [145]:

$$L = \frac{l^2}{D_\mu^0} \left\{ \frac{1}{\ln(1 + bP_0)} \left[\frac{1}{2} - \frac{1}{(1 + bP_0) \ln^2(1 + bP_0)} - \frac{\ln(1 + bP_0) - 1}{\ln^2(1 + bP_0)} \right] \right\} \quad (6-10)$$

The steady state permeation flux is obtained by integrating Eq. 6-4 at the time of infinity:

$$J_\mu^\infty = \frac{1}{l} \times \int_0^{P_0} D_\mu f'(P) dP \quad (6-11)$$

Therefore, the permeability (normalized flux) will take the form of:

$$P_e = \frac{J_\mu^\infty}{\Delta P/l} = \begin{cases} \frac{C_{\mu s} D_\mu^0}{P_0} \ln(1 + bC_0) & n = 1 \\ \frac{C_{\mu s} D_\mu^0}{P_0} \times \frac{(1 + bC_0)^{(n-1)} - 1}{n-1} & n \neq 1 \end{cases} \quad (6-12)$$

Eq. 6-9 and Eq. 6-12 will be used to compare with the experimental data of time lag and permeability, respectively. The purpose of this modeling is to take an integral approach for both transient and steady state permeation processes. The surface is assumed to be homogeneous for adsorption (a Langmuir isotherm is used) so that the diffusion anomalies were solely contributed by the heterogeneity factors in the diffusion process, represented by the parameter ' n ' in Eq. 6-7.

6.3.2 Results and discussion

The sorption isotherms of Ar were measured at 308 K, 333 K, and 363 K, respectively, and plotted in Figure 6-3a and 6-3b as symbols. It is seen in Figure 6-3a that, with pressures up to 10 atm, the isotherms are largely linear. Figure 6-3b shows the high pressure isotherm of Ar at 333 K on the logarithmic scale, from which we can see that the sample is still far from the saturation at the pressure of 40 atm. The experimental data were fitted to Langmuir isotherm (shown as continuous lines in Figure 6-3a and 6-3b), and the optimal isotherm parameters were listed in Table 6-2. It can be seen that Langmuir isotherm adequately fits the experimental data at all three temperatures. In the fitting procedure, the sorption capacities are set as the same, so that the high pressure isotherm data can exert constraint for the sorption capacity, as proposed by other researchers [146] in the modeling of high pressure and multiple-temperature isotherms.

Figure 6-3 Isotherm data of Ar (dots) and the fittings of the Langmuir isotherm (lines) at (a). 308 and 363K. (b) 333 K (logarithm scale).

Table 6-2 The optimal isotherm and diffusion coefficients

T (K)	Isotherm		Time lag		Permeability	
	$C_{\mu s}$ (mmol/g)	b (kPa ⁻¹)	D_{μ}^0 (cm ² /s)	n	D_{μ}^0 (cm ² /s)	n
308	0.281	1.18×10^{-3}	1.53×10^{-10}	1.84	3.33×10^{-8}	1.86
333	0.281	6.61×10^{-4}	3.63×10^{-10}	1.71	7.57×10^{-8}	1.7
363	0.281	3.59×10^{-4}				

6.3.3 Permeability and irregular channels

Ar permeations was measured at 308 K and 333 K, respectively, with permeation (upstream) pressures up to ~15 atm. The permeation time lags are shown in Figure 6-4 as symbols. The modified HIO model (Eq. 6-7) is fitted to the experimental data via the least square scheme and presented as continuous lines in Figure 6-4. It is seen that the model adequately fits the pressure dependence of the time lag data. On the other hand, attempting to fit the data with the traditional Darken model (Eq. 6-8 with $D_{\mu}^0=1.55 \times 10^{-10}$ cm²/s) results in a curve (dashed line), which considerably underestimates the pressure dependence of the experimental data. The optimal parameters for the modified HIO model are listed in Table 6-2 with $n = 1.8$ in Eq. 6-7. This proves that Ar permeation at transient state presents strong pressure dependence and the apparent diffusion coefficient shows a functional dependence on loading which is stronger than the traditional Darken relation. Such diffusion anomalies were also observed by Wang [134] for other species (N₂ and CO₂) on the same membrane and have been attributed (on the microscopic scale) to the existence

of blind pores in the membrane matrix. Strano and Foley have also observed similar phenomena on a supported CMS membrane [145]. Table 6-3 compares the sorption and permeation properties of Ar, N₂ and CO₂.

Table 6-3 Sorption/permeation properties of Ar, CO₂, and N₂ on KP800 at 308 K

Gas	σ (Å)	$D_{\mu 0}$ (cm ² /s)	N	$C_{\mu s}$ (mmol/g)	b (1/kPa)	ϵ_{SLP} (kJ/mol)	H_{ads}/ϵ_{SLP}
Ar	3.54	1.5×10^{-10}	1.8	0.28	1.18×10^{-3}	9.0	2.2
CO ₂	3.30	1.3×10^{-8}	1.6	4.6	1.16×10^{-2}	16.8	1.3
N ₂	3.64	3.6×10^{-9}	1.9	0.25	1.25×10^{-3}	8.8	1.6

Note: ϵ_{SLP} = Theoretical heat of adsorption for a species on a graphite

basal plane noted by Rao et al. [147].

Table 6-3 indicates that the sorption capacity and affinity of Ar are comparable to that of N₂. An Arrhenius plot of the sorption affinities ($b = b_{\infty} \exp (H/RT)$) gives a sorption energy (H_{ads}) of ~20 kJ/mol for Ar, which is about 2.2 times the heat of adsorption of Ar on a graphite basal plane (ϵ_{SLP} , listed in Table 6-3). In comparison, CO₂ presents a heat of adsorption of $\sim 1.3 \times \epsilon_{SLP}$ while this value for N₂ is $1.6 \times \epsilon_{SLP}$. The derived diffusion heterogeneity (n) follows the order of molecular sizes of the three gaseous species, i.e., N₂ > Ar > CO₂. Under the assumptions that the micropores are essentially slit-shaped with layers of graphite basal planes and that adsorbate-pore interactions are predominantly dispersive, these apparent discrepancies can be qualitatively explained as follows: (1) the small CO₂ molecules experience less diffusion barrier ($n = 1.6$) and weaker overlapping ($1.3 \times \epsilon_{SLP}$) of the sorption potentials from opposite

walls of micropores, (2) the large N_2 molecules experience strong diffusion barrier and some strong repulsion interaction from the micropores, and (3) Ar presents strong potential overlapping in micropores with the width of $\sim 2\sigma_{sk}$ ($\sim 10 \text{ \AA}$, calculated from the 10-4-3 potential, where σ_{sk} is the collision diameter). The above analysis is consistent with the pore size distribution of the membrane (5-12 $\text{\AA}$) as revealed by N_2 sorption and molecular probe experiments [123]. Another interesting phenomenon is that, N_2 , which has larger dimensions than Ar, has a permeability comparable to that of Ar (Table 6-1). This observation suggests that sorptivity is as important as the molecular sieving (diffusion barrier) for gas permeation in the microporous CMS membrane (because the sorptivity, $b_{N_2} > b_{Ar}$), which is consistent with the observation (Table 6-1) that H_2 (2.89 $\text{\AA}$) presents a permeability three times that of helium (2.6 $\text{\AA}$). The above analysis suggests that the sorption and permeation characteristics of Ar, N_2 and CO_2 are consistent to their molecular properties and Ar can be used as a reference molecule for the estimation of permeation properties of other gaseous species.

The steady state permeation fluxes (permeabilities) of Ar were also measured at the permeation pressures up to 15 atm and at the temperatures of 308 K and 333 K, respectively. The experimental data were plotted in Figure 6-5. The data were fitted with Eq. 6-10. The diffusion coefficients and heterogeneity parameters were optimally derived for the steady state data and listed in Table 6-2. It can be seen that the pressure dependence of the permeability is well described by the modified HIO model and the diffusion heterogeneities (n) are close to the values derived from the transient state permeation time lags. The

derived diffusion coefficients at zero loading ($D_{\mu 0}$), however, show considerable discrepancy (orders of magnitude) between the transient state ($1.53 \times 10^{-10} \text{ cm}^2/\text{s}$ at 308 K) and steady state ($3.33 \times 10^{-8} \text{ cm}^2/\text{s}$). Such a difference has been observed for gas permeations in microporous media by a number of researchers [11, 12, 131, 148]. The main reason for this disparity was attributed to the structural heterogeneity and pore connectivity in the CMS membrane. The complicated 3D microporous network (the turbostratic structure) forms graphite pores with various connectivities and sizes so that the porous networks involved in the mass transport can be very different for the transient and steady states. For example, the “blind pores” (ink-bottled pores or dead-end pores) which function as “adsorbate sinks” during transient permeation process will reach the sorption equilibrium at the steady state (cease to adsorb in gas adsorbates). This will considerably decrease the overall diffusion coefficient at the blind pores account for the majority of sorption capacity of the CMS membrane [123]. However, as Table 6-2 suggests, because the membrane structure is formed by the controlled thermal pyrolysis, the porous network is relatively homogeneous on macroscopic level so that the diffusion heterogeneity felt by the penetrating molecules can be of the similar degree for the transient and steady states. This is in support of the experimental results that the degree of diffusion heterogeneity is approximately the same for transient and steady states.

Figure 6-4 The permeation time lag (symbols) versus permeation pressure. The solid line is the fitting of the modified HIO model; dashed line is the Darken model.

Figure 6-5 The steady state permeability (symbols) versus the upstream permeation pressure. The solid line is the fitting of Eq. (6-12). (1 Barrer = 1×10^{-10} cc(STP)cm/(cm²scmHg))

6.4 Summary

The sorption and permeation properties of CO₂ and Ar were measured on microporous CMS membrane (KP1000 and KP800, respectively) over a range of temperature and permeation pressure. The adsorption/desorption isotherms of CO₂ data were fitted reasonably well by the Langmuir isotherm as well as by the Toth isotherm. Isotherm analysis suggests that: (1) the micropore hysteresis is not significant at high pressure; (2) the membrane sample has a relatively uniform structure with a portion of small micropores; and (3) the surface barrier is significant at low sorption pressure.

For Ar permeation, the diffusion coefficient was found to present stronger pressure dependence than the traditional Darken relation at both transient and steady state permeation processes. It is further demonstrated that the degree of this deviation can be represented in a heterogeneity parameter in the modified HIO model and is approximately the same for the transient and steady states. Comparison analysis reveals that this heterogeneity is dependent on the molecular properties and the sorption properties of the penetrating gas molecules.

Chapter 7. Characterizing the structure of CMS membrane by adsorption and permeation

7.1 Introduction

CMS materials comprise micropores of relatively uniform size, which enable the discrimination of gas molecules with very similar dimensions [1, 3, 8]. Due to the structural characteristics (ultramicropores with narrow pore size distribution, or PSD), it is impractical to characterize their structure via traditional methods such as N₂ sorption at -196 °C because of the extremely slow sorption rate. An alternative method is to analyze, at ambient temperature, the sorption isotherm of a suitable adsorbate whose rate of adsorption is much faster [122]. CO₂ sorption at room temperature appears to be a good choice because: (1) the CO₂ molecule is small in size and is capable of penetrating very small micropores, and (2) the sorptivity of CO₂ is high at room temperature. The drawbacks of CO₂ sorption may be: (1) nonideality at high pressure; (2) the molecule is not spherical in shape; and (3) CO₂-pore interaction is not purely dispersive. These factors, however, can be adequately addressed by taking into account a number of thermodynamic properties of the sorption system.

As the “sorption-diffusion” is the mechanism for gas permeation in such membranes, it is desirable that we characterize the sorption as well as the

diffusion properties of a membrane sample using a reference gas, and based on which the prediction/estimation can be made for other gases. Helium gas was popularly used in characterizing gas permeation in microporous media, which is spherical, non-polar and fast penetrating. However, helium, being a small molecule ($\sigma = 2.6 \text{ \AA}$), cannot effectively probe large micropores and the sorption properties, as it is virtually non-adsorbing at room temperature. In contrast, Ar is large in size ($\sigma = 3.54 \text{ \AA}$) and strong in sorption (comparable to N_2) so it is potentially a good candidate to probe a microporous membrane for its sorption and diffusion properties. The popular approach to characterize a porous media is to simulate the observed isotherm using the local pore isotherm (or density) generated with various theories (such as DFT or GCMC), and to derive the pore size/volume distributions. Such approaches are theoretically sound, but give no information about the pore connectivity, which is critical to the separation performance of a porous membrane.

In the previous chapter, the diffusion anomalies were attributed to the surface heterogeneity in term of a heterogeneity parameter in modified HIO model. Intrinsically, this heterogeneity should arise from the porous network of the membrane itself and be reflected in the adsorption as well as mass transport behaviors. Therefore, this chapter will characterize this structure of a CMS membrane based on the sorption as well as the permeation properties of gas permeate.

7.2 Theories

The porous structure of the membrane can be derived from the analysis of multiple adsorption isotherms with the mathematical model proposed by Nguyen, Do, Haraya and Wang [121, 122]. The blind pore characteristics of the membrane, which has been known to cause the observed diffusion anomalies, can be characterized via the transient permeation kinetics using the mathematical model proposed by Wang [134]. Details of those models can be found in the original publications, and we only briefly present the essential features of the models here.

The observed isotherm is the contribution of local isotherms (assumed to be Langmuir) of all pores:

$$C_{\mu}(p) = \int_0^{\infty} C_{\mu s}(r) \frac{b_{pore}(r) p_{pore}(r)}{1 + b_{pore}(r) p_{pore}(r)} f(r) dr \quad (7-1a)$$

where r is pore size, P is pressure, b is sorption affinity, C_{μ} is adsorbed phase concentration, $C_{\mu s}$ is sorption capacity. The subscript 'pore' represents the property in pore phase. The pore pressure relates to the bulk pressure via:

$$p_{pore} = p_{bulk} \exp\left(\frac{-E_{pore}^g}{RT}\right) \quad (7-1b)$$

where T is temperature, E_{pore}^g is potential energy of the gas phase molecules confined in the pore interior. The sorption affinity of the pore, b_{pore} , is:

$$b_{pore} = b_s \exp\left(\frac{E_{pore} - E_s}{RT}\right) \quad (7-1c)$$

with $b_s = \frac{\beta}{\sqrt{MT}} \exp(E_s / RT)$ where E_s and b_s are the heat released and the affinity of adsorption on a flat surface, respectively; E_{pore} is sorption energy in a pore (related to the sorption potential at the mid-plane). M is the molecular weight, β is a parameter characterizing the solid surface. The model parameters can be calculated from molecular properties and surface properties of the adsorbate/adsorbent with the assumptions that micropores are slit-shaped while adsorbate-pore interaction is dispersive [122]. This model was used by Nguyen et al. and Lagorsse et al. [149] to characterize the structure of CMS membranes.

By matching the theoretical equation (Eq. 7-1) to the experimental data of multiple isotherms, we can derive the pore size distribution $f(r)$.

Eqs. 7-1 states that the overall isotherm is the contribution of pores of different size. However, the derived pore size distribution does not discriminate the two types of pores (through pores and blind pores) and therefore it does not contain any information about pore connectivity (other models such as DFT, GCMC, HK, etc., have the same problem). To discriminate between through pores and blind pores, we resort to the transient permeation kinetics because the roles that these pores play are different [134]. The mass balance equation for gas permeation in a slab membrane with the thickness of l is:

$$\varepsilon_T \frac{\partial C_\mu^T}{\partial t} + (1 - \varepsilon_T) \frac{\partial C_\mu^B}{\partial t} = \frac{\partial}{\partial z} \left(\varepsilon_T D(C_\mu^T) \frac{\partial C_\mu^T}{\partial z} \right) \quad (7-2a)$$

where t is time, z is diffusion coordinate, and ε is porosity. The subscripts 'T' and 'B' represent the through pore and blind pore, respectively. D_μ is the

diffusion coefficient following the Darken type concentration dependence, $D_{\mu} = D_{\mu}^0 \left(\partial \ln P / \partial \ln C_{\mu} \right)_T$, D_{μ}^0 is the diffusion coefficient at zero surface loading. The overall sorption isotherm is then the combination of the isotherms in blind and through pores, represented by Langmuir isotherms:

$$C_{\mu}(p) = \varepsilon_T C_{\mu}^T + (1 - \varepsilon_T) C_{\mu}^B = \varepsilon_T C_{\mu}^T \frac{b_T p}{1 + b_T p} + (1 - \varepsilon_T) C_{\mu}^B \frac{b_B p}{1 + b_B p} \quad (7-2b)$$

The analytical expression of permeation time lag (L) was derived from Eqs. 7-2 using the method of Frisch and shown in Appendix A. Eq. A-1 together with Eq. 7-2b are used to compare with the permeation time lag data and isotherm data, respectively, to derive the contribution of blind pores and through pores.

The idealized structural model of the CMS membrane can be schematically shown in Figure 7-1.

Figure 7-1 The idealized structural model of the CMS membrane.

7.3 Results and discussion

Figure 7-2a shows the sorption isotherms (symbol) of Ar measured at 308 K, 333 K and 363 K. Eq. 7-1 were used to fit all three isotherms simultaneously and shown in the same figure as the solid line. The resulting pore size distribution is shown in Figure 7-2b.

It is seen that Eq. 7-1 adequately fits the isotherm data over the wide experimental pressure range. Figure 7-2b shows that the membrane is predominantly microporous, with a major capacity at 7-10 Å and smaller capacities at 6 Å and 18-20 Å. This is expected as the controlled pyrolysis of a polymeric precursor will generate pores of relatively uniform sizes and this uniformity largely depends on the soaking temperature [3, 10].

Figure 7-2 (a) Ar isotherm (symbols) at 308K, 333K and 363K. (— Eqs. 7-1, -- Eq. 7-2b) and (b) The distribution of the Ar sorption capacity of the membrane sample.

To further discriminate the contribution of blind pores and through pores within the membrane structure, Eq. A-1 was used to study the permeation time lag of Ar measured at 303 K and 333 K. The experimental data were plotted in Figure 7-3 as symbols while the model simulations were presented as solid lines. It is seen that the time lag model with blind pore characteristics (solid line) correctly simulated the pressure dependence of the experimental data. In comparison, the time lag model with a Darken type concentration dependence and with no blind pore contribution (the dashed line in Figure 7-3, represented by the L_T term in Eq. A-1) considerably underestimates the pressure dependence of the time lag data. The simultaneous fittings of the isotherm data with Eq. 7-2b are shown in Figure 7-2a as dashed lines, where we see the fit is satisfactory.

Figure 7-3 The permeation time lag (symbols) versus permeation pressure. The solid lines are the simulation of time lag model with blind pore characteristics, Eq. A-1; Dashed line is the time lag model with Darken type concentration dependence only, or time lag in through pore (L_T term in Eq. A-1).

The derived blind pore contributions were listed in Table 7-1. It is seen that, at 308 K, blind pores have a sorption capacity of 8 times and an affinity of 5 times those of through pores. As temperature increases, these ratios increase to 14 times and 7 times, respectively. These indicate that the majority of the sorption capacity is contributed by blind pores (or sorption pores). As these blind pores occupy a major volume fraction in the overall network, they function as the “concentration sinks” in transient permeation processes and cause the diffusion anomalies [11]; the through pore, on the other hand, behave more like “bottle necks”, which present diffusion barrier and high selectivity for different molecules (Table 3-4). With the information of probe permeation experiments

(Table 3-4) and the blind pore characters (Table 7-1), we further discriminate the porous network of the membrane into the following categories for Ar permeation:

Table 7-1 The optimal isotherm parameters and diffusion coefficients

T	$C_{\mu s}^B$	b_B	$C_{\mu s}^T$	b_T	D_{μ}^0
K	mmol/g	kPa ⁻¹	mmol/g	kPa ⁻¹	cm ² /s
308	0.262	1.33×10^{-3}	2.98×10^{-2}	2.57×10^{-4}	1.96×10^{-7}
333	0.267	7.05×10^{-4}	1.87×10^{-2}	9.43×10^{-5}	1.19×10^{-6}

Blind pores ($r \geq 7 \text{ \AA}$)

This is estimated from the permeation probe experiments, in which the membrane sample was found impermeable to CF₄. As CF₄ is a spherical molecule with the dimension of 4.7 Å, this put the size limit for the through pores at ~ 7 Å. This value is calculated in this way: for a slit-shaped pore with 10-4-3 potential configuration, the smallest pore that an adsorbate can enter is the one with zero sorption potential, i.e., pore width $d = 2 \times 0.815 \times \sigma_{sk} \sim 7 \text{ \AA}$ (center to center distance) [150]. Therefore, based on probing experiments, pores with size of 7 Å and above in Figure 7-2b can be regarded as blind pores. They contribute the major sorption capacity of the membrane.

Main peak of through pores ($6 \text{ \AA} < r < 7 \text{ \AA}$)

This is the size range where the majority of through pores can be found. Ar sorption affinity in such pores change drastically from very low at 6 Å to very high at 7 Å. As the sorption capacity in through pores is about 10% that of blind pores and the sorption affinity is about 20% that of blind pores (Table 7-1), we

can deduce that most through pores are around 6 Å while the pore size of most blind pores is about 7 Å. The variation of pore size of the through pores is further supported with the perm-selectivity of the membrane of different gas pairs (Table 3-4). A simple computation shows that $P_{N_2}/P_{CO_2} = 33$ for KP800, which is much lower than $P_{N_2}/P_{CO_2} = 93$ in the other CMS membrane [3, 10], suggesting there is a size distribution of through pores in KP800 membrane.

Ink-bottle pores ($14 \text{ Å} < d < 20 \text{ Å}$)

The pore size distribution obtained from the analysis of Ar isotherms show some modest contribution from large pores, on the other hand, the analysis of N_2 adsorption isotherms on the same membrane did not find any contribution from pores larger than 12 Å [134]. From this, we can attribute pores having sizes behavior 14-20 Å as ink-bottle pores which have narrow necks accessible only to the smaller Ar molecules.

The results of the above analysis are summarized in Figure 7-4, in which the sorption capacity of Ar was classified into ink-bottle pores, through pores, blind pores and mixed regions. Also shown in the same figure is the magnitude of sorption potential energy in micropores (calculated from 10-4-3 potential [150]) for Ar molecule. If these energy values roughly approximate the sorption energy in the local pores, we conclude that our classification is consistent with the structural characteristics revealed by the permeation probe experiments as well as the blind pore characteristics derived from the transient gas permeation data. We expect that more accurate structural characterization is possible if adsorption and permeation data of more adsorbates are available. The two

mathematical models used in this work will serve as useful tools in such application.

Figure 7-4 The discrimination of the pores in KP800 CMS membrane. The dotted line is the magnitude of potential energy in pores of different sizes.

7.4 Pore irregularity and steady state permeation flux

7.4.1 Theory

In term of gas permeation, the structure of a CMS membrane can be grouped into two types of pores: through pores and blind pores. In the last section, the effect of each type of pore was studied based on the ideal structural model. This model is successful in modeling the diffusion anomalies at the transient state permeation. However, the steady state permeation properties were not taken into account, in which the pore structures as well as the pore connectivities play the dominant role. To account for such factors, a structural model was setup for

the permeation in CMS membrane at the steady state and was shown in Figure 7-5.

Figure 7-5 The schematic diagrams of CMS membrane and the 3-section model.

At steady state permeation, the dead-end pores (blind pores) will be filled and the permeation only takes place in through pores. The permeation channel is assumed to take the form shown in Figure 7-5, in which a big volume (or bottle) is connected by two small necks. The bottle is mainly responsible for the sorption capacity of the membrane while the necks present molecular sieving effect for the permeation selectivity. This is a reasonable picture, as many CMS materials have ‘ink-bottle’ pores with relatively homogeneous size in pore necks.

Based on such a model, the overall isotherm again takes the Dual-Langmuir equation:

$$C_{\mu} = \varepsilon_T C_{\mu}^T + (1 - \varepsilon_T) C_{\mu}^B = \varepsilon_T C_{\mu s}^T \frac{b_T P_T}{1 + b_T P_T} + (1 - \varepsilon_T) C_{\mu s}^B \frac{b_B P_B}{1 + b_B P_B} \quad (7-3)$$

where C_{μ} is the adsorbed phase concentration with the capacity of $C_{\mu s}$, b is the sorption affinity, ε_T is the volume fraction of through pores, P is the hypothetical bulk pressure in micropores. To keep the consistence with the previous blind pore model, the subscripts ‘ T ’ and ‘ B ’ are again used to

represent the ‘Throat’ pore and ‘Bottle’ pore, respectively. The volume fraction of each type of pore will combine with the maximum capacity to form the apparent capacity of its own category of pores. The contribution of the blind pores (which functions only as the concentration sink for sorption equilibrium, but no contribution to transport) will be lumped into the ‘Bottle’ pores. The diffusion in the channel follows the Darken relation,

$$D_{\mu}(r) = D_{\mu}^0(r) \left(\frac{\partial \ln P}{\partial \ln C_{\mu}} \right)_T = \frac{D_{\mu}^0(r)}{1 - \theta_T} \quad (7-4)$$

and

$$D_{\mu}^0(r) = D_{\mu\infty}^0 \exp \left(- \frac{aE(r)}{R_g T} \right) \quad (7-5)$$

where t is the time, r is the diffusion coordinate and D_{μ} is the diffusion coefficient, D_{μ}^0 is the diffusion coefficient at zero loading and θ_T is the fractional surface loading in through pores. $D_{\mu\infty}^0$ is the surface diffusivity at infinite temperature, and ‘ a ’ is the ratio of activation energy to sorption energy. The boundary conditions for Eq. 7-3 are:

$$P = P_0 @ r = 0; P = 0 @ r = l; C_{\mu}^T = 0 \text{ and } C_{\mu}^B = 0 @ t = 0 \quad (7-6)$$

The sorption affinity, $b(r)$, is a function of pore size and has been derived from the kinetic theory of gas adsorbing in porous media as [151]:

$$b(r) = \frac{\beta}{\sqrt{MT}} \exp \left(\frac{E(r)}{RT} \right) \quad (7-7)$$

where β is the affinity parameter specific to the surface properties of AC, M is the molecular weight, and $E(r)$ is the adsorbate-pore interaction energy taken as the modulus of the sorption potential minimum (e.g. 10-4-3 potential).

$$\varphi(r,z)=\frac{5}{3}\varepsilon_{sk}^*\left\{\frac{2}{5}\left[\left(\frac{\sigma_{sk}}{r+z}\right)^{10}+\left(\frac{\sigma_{sk}}{r-z}\right)^{10}\right]-\left[\left(\frac{\sigma_{sk}}{r+z}\right)^4+\left(\frac{\sigma_{sk}}{r-z}\right)^4\right]-\left[\left(\frac{\sigma_{sk}^4}{3\Delta(0.6\Delta+r-z)^3}\right)+\left(\frac{\sigma_{sk}^4}{3\Delta(0.6\Delta+r-z)^3}\right)\right]\right\} \tag{7-8}$$

where r is the pore radius (or half-width), z is the distance between the adsorbate and a pore wall, $\varepsilon_{sk}^* = \frac{6}{5}\pi\rho_s\varepsilon_{sk}\sigma_{sk}^2$, Δ represents the interaction energy minimum between the adsorbate molecule and a side wall, ρ_s is the number density of carbon molecule per unit volume. Δ and ρ_s are generally have the values of 0.335 nm and 114 nm⁻³, respectively.

ε_{sk} and σ_{sk} are the cross Lenard-Jones parameters calculated using a geometric mean and arithmetic mean (Lorentz-Berthelot rule), respectively:

$$\varepsilon_{sk} = \sqrt{\varepsilon_{ss} \times \varepsilon_{kk}}, \quad \sigma_{sk} = \frac{\sigma_{ss} + \sigma_{kk}}{2} \tag{7-9}$$

Table 7-2 shows the Lennard-Jone parameters for some molecules

Table 7-2 Lenard –Jones parameters

	σ (Å)	ε/k (K)
C	3.4	28
CO ₂	3.3	195
N ₂	3.64	71
Ar	3.54	93

At steady state, the permeance (mole/s), P_M , of the membrane is fixed. For the structural model in Figure 7-5, we have:

$$P_M = S_1J_1 = S_2J_2 = S_3J_3 \tag{7-10}$$

where S_1, S_2, S_3 are the cross sectional areas of the throat-1, bottle and throat-2, respectively. J_1, J_2, J_3 are the corresponding steady state flux in each section,

respectively. The detailed model derivation and model solution for Eq. 7-10 are shown in the Appendix B.

By simultaneously solving Eq. 7-3 with the experimental isotherm data and Eq. 7-10 with the measured permeance data, we can optimize the characteristic pore sizes of the throat pores and bottle pores, respectively.

7.4.2 Results and discussion

The first data set were taken from Wang et al [10], in which CO₂ adsorption and permeation were conducted on a CMS (KP950) at 298K. Figure 7-6a and 7-6b show the isotherm data (dots) and permeance of CO₂ (dots) on the membrane (with the thickness of 23 μm) over a wide pressure range (upto 30 bar). The experimental data were fit by Eq. 7-3 and Eq. 7-10 simultaneously and the simulation results were shown in the related figures as solid lines. We see that the 3-section model (solid lines) successfully fit both the isotherm data and steady state permeation simultaneously.

Figure 7-6 CO₂ isotherm (a) and permeance (b) on KP950 at 298K.

On the other hand, the single section model, which can be regarded as the 3-section model with the same dimensions in all the three sections, would overestimates the isotherm linearity and the pressure dependence of the steady state flux. The broken lines in Figure 7-6a and 7-6b shows the optimal fittings

of the single section model for the experimental data, which proves that the single section model is unable to cope with the pressure dependence of the steady state permeance (or permeation flux) of CO₂ on KP950.

Table 7-3 lists the isotherm and permeation parameters of CO₂ on KP950 at 298K. We see that, for the 3-section model, the pore size (radius) of the throat pore is smaller than that of the bottle pore, which is in agreement with the structural model depicted in Figure 7-5 and is consistent with the physical pore structure of CMS membranes. The other important information is that the adsorption capacity of the CMS membrane resides mostly in the bottle pores, which is in line with our expectation. Because the bottle pore is the lumped effect of all the filled blind pores, sorption pores and large diffusive channels, they are mainly responsible for the overall sorption capacity of the CMS membrane, according to the PSD we derived previously from Figure 7-4.

Table 7-3 The optimal derived isotherm and kinetics parameters

	$D_{\mu\infty}^0$ (cm ² /s)	$C_{\mu s}^T$ (mmol/g)	$C_{\mu s}^B$ (mmol/g)	r_t (Å)	r_b (Å)
3-section model	5.32×10^{-9}	0.149	3.51	3.01	3.66
Single section model	4.77×10^{-10}	4.61		6.58	

The characteristic half-width (radius) of the throat and bottle pores of the CMS membrane are 0.3 nm and 0.37 nm, respectively. Compared with the physical pore size of the KP950 membrane (0.7 nm by molecular probe experiment, which is the center to center distance between the graphite pore walls), this pore size of throat (0.6 nm) is a little bit deviated but close. On the other hand, using

a single section pore model ($r_t = r_b$) would give a pore radius size of ~ 0.66 nm (the full pore size of 1.2 nm), which overestimates the real pore size of the membrane. Such a single pore model also fails to simulate the pressure dependence of the experimental sorption isotherm and permeance. These discussions strong support that the 3-section model (which addresses the issues of pore connectivity and pore irregularity) for the steady state permeation is a more realistic picture and mathematical formulation for the permeation in CMS membranes.

Next, adsorption and permeation data on KP800 CMS are employed to further investigate the performance of the 3-section model. Compared with CO₂, Ar is a weakly adsorbed molecule with spherical geometry and slightly large molecular size (~ 0.35 nm). As discussed previously, Ar is a good ‘ruler’ for characterizing permeation in porous media.

Figure 7-7a and 7-7b present the simulation results of Ar sorption and permeation on KP800 membrane at 308K. It is seen that the 3-section model (solid lines) again gives a satisfactory fittings to both the sorption isotherm and permeance data at this temperature (symbols). The single section model (broken line) slightly overestimates the isotherm data at the high pressure, but considerably deviate from the permeation data (Figure 7-7b) at the high permeation pressure.

Figure 7-7 Ar on KP800 CMS at 308 K. (a) isotherm, (b) permeance.

Table 7-4 lists the optimal data of the model fittings for the Ar sorption and permeation on KP800 at 308K, which shows that, 1) the proposed 3-section

model gives a much higher capacity in the bottle pores than throat pores (0.5 vs. 0.28 mmol/g), and 2) the pore radius for the bottle pore is bigger than that of the throat pore (0.5 vs. 0.34 nm). Compared with CO₂ data on KP950 CMS in Table 7-3, those data are in good agreement with each other because KP800 CMS possesses bigger average pore size than the KP950 CMS. The difference in the capacity ratio (bottle /throat) are less than that of CO₂ on KP800, because Ar is much weaker in adsorption so the effect of isotherm non-linearity is much less significant. One more thing to note is that the diffusivity at infinite temperature, $D_{\mu\infty}^0$, is much larger for Ar than that for CO₂ (i.e. 10⁻⁹ vs. 10⁻⁶). The reason is that KP800 has a larger average pore size and much higher permeability (but with a lower selectivity) than KP950, so that this high throughput is factored into the overall diffusivity and results in an apparently high value for $D_{\mu\infty}^0$.

Table 7-4 The optimal derived isotherm and kinetics parameters

	$D_{\mu\infty}^0$ (cm ² /s)	$C_{\mu s}^T$ (mmol/g)	$C_{\mu s}^B$ (mmol/g)	r_t (Å)	r_b (Å)
3-sectioned model	3.76×10 ⁻⁶	0.28	0.5	3.4	5.0
1-sectioned model	4.63×10 ⁻⁶	0.18		3.6	

Figure 7-8a and 7-8b further show Ar adsorption and permeation data on KP800 CMS at 363K (symbols) and the fittings by the two models (solid lines for 3-section model, broken line for single-section model). We see that, even the isotherm and permeance of Ar is largely linear when plotted against the experimental pressure at this experimental temperature, the 3-section model still outperforms its counterpart in fitting both the isotherm and permeance data.

Figure 7-8 Ar on KP800 CMS at 363 K. (a) isotherm and (b) permeance.

7.5 Summary

Adsorption/desorption isotherms of CO₂ were measured on a CMS membrane at three temperatures and over a wide range of pressures. The data were fitted reasonably well by the Langmuir isotherm and better by the Toth isotherm, which suggests a strong surface heterogeneity of the CMS membrane. The diffusion barrier (micropore resistance) was significant on at low experimental temperature (77 K) but less important at ambient experimental temperature and high pressures.

The structure of the CMS membrane were characterized by the high pressure, multiple-temperatures isotherm data and further discriminated into blind pores and through pores via the transient state permeation time lag data, and into throat pores and bottles pore by the steady state permeance data. The main sorption capacity of the CMS membrane was found to reside in blind/bottle pores.

A 3-section model was proposed to characterize the structure CMS membrane for steady state permeations. It was demonstrated that, by addressing the pore connectivity and pore irregularity, the model is able to cope with the CO₂ and Ar isotherm and permeance data measured on different CMS membranes at various experimental temperatures. Assuming a straight diffusion channel (single pore model) would fail to model accurately the overall isotherm and permeance data.

Chapter 8. Conclusions and recommendations

8.1 Conclusions

CS based nanocomposite fibers were successfully fabricated by the phase inversion/wet-spinning method with three types of nanofillers: lignin, POSS, and CNT. The structure and the mechanical properties of the fibers were characterized by a number of techniques. It was found that lignin, OA, and OA-disperse well in CS matrix, while the OAPS, ONPS and SWNT, which are hydrophobic, disperse less homogeneously. For the mechanical properties, the maximum stress, strain at break, Young's modulus and toughness can all be improved by the three types of fillers, with the optimal compositions for each filler of: 3% of CS-lignin, 7% of CS-OA, 5% of CS-ONPS, and 1% of CS-SWNT. Further increasing or decreasing the concentration of fillers in CS matrix will result in decrease in the mechanical properties.

For the CS-based nanocomposite (OA- and OAPS) membranes, the permeability and flux increase with the increasing concentration of POSS in the CS matrix and so is the diffusivity. A novel experimental method was proposed to study the permeation/separation properties of gas-vapor mixtures or gas mixtures with very different boiling points. This technology can simultaneously measure the transport properties for the mixture as well as for each component.

Adsorption isotherm, permeation time lag, and steady state permeability were measured for CO₂ and Ar gases on a few CMS membranes. Strong surface barriers were found at low sorption pressure for CO₂ gas at 77 K, but the micropore hysteresis was not seen at high sorption pressure and ambient temperature. The Ar sorption and permeation properties were used to characterize the structure of CMS membrane. The pore size distribution derived from equilibrium information was further discriminated by the permeation properties at transient and steady states. It was found that blind pores contribute the majority of the total pore volume while through pores and ink-bottled pores do exist in small volume fraction.

A structural model was proposed for the steady state permeation in CMS membranes. The model successfully simulated the pressure dependence of the steady state permeance by the 3-sectional diffusion path. On the other hand, the single section model would fail to simulate this pressure dependence of the permeance and the isotherm data. It was demonstrated that, at steady state, adsorption capacities of the CMS membrane reside mostly in the bottle pores.

8.2 Recommendations

The homogeneous dispersion of nanofillers in polymer solution still remains a big challenge, which is critical for the quality of the synthesized fibers. In future, other techniques such as in-situ polymerization instead of solution blending can be used. Using crosslinking agent such as epichlorohydrin or high-power ultrasonification can improve the polymerization and help to break apart the CNT bundles into finer tubes before curing of the CS. The mathematic

model of dispersion of nanofillers in CS matrix would be proposed to study the dispersion effect on the mechanical properties. Moreover, the array of CNT bundles and CNT finer tubes in the matrix would be compared in the mathematically model as well. Mathematically model the process of dispersion and the arrange of fillers in the CS matrix could be a valuable addition towards a better understanding how fillers effect on the CS matrix.

For permeation in CS nanocomposite membranes, more experiments should be conducted for vapor-gas mixtures, such as water-CH₄, water-SO₂, etc., at different condensation temperatures for potential application in packaging industry and for bio-gas/natural gas cleaning. Besides, by controlling the cold trap temperature and choosing the gases with different boiling temperature, more binary gas mixtures should be studied. Such as if we kept liquid nitrogen (-196°C) in the cold trap, and then the system can be used to separate CO₂-He, O₂-He, CO₂-H₂ and CH₄-H₂ gas mixtures. (The boiling points: He: -269°C, O₂: -183°C, H₂: -252.8°C and CH₄: -182.5°C). The study of the binary permeation time lag is another important area. For more multi-component gas mixture, more cold traps could be used. However, the novel method have some vulnerabilities, such as just separate two gases at one time, and the gases need have very different boiling points. Since the system is easy and convenient for binary gas separation and the vulnerabilities limit the multi-component gas separation, new idea should be proposed to fit the multi-component gas mixtures.

For the structural characterization of CMS membrane, the two models (blind pore model and 3-section model) should be integrated to describe the transient state and steady state permeation simultaneously. This new model (it should be a 2-D model then) will take into account of blind pore characteristics and pore irregularity to cope with the diffusion anomalies at both transient and steady states.

Appendix

Appendix A

The overall time lag is the sum of the time lags in through pores and blind pores,
i.e.

$$L = L_T + L_B = \frac{l^2}{D_\mu^0} \left\{ \frac{1}{\ln(1+b_T P_0)} \left[\frac{1}{2} - \frac{1}{(1+b_T P_0) \ln^2(1+b_T P_0)} - \frac{\ln(1+b_T P_0)-1}{\ln^2(1+b_T P_0)} \right] \right\} +$$

$$\frac{l^2}{D_\mu^0} \times \frac{C_{\mu s}^B}{C_{\mu s}^T} \frac{\left[2di \log\left(\frac{k}{k-1}\right) - 2di \log\left(\frac{k w}{k-1}\right) - 2 \ln(1-k+k w) \ln\left(\frac{k w}{k-1}\right) + k \ln^2 w \right]}{2(k-1) \ln^3 w}$$

where $w = (1+b_T P_0)$, $di \log(x) = \int_0^x \frac{\ln(t)}{1-t} dt$ is the dilogarithm function, and

$$k = \frac{b_B}{b_T} > 1.$$

Appendix B

The 3-section pore model and related properties are shown schematically in
Figure B-1.

Figure B-1 Pores with ink-bottled structure

The boundary conditions for the model are:

$$C(0,t) = C_0; C(L,t) = 0; C(r,0) = 0$$

Where L is the length of the membrane, r is the diffusional path. With the adsorption in each pore:

$$C_\mu^1 = C_{\mu s}^1 \frac{b_1 P}{1 + b_1 P}, \quad C_\mu^2 = C_{\mu s}^2 \frac{b_2 P}{1 + b_2 P}, \quad C_\mu^3 = C_{\mu s}^3 \frac{b_3 P}{1 + b_3 P}$$

Where P is the (hypothetical) bulk phase pressure (a function of r), C_μ is adsorbed phase concentration in the pore. At steady-state:

$$J_\mu^\infty = -D_\mu \frac{dC_\mu^\infty}{dr}$$

where surface diffusivity is described by the Darken relation

$$D_\mu = \frac{D_\mu^0}{1 - \theta} = \frac{D_\mu^0}{1 - C_\mu / C_{\mu s}}$$

In Section 1 (or the throat)

$$J_1 = -\frac{D_{\mu 1}^0}{1 - \frac{C_\mu^1}{C_{\mu s}^1}} \frac{dC_\mu^1}{dr}, \quad \int_0^{l_1} J_1 dr = -\int_{C_{\mu end}^1}^{C_{m1}^1} \frac{D_{\mu 1}^0}{1 - \frac{C_\mu^1}{C_{\mu s}^1}} dC_\mu^1$$

$$\text{So } J_1 l_1 = D_{\mu 1}^0 C_{\mu s}^1 \ln\left(\frac{C_{\mu s1} - C_{m1}}{C_{\mu s1} - C_{\mu end}}\right) \text{ where } C_{\mu end} = \frac{C_{\mu s1} b_1 C_0}{1 + b_1 C_0}$$

Similar relations can be derived for section 2 and 3.

$$J_2 l_2 = D_{\mu 2}^0 C_{\mu s}^2 \ln\left(\frac{1 - C_{m2}/C_{\mu s}^2}{1 - C_{m1}/C_{\mu s}^2}\right), \quad J_3 l_3 = D_{\mu 3}^0 C_{\mu s}^3 \ln\left(\frac{C_{\mu s}^3}{C_{\mu s}^3 - C_{m2}}\right)$$

At steady state, we have :

$$J_{\mu 1} S_1 = J_{\mu 2} S_2 = J_{\mu 3} S_3$$

With above equations, the concentrations between different sections can be derived and flux/permeance can be calculated.

Appendix C

The main MATLAB program for the 3-section model is listed below:

```
close all; clear all; clc; format short e;
global iso_data perm_data beta t_temp m_w d_dia eps_i n_section flag_ads L_ratio LL C_ratio
perm_len area_mem

[iso_data, perm_data, LL, t_temp, sample] = KP950data;
area_mem = pi.*(2.0).^2;
permeance = perm_data(:,2).*area_mem;
perm_data(:,2) = permeance;
C_ratio = 1./8.314./t_temp;
L_ratio = 1./3;
x_axis = [1, 1-(1-L_ratio)./2, (1-L_ratio)./2, 0] ;
perm_len = length(perm_data(:,1));
beta = 1.2e-4;

if sample == 1 ;
    m_w = 44;
    d_dia = 3.3;
    eps_i = 12;

elseif sample > 1 & sample < 5;
    m_w = 40;
    d_dia = 3.54;
    eps_i = 7.6 ;
end

d_dia = (d_dia + 3.4)./2 ;
flag_ads = input('--Adsorption or NonAdsorption 1/0: ');
n_section = input('One/Three Section (1/3): ');

a0_ini = input('D0 Cut r_t/[ D0 Cut0 Cub0 r_t r_b]: ');

if n_section ==1
    a0_ini = [a0_ini(1) a0_ini(2) a0_ini(2) a0_ini(3) a0_ini(3)];
end

k = 1;

while k == 1;
    [y_iso, y_perm, C_dis, J_flux] = feval('isoperm', a0_ini);

    figure (1); plot(iso_data(:,1), iso_data(:,2), 'o', iso_data(:,1), y_iso);
    figure (2); plot(perm_data(:,1), perm_data(:,2), 'o', perm_data(:,1), y_perm(:,1));
    figure (3); plot(x_axis, C_dis(1:perm_len,:));
```

```

iyes = input('Do you wish to further change the guessing parameters? = ','s');

if      iyes=='y' | iyes=='yes' | iyes=='Y' | iyes=='Yes'

    a0_ini  = input('[ D0 Cut0 Cub0 r_tr_b] / [D0 Cut r_t] : ');

    if      n_section ==1
        a0_ini = [a0_ini(1) a0_ini(2) a0_ini(2) a0_ini(3) a0_ini(3)];
    end
else;
    k=0;
end;

end;

iyes=input('Do you want to plot/optimization (0/1) ?');

if iyes==1;

    options(1)=0; options(2)=1e-3; options(3)=1e-3; options(4)=1e-4; options(14)=8000;

    disp('*****');
    disp('*   The program is RUNNING !!!!! Thank you   *');
    disp('*   Using relative error as object function   *');

    disp('*****');

    [a_optimal,options] = fminsearch('residualflux',a0_ini);

elseif iyes==0;
    a_optimal = a0_ini;
else ;
    break;
end;

disp(' ')
disp(' %----- The Pore model is ----- % ');
disp(' ')

if n_section ==1
    disp('***** Single section --> Uniform size *****')
else
    disp('***** Three section --> Neck and volume *****')
end

[y_iso, y_perm, C_dis, J_flux] = feval('isoperm', a_optimal);

disp(' '); disp(' ')

if n_section ==1;
    a_optimal = [a_optimal(1), a_optimal(2).*2, a_optimal(3)];
    disp('--- D0 -----Cust0+ Cusb0 ----- rt(A)')
    disp(a_optimal);
else
    disp('--- D0 ----- Cust0 ----- Cusb0 ----- rt(A) ----- rb(A) ')
    disp(a_optimal);
end

disp(' note: if single section, Cusb0, rb are not used !')
disp(' if no adsorption, Cust0 & Cusb0 are not used !')

```

```
disp(' %-----% ');

figure (1); plot(iso_data(:,1),iso_data(:,2),'o',iso_data(:,1),y_iso)
figure (2); plot(perm_data(:,1), perm_data(:,2),'o', perm_data(:,1),y_perm(:,1));
figure (3); plot(x_axis, C_dis(1:perm_len,:))

iso_out = [iso_data,y_iso];
perm_out = [perm_data,y_perm(:,1)];

save iso_out.txt iso_out-ascii;
save perm_out.txt perm_out-ascii;
```

This is the sub-program to calculate the flux/permeance

```
function [y_iso, y_perm, C_dis, J_flux] = isoperm(a0_ini);

global iso_data perm_data beta t_temp m_w d_dia eps_i n_section flag_ads L_ratio LL C_ratio
perm_len bb Du l1 l2 l3 S1 S2 S3 Cus Cu_end area_mem

D0 = a0_ini(1);

If n_section == 1
    cus_t = a0_ini(2);
    cus_b = cus_t;
    r_t = a0_ini(4)/d_dia;
    r_b = r_t;
else
    cus_t = a0_ini(2);
    cus_b = a0_ini(3);
    r_t = a0_ini(4)/d_dia;
    r_b = a0_ini(5)/d_dia;
end

S1 = pi.*(r_t.*1e-8).^2;
S2 = pi.*(r_b.*1e-8).^2;
S3 = S1;
l2 = L_ratio .* LL ;
l1 = (1-L_ratio).*LL./(n_section-1);
l3 = l1;

if n_section == 1;
    l1 = l2; l3 = l1;
    S2 = S1; S3 = S1;
end

Cus = [cus_t cus_b];
Cus1 = Cus(1); Cus2 = Cus(2); Cus3 = Cus1;

If flag_ads == 0;

    pp = perm_data(:,1);
    Du01 = D0;
    Du02 = D0;
    Du03 = D0;
    y_iso = iso_data(:,2);

    for i = 1:perm_len;

        C0 = pp(i).*C_ratio;
```

```

C_mid1 = C0./(S1.*Du01.*I3./S3./Du03./I1 + S1.*Du01.*I2./S2./Du02./I1 + 1) ...
+ C0./(S2.*Du02.*I3./S3./Du03./I2 + S2.*Du02.*I1./S1./Du01./I2 + 1);
C_mid2 = C0./(S1.*Du01.*I3./S3./Du03./I1 + S1.*Du01.*I2./S2./Du02./I1 + 1);

J1 = C0./(S1.*I3./Du03./S3 + I1./Du01 + S1.*I2./Du02./S2);
J2 = C0./(S2.*I3./Du03./S3 + S2.*I1./Du01./S1 + I2./Du02);
J3 = C0./(S3.*I1./Du01./S1 + S3.*I2./Du02./S2 + I3./Du03);

C_dis(i,:) = [C0, C_mid1, C_mid2, 0];
J_flux(i,:) = [J1, J2, J3];
y_perm(i,:) = [J1.*area_mem, J1.*S1, J2.*S2, J3.*S3];
end

else

[ep, yp] = potenti([r_tr_b], l43, d_dia);
bb = beta./sqrt(t_temp.*m_w).*exp(- eps_i.*ep.*1000./8.31./t_temp);
p_iso = iso_data(:,1);

for i = 1:2;
    y_iso(:,i) = Cus(i).*bb(i).*p_iso./(1+bb(i).*p_iso);
end

y_iso = sum(y_iso)';
pp = perm_data(:,1);
Du = D0.*exp(0.5.*eps_i.*ep.*1000./8.31./t_temp);

Du01 = Du(1); Du02 = Du(2); Du03 = Du(1);
Cu_end0 = Cus(1).*bb(1).*pp./(1+bb(1).*pp);

For i = 1: perm_len
    Cu_end = Cu_end0(i);

    If n_section == 1

        C_mid1 = Cus(1).*(1-(1+bb(1).*pp(i)).^(-(1-L_ratio.*1)));
        C_mid2 = Cus(1).*(1-(1+bb(1).*pp(i)).^(-(1-L_ratio.*2)));
        C_mid = [C_mid1 C_mid2];

        Ju1=Cus(1).*Du01.*log(1+bb(1).*pp(i))./(I1+I2+I3);
        Ju2 = Ju1;
        Ju3 = Ju2;

    else

        C_mid = fsolve(@(xx) bsbmiddle(xx),[Cu_end.*(0.75), Cu_end.*(0.3)], ...
optimset('Display','off', 'TolFun',1e-3));

        Ju1 = Cus1.*Du01.*log((C_mid(1)-Cus1)./(Cu_end-Cus1))./I1;
        Ju2 = Cus2.*Du02.*log((Cus2-C_mid(2))./(Cus2-C_mid(1)))./I2;
        Ju3 = Cus3.*Du03.*log(Cus3./(Cus3-C_mid(2)))./I3;

    end

    C_dis(i,:) = [Cu_end,C_mid,0];
    J_flux(i,:) = [Ju1, Ju2, Ju3];
    y_perm(i,:) = [Ju1.*area_mem, Ju1.*S1, Ju2.*S2, Ju3.*S3];

end
end

```

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List of publications

- 1) Chen, J.; Loo, L. S.; Wang, K., High-Pressure CO₂ Adsorption on a Polymer-Derived Carbon Molecular Sieve. **Journal of Chemical & Engineering Data**, 2007, 53, (1), 2.
- 2) Chen, J.; Loo, L. S.; Wang, K.; Do, D. D., The structural characterization of a CMS membrane using Ar sorption and permeation. **Journal of Membrane Science**, 2009, 335, (1-2), 1.
- 3) Chen, J.; Loo, L. S.; Wang, K., Experimental Measurement and Modeling of Diffusion Anomalies in a CMS Membrane. **Chemical Product and Process Modeling**, 2010, Vol. 5 (1), 3.
- 4) Chen, J.; Loo, L. S.; Wang, K., Enhanced Mechanical Properties of Novel Chitosan Nanocomposite Fibers. **Carbohydrate Polymers**, 2011, Vol. 86 (3), 1151.
- 5) Chen, J.; Loo, L. S.; Wang, K., An IAST study of binary mixtures of methane and ethane on a templated carbon. **Journal of Chemical & Engineering Data**, accepted, 2011.
- 6) Chen, J.; San, H.; Loo, L. S.; Wang K., A novel method for measuring permeation properties of gas-vapor mixtures. **Submitted to Journal of Membrane Science**
- 7) Chen, J.; Loo, L. S.; Wang, K., Enhanced Mechanical Properties of Novel Chitosan/Lignin Nanocomposite Fibers. **Submitted to Journal of Material Science**.
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