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PERFLUOROCYCLOBUTYL POLYMER THIN-FILM COMPOSITE MEMBRANE FABRICATION, PLASTICIZATION AND PHYSICAL AGING

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PERFLUOROCYCLOBUTYL POLYMER THIN-FILM COMPOSITE MEMBRANE FABRICATION, PLASTICIZATION AND PHYSICAL AGING

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemical Engineering

by
Jinxiang Zhou
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Accepted by:
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ABSTRACT

Membrane technologies have been used widely in industrial practices such as waste water treatment, sea water desalination, gas separations, pharmaceutical separations, and food and beverage processing to name a few. Among the features that make them attractive are that they are cost effective, highly efficient, scalable, and environmentally benign. The focus of this dissertation is to contribute to the understanding and use of polymeric membranes for carbon dioxide separations.

Currently, the largest carbon capture demand lies in the natural gas industry. However, since global warming has become a severe concern for human existence, flue gas cleaning is potentially another very important market for carbon capture. Therefore, I chose to address the membrane-based separation of carbon dioxide from nitrogen, a mixture that results from post-combustion processes using air as the oxygen source.

The work was done in close collaboration with Tetramer Technologies, LLC (Pendleton, SC). In addition to intellectual capital, Tetramer provided their perfluorocyclobutyl (PFCB) polymers, which are a new class of fluorinated polymers with promising application in O$_2$/N$_2$, CO$_2$/methane, and flue gas separations. I used a representative polymer, biphenylvinyl-PFCB, as the selective layer in the development of thin-film composite membranes for CO$_2$/N$_2$ separations.

Different from ultrafiltration and microfiltration membranes, polymeric thin-film composite (TFC) membranes usually are nonporous. Their separation ability is not just size based but also based on the interactions between gases and the polymer(s). A solution-diffusion mechanism is the most popular theory explaining the transport
phenomena inside these membranes. Oftentimes, glassy polymers such as PFCB are used as the selective layer in TFC membranes, as they have higher selectivity than rubbery polymers. However, glassy polymers, including PFCB, are associated with the problems of physical aging and plasticization. Many researchers have found that these two phenomena are more significant in thin polymer films. Unfortunately, flux of gas through polymeric membranes is inversely related to polymer thickness; thus, thin polymer films (<1000 nm) are more practical than bulk films for industrial applications. A goal of my work was, therefore, to elucidate structure-property relationships for Tetramer PFCB polymers that provide a foundation for TFC membranes with resistance to CO₂ plasticization and physical aging. Specifically, my doctorate research consists of three parts: 1) study of PFCB thin film formation, 2) development and characterization of PFCB thin-film composite membranes, and 3) elucidation of the roles that plasticization and physical aging play on PFCB thin-film performance.

In part 1, I conducted comprehensive research to understand how PFCB thin films form by the method of dip coating. Through the control of solvents, polymer solution concentrations, and withdrawal speeds, a series of PFCB thin films were formed on silicon wafers. Film thickness and refractive index were characterized by ellipsometry. Results suggested that when the withdrawal speeds are higher than 50 mm/min, film thickness increases with increasing withdrawal speeds, as it is predicted in the proposed extension of the Landau-Levich model. When the withdrawal speeds are lower than 50 mm/min, film thickness increases with decreasing withdrawal speeds, which could be explained by the phenomenon of PFCB surface excess. Subsequent surface tension
studies proved the existence of this surface excess. Surface images of these films were measured by atomic force microscope. Films prepared from tetrahydrofuran and chloroform yielded uniform nanolayers. However, films prepared using acetone as solvent yielded a partial dewetting pattern, which could be explained by a surface depletion layer of pure solvent between the bulk PFCB/acetone solution and the substrate.

Based on the knowledge generated in part 1, I developed, from scratch, procedures to prepare PFCB TFC membranes that were free of major defects. I used mathematical models based on resistance in series to predict composite membrane performance. In many cases, surface defects are the major reason for poor separation ability of TFC membranes. Mathematical analysis showed that the surface defects are less critical in thinner films but are still an important factor causing selectivity loss. Surface defects occur mainly from polymer dewetting on the support substrate. A method of plasma treatment was developed to modify the surface of the proprietary gutter layer, which is highly permeable but not very selective. Forced wetting was proposed to guide the degree of surface modification that was needed. Finally, PFCB TFC membranes were successfully produced with excellent reproducibility. The selective PFCB layers were between 10 and 59 nm. Measured CO₂ permeance through PFCB layers were as high as 1700 GPU (gas permeation units) with CO₂/N₂ selectivity close to 20. Membrane performance was highly reproducible.

In the last part of this dissertation, plasticization and physical aging were evaluated on different PFCB thin-film selective layers. Measurement of plasticization curves was the focus of this part of the study. PFCB thin-film selective layers were prepared from
solutions with different PFCB concentrations using four different dip-coating withdrawal speeds. I discovered that thickness played a more important role than coating solution concentration on PFCB thin-film plasticization when film thickness is below 35 nm; whereas, concentration played a more important role when film thickness is above 35 nm. Impacts of different thermal treatments and physical aging on film plasticization also were analyzed. Thermal annealing effectively enhanced the plasticization pressure at the expanse of permeance loss. PFCB films aged for longer times had lower plasticization pressure. Long-term flux studies revealed a complicated relationship between plasticization and physical aging and their roles on membrane permeance. During the early stage of membrane exposure to CO₂, plasticization has a competing effect with physical aging, but, at longer times, plasticization appears to accelerates physical aging.

In all, my doctorate research provides a systematic method to fabrication TFC membranes with high performance and protocols to evaluate PFCB polymer thin film plasticization and physical aging.
DEDICATION

This dissertation is dedicated to my beloved father Mr. Zhenkai Zhou and mother Mrs. Qinghua Zeng.

本论文献给我伟大的以及挚爱的父亲周镇凯先生以及母亲曾清华女士。
ACKNOWLEDGEMENTS

My first thanks should be given to my great parents. As an only child of my parents, I was supposed to stay with them to oblige the traditional Chinese filial piety. But, thanks to their trust, understanding, and encouragement, I was able to use their support to come to this faraway country to finish my Ph.D. I am sorry for all that they have had to suffer for my journey. Here, I sincerely appreciate their love again. I will use all of the abilities that I learned to make my parents feel happy and healthy in the future. Especially, I would like to thank my uncle Mr. Jinzhong Zeng, who provided a significant amount of financial support for all my years of study since I was a young kid. In addition to his financial support, he is also a great friend and mentor. I also would like to thank all my other family members in China for their care and prayers.

I would like to express my special thanks to my advisor Dr. Scott Husson. I will never forget his patient support on my research progress and his careful guidance on my paper and dissertation development, as well as his very responsible working attitude and extremely organized working methodology on helping me become a qualified researcher. Dr. Husson is the most helpful mentor I have ever met.

I also would like to thank Dr. Earl Wagener, Dr. Jianyong Jin, and Adam Haldeman from Tetramer Technologies for providing guidance and help in my project development. I thank Dr. Christopher Kitchens for helping me design the high pressure cell for CO₂ swelling study. I thank Dr. Earl Wagener, Dr. Christopher Kitchens, and Dr. Douglas Hirt as my committee members for their cooperation and for spending time reading my dissertation and giving comments. I thank Dr. Ruslan Burtovyy and Dr. Valery Bliznyk
for giving me guidance on AFM measurements. I also thank Brandom Abott, Scott Winkler and Ming-Ming Tran from Research Experience for Undergraduates program for membrane testing.

In my opinion, loneliness is one of the difficulties one would have to deal with in PhD study. However, attributed to our past and current group members – Azi, Bahrat, Daniel, Heather, Joe, Juan, Kristine, Milagro, and Nikki – all frustrations and miseries from my study and research have always been turned into fun and joys. I would like to thank them again for helping me think positively during any rough times I have encountered. I would like to thank all the faculty, staff and Chemical Engineering students to give me such a friendly and multicultural environment.

Finally, I would like to sincerely thank National Science Foundation for providing funding to support my project and enable me to explore all the interesting topics described in this dissertation.
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1.1 Carbon capture and membrane opportunities

Humans have accounted for about half of one trillion tons of carbon emitted into the atmosphere in total since their origin, from sources including combustion of fossil fuels, deforestation, and biomass burning, which is the primary cause of a global rise in temperature [Luis et al., 2012]. One solution is to reduce carbon dioxide emissions associated with fossil fuel combustion using four main strategies: post-combustion capture, pre-combustion capture, oxyfuel combustion, and electrochemical separation. The first of these arguably is easiest to implement because it can be adapted readily to an existing plant; however, it presents challenges [Luis et al., 2012]. Foremost, CO\textsubscript{2} is diluted in a large volume of gas needing treatment (10-14 vol\% CO\textsubscript{2}), making separation more difficult and energy-intensive.

Another CO\textsubscript{2} capture application lies in the natural gas industry. Since human demand for natural gas is experiencing rapid growth, unconventional, stranded and contaminated gas reserves have drawn recent attention [Rufford et al., 2012]. The occurrence of CO\textsubscript{2} in the natural gas corrodes pipelines and lowers the heating value. Therefore, CO\textsubscript{2} removal is an important step in natural gas processing. Specifically, this removal step is called natural gas sweetening. Usually, CO\textsubscript{2} must be removed to levels below 2 vol.\%. The composition of raw natural gas varies over a broad range for different
wells, with relatively high pressures between 20 to 70 bar. Natural gas sweetening is the largest CO$_2$ separation market [Peters et al., 2011; Baker, 2002].

Membrane technologies have attracted broad interest from many industries and research groups. Freemantle [Freemantle, 2005] points to a significant intrinsic advantage of using membranes for gas separations relative to more conventional techniques: Membranes do not require an energy-intensive gas-to-liquid phase change in the gas mixture that is to be separated. Other cited advantages include smaller footprints and lack of mechanical complexity. The former is particularly important in environments such as offshore gas-processing platforms.

If membranes are used for the separation, expensive compression technology is needed to generate the required pressure difference across the membrane. However, post-combustion capture may be a practical choice using thin-film composite membranes.

A common approach to develop a gas separation membrane is to form a polymer thin-film composite (TFC) comprising a selective layer coated on a support layer. There may also be a highly permeable gutter layer between the selective and support layers that provides a smooth surface on which to deposit the selective layer. Finally, another permeable protective layer may be deposited on the selective layer to protect it from chemical or physical attack. An advantage of using multiple layers of different materials is that this approach uses much less of the often expensive selective layer polymer than an asymmetric membrane made of the selective polymer alone (< 1 g/m$^2$ compared to 40-60 g/m$^2$) [Baker, 2002; Robeson, 2008; Merkel et al., 2010].
1.2 Thin film composite membrane fabrication

Because natural gas sweetening normally is done at high feed pressures (>50 bar) [Ahmad et al., 2013], the permeance of commercial membranes for natural gas sweetening (>100 GPU) does not need to be as high as that needed for membranes used for flue gas separations (1000 GPU) [Merkel et al., 2010]. The U.S. Department of Energy (DOE) has set a goal to separate 90% of the CO$_2$ from flue gas at a price cheaper than $40/ton for the second generation technologies [USDOE, 2013]. Merkel and coworkers [Merkel et al., 2010] have pointed out that the CO$_2$ capture cost can be as low as $23/ton if membranes are used with CO$_2$ permeance of 1000 GPU and CO$_2$/N$_2$ selectivity of 50 using a feed pressure of 2 bar. Noteworthy is that the capture cost using amine scrubbing is in the range of $40-100/ton. From Merkel and coworkers’ data, one can find conditions needed to meet the target of $40/ton: CO$_2$ permeance > 1000 GPU and CO$_2$/N$_2$ selectivity > 20 at 1.1 bar feed pressure. If the feed pressure can be increased to 2 bar, then membranes with lower performance metrics may potentially meet the DOE target capture cost.

The CO$_2$ permeability of most polymeric membranes with selectivity larger than 20 is between 1 and 100 Barrer (1 Barrer = $10^{-10}$cm$^3$(STD)·cm/(cm$^2$·cmHg·s)) [Robeson, 2008]. To achieve high permeation rates, the selective layer of the membrane must be very thin—typically less than 0.5 μm [Baker, 2002]. For example, MTR [Merkel et al., 2010] and GKSS [Yave et al., 2010] reported TFC membranes with CO$_2$ permeance larger than 1000 GPU (1 GPU = $10^{-6}$cm$^3$(STD)/(cm$^2$·cmHg·s)). In the case of the GKSS Polyactive® product, the membrane selective layer could be as thin as 30 nm. Ren et al.
[Ren et al., 2012] prepared multilayer polyetherimide (PEI) (support layer)-polydimethylsiloxane (PDMS) (gutter layer)-Prebax (selective layer)-PDMS (protective layer) membranes. Chendake et al. [Chendake et al., 2010] reported TFC membranes based on polyarylate and PDMS. While these two groups gave details on the preparation of their TFC membranes, the thinnest films they prepared were around 500 nm. Peter and Peinemann [Peter and Peinemann, 2009] used crosslinked poly(1-trimethylsilyl-1-propyne) (PTMSP) as the gutter layer and partially crosslinked Matrimid® 5218 as the selective layer. A 500 nm thick UV crosslinked PTMSP was found to be much more stable than the original PTMSP; however, its permeance was only 500 GPU. The thinnest Matrimid layer that they have prepared was 110 nm, but its selectivity was impaired substantially by defects. An important part of this PhD work was to develop a procedure to fabricate TFC membranes using perfluororcyclobutyl (PFCB) glassy polymers developed by Tetramer Technologies. The target was on the one hand to produce selective layers thinner than 100 nm without major defects, and on the other hand to produce such membranes with high reproducibility. I used CO₂ and N₂ as the model gas separation to evaluate PFCB TFC membranes.

1.3 Physical aging and plasticization problems associated with glassy polymers

Glassy polymers have been long favored for gas separations because they have a good balance of permeability and selectivity. Plasticization generally reduces selectivity. It is caused by polymer swelling induced by penetrants like CO₂ and hydrocarbons that can be absorbed strongly by the polymer. Due to the expanded free volume that is caused
by CO₂ plasticization, the permeabilities of other gas penetrants also increase, oftentimes more so than that of CO₂ [Wang et al., 2002; Reijerkerk et al. 2011]. The result is a decreased selectivity for CO₂ over the other penetrants. Membranes prepared from glassy polymers start out in their nonequilibrium states. As polymer chains relax towards their equilibrium states, the free volume decreases, which can lead to permeability reduction. This process is called physical aging.

Usually, CO₂ permeabilities or permeances of glassy polymer films are measured as a function of pressure to evaluate their susceptibility to plasticization. When plotted, these data yield a so-called plasticization curve. To understand the shape of a typical plasticization curve, one needs to say something both about gas solubility and diffusivity. Solubility of CO₂ in polymeric membranes can be described by dual-mode sorption proposed by Koros [Koros, 1980]. By this mechanism, both surface adsorption and bulk absorption may occur as a result of gas-polymer interactions. The solubility coefficient decreases with increasing pressure, but not significantly [Hachisuka et al., 1991]. There are competing effects between decreasing solubility and increasing diffusivity at all pressures, and, at a critical pressure, these effects are balanced. Thus, a typical plasticization curve would exhibit a minimum in CO₂ permeability or permeance of the membrane [Horn and Paul, 2012]. The corresponding pressure at the minimum permeance on the plasticization curve is called the plasticization pressure [Wessling et al., 1995; Bos et al., 1999]. Degree of plasticization is another term mentioned in the literature [Horn and Paul, 2011; Ismail and Lorna, 2002; Dong et al., 2011; Zhou et al. 2003]. It describes the relative permeance increase under pressure above the
plasticization pressure. Horn and Paul [Horn and Paul, 2012] suggested that degree of plasticization is related to CO$_2$ solubility. Dong et al. [Dong et al., 2011] proposed a nodule structure model to understand plasticization. In this model, a nodule is defined as the basic structural unit of the membrane. The free volume within the nodule represents the location of Henry’s law sites for CO$_2$ sorption, while the larger free volume between nodules represent the location of Langmuir adsorption sites. Based on this theory, they submit that polymer swelling and plasticization are due to an increase in Henry’s law sites, and are related weakly to Langmuir adsorption sites. They argue that degree of plasticization is determined by the competition between sorption to Henry’s law and Langmuir adsorption sites.

In the industrial practice, thin selective polymer films are coated onto a support membrane. The thickness of the selective layer in the composite membrane structure usually is below 100 nm. Earlier work in this field demonstrated that properties of nanothin films and bulk films are quite different. Of particular relevance to this work, plasticization and physical aging were found to be more significant in polymer thin films than bulk films [Horn and Paul, 2012; Horn and Paul, 2011; Dong et al., 2011; Horn and Paul, 2011; Zhou et al., 2003; Scholes et al., 2010; McCaig and Paul, 2000; Cui et al. 2011; Huang and Paul, 2004]. For non-crosslinked polymers reported in the literature, the bulk polymer plasticization pressure ranges typically from 10 to 40 atm [Bos et al., 1999]. Plasticization pressures of thin films (<500 nm) usually are much lower, with values typically ranging from 5 to 25 atm. Previous studies [Horn and Paul, 2011; Zhou et al., 2003; Scholes et al., 2010] suggested that both plasticization pressure and degree of
plasticization are a function of film thickness. Zhou et al. [Zhou et al., 2003] found significant decrease of glass transition temperature ($T_g$) in ultra-thin films and suggested that mechanical properties decreased significantly from bulk to micro-scale, which resulted in the higher degree of plasticization of the thinner films, even though they absorbed the same amount of CO$_2$ as the bulk film. McCaig and Paul [McCaig and Paul, 2000] discovered that O$_2$ rate of permeability loss (i.e., aging) depends on thickness when the thicknesses of polyarylate films are less than 2.5 μm. Accelerated aging in thinner films have been explained by the higher polymer chain mobility near free surfaces [McCaig and Paul, 2000; Cui et al. 2011; Huang and Paul, 2004]. Dong et al. [Dong et al., 2011] observed that asymmetric membranes had lower plasticization pressures than dense membranes. They attributed the difference to longer nodule growth time in dense membrane preparation, resulting from longer solvent evaporation time. Longer growth time usually produces larger nodules, which would increase the Langmuir adsorption sites. Scholes et al. [Scholes et al., 2010] recommends tracking $T_g$ changes and quantifying interactions between CO$_2$ and polymeric chains in thinner films to better understand why they have lower plasticization pressures. I have done studies in my PhD research to contribute my understanding of plasticization and physical aging of thin PFCB films.

Among the widely studied thin-film gas separation polymers to date are polyetherimide, Matrimid® 5218, poly(2,6, dimethyl-1,4-phenylene)oxide (PPO), polysulfone (PSF), and 6FDA polyimide [Zhou et al., 2003; Horn and Paul, 2011; Scholes et al., 2010; Xia et al., 2012; Simons et al., 2010; Wind et al., 2003]. Most
studies have used films with thicknesses of 150–500 nm. In my PhD research, I evaluated CO₂ plasticization and aging of thin PFCB selective layers, which are below 100 nm.

1.4 Tetramer Technologies’ Perfluorocyclobutyl (PFCB) polymers

My PhD project was done in close collaboration with Tetramer Technologies, LLC (Pendleton, SC). In addition to intellectual capital, Tetramer provided their perfluorocyclobutyl (PFCB) polymers, which are a new class of fluorinated polymers with promising application in O₂/N₂, CO₂/methane, and flue gas separations. The simplest PFCB polymer, biphenylvinylether-perfluorocyclobutyl (BPVE-PFCB) polymer (Figure 1.1), has CO₂ permeability of 38 barrer and CO₂/N₂ selectivity of 21 at 35 °C. PFCBs have a significant percentage of fluorine in the backbone and molecular architecture designed to increase free volume. PFCB polymers typically are amorphous and are easy to process, which enable composite membrane fabrication.

BPVE-PFCB was used in this work as a model PFCB for fundamental research.

![Figure 1.1 Chemical structure of PFCB BPVE polymer repeat unit.](image)
No previous plasticization or physical studies have been performed on these polymers. Fundamental investigation into the plasticization and aging phenomena that occur with PFCB polymers, particularly with high partial pressure CO$_2$, would add to our understanding of these phenomena.

1.5 Outline of the dissertation

A goal of my doctorate work was to elucidate structure-property relationships for Tetramer PFCB polymers that provide a foundation for PFCB TFC membranes with resistance to CO$_2$ plasticization and physical aging. Specifically, my dissertation consists of three parts: 1) study of PFCB thin film formation, 2) development and characterization of PFCB thin-film composite membranes, and 3) elucidation of the roles that plasticization and physical aging play on PFCB thin-film performance. They will be addressed in Chapters 2–5.

To measure fundamental specific physical change data for PFCB-based composite membranes, one first needs to understand how coating conditions affect the formation of PFCB thin films. Thus, the objective of Chapter 2 was to determine the thin film formation characteristics of PFCB polymer thin films to guide our development of PFCB thin-film composite membranes. In this chapter, PFCB thin films were formed by dip coating onto silicon wafer. Variables studied in this work were withdrawal speed, solvent type, and concentration of polymer solution. PFCB films were characterized by measurements of thickness, refractive index, and surface morphology using ellipsometry and atomic force microscopy. The Landau-Levich equation was extended to correlate
film thickness and coating conditions. Results show that polymer thickness and morphologies could be well controlled. These results are being used to guide the development of PFCB thin-film composite membranes for fundamental studies on plasticization and physical aging.

In Chapter 3, a systematic method of composite membrane fabrication was developed. Performance measurements were done to understand the effects of coating conditions on CO$_2$ and N$_2$ permeance and CO$_2$/N$_2$ selectivity. Precautions were taken to ensure that all films experienced the same thermal history prior to characterization to avoid measurement artifacts due to physical aging. As a brief overview, CO$_2$ permeance for membranes prepared with the thinnest PFCB selective layer was measured to be 1000 GPU with a CO$_2$/N$_2$ selectivity of 15. The estimated PFCB layer CO$_2$ permeance is 1700 GPU with a CO$_2$/N$_2$ selectivity of 20, which is very close to selectivity of the bulk (intrinsic) PFCB polymer and suggests that the membrane fabrication yields PFCB TFCs with no major defects. The use of other PFCB polymers and copolymers with superior separation characteristics may be used to prepare composite membranes with improved performance.

Chapter 4 described the efforts on plasticization and physical aging effects of PFCB selective thin layers on TFC membranes. PFCB selective layers in this study had thicknesses from 10 to 60 nm. The objectives of this study were to evaluate CO$_2$ plasticization and aging of thin PFCB selective layers. Specifically, by comparing plasticization curves of different PFCB thin layers controlled by changing polymer concentrations and dip-coating withdrawal speeds, our aim was to elucidate the roles of
solution concentration and film thickness on plasticization and physical aging. We also studied the effects of thermal annealing and long-term physical aging on plasticization. Permeance values of PFCB thin-film selective layers were tracked over 1000 h under different CO$_2$ pressures. These data provide baselines for comparison with next-generation PFCB polymer selective layers with improved resistance to plasticization and physical aging. Finally, a correlation is proposed between polymer plasticization pressure and polymer properties for a wide range of polymer types. My hope is that this correlation will aid in the development of strategies to mitigate the negative effects that plasticization and physical aging have on performance in thin-film composite gas separation membranes.

Chapter 5 summarizes the conclusions from my PhD research and presents recommendations for future work.

Publications from this work at the time of dissertation submission include:


3) J. Zhou, A. T. Haldeman, E. H. Wagener, S. M. Husson, CO$_2$ plasticization and physical aging of perfluorocyclobutyl polymer thin films, in preparation. (Associated with Chapter 4)
1.6 References


CHAPTER 2

FORMATION AND CHARACTERIZATION OF PERFLUOROCYCLOBUTYL POLYMER THIN FILMS

2.1 Introduction

Perfluorocyclobutyl (PFCB) polymers are a new class of materials that show promise as selective layer materials in the development of composite membranes for gas separations, such as carbon dioxide/methane and oxygen/nitrogen separations. In many of the flat sheet applications, a thin film of the selective layer that is free of major defects must be coated onto a support membrane. A focus of this study was to elucidate the impacts of solvents, polymer concentration, and dip-coating withdrawal speed on PFCB thin film thickness and uniformity. An extension was proposed to the Landau-Levich model to estimate the polymer film thickness. The results show that the extended model fits the thickness-withdrawal speed data well above about 55 mm/min, but, at lower withdrawal speeds, the data deviated from the model. This deviation could be explained by the phenomenon of polymer surface excess. Static surface excesses of polymer solutions were estimated by applying the Gibbs adsorption equation using measured surface tension data. Prepared films were characterized by ellipsometry. Refractive index was found to increase with decreasing film thickness below about 50 nm, indicating densification of ultrathin films prepared from PFCB solutions below the overlap concentration. Atomic force microscopy was used to characterize surface morphologies.
Films prepared from tetrahydrofuran and chloroform yielded uniform nanolayers. However, films prepared using acetone as solvent yielded a partial dewetting pattern, which could be explained by a surface depletion layer of pure solvent between the bulk PFCB/acetone solution and the substrate.

2.2 Experimental
2.2.1 Materials

These chemicals were used as received: acetone (anhydrous, 99.8%, Acros Organics), THF (anhydrous, 99.9%, Acros Organics), chloroform (anhydrous, 99.9%, Acros Organics), hydrogen peroxide (30% in water, Fisher Scientific), and sulfuric acid (≥ 96%, Sigma-Aldrich). Tetramer Technologies, LLC provided the biphenylvinylether-perfluorocyclobutyl (BPVE-PFCB) polymer with $M_w = 110000$ Da and PDI = 1.4. Figure 1.1 illustrates the molecular structure of the PFCB polymer repeat unit.

Silicon wafers (Silicon Quest International, Inc.) were diced into 1 cm × 3 cm sample sizes. Prior to dip coating studies, the silicon wafers were cleaned by sonication (VWR, B3500A-MTH) in distilled, deionized water for 15 min and then treated by immersion in a 3:1 v/v mixture of sulfuric acid and hydrogen peroxide for 1 h at 80 °C. (Caution: To prepare this ‘Pirahna’ solution, hydrogen peroxide was poured slowly into the concentrated sulfuric acid under a hood. This solution is a very strong oxidant that may react violently if mixed with organics.)
2.2.2 PFCB solution preparation

PFCB solutions were prepared with concentrations of 0.25–1.00 wt % in chloroform and THF. Additional 1.00 wt % PFCB solutions were prepared in acetone. Each PFCB solution was mixed by magnetic stirrer at room temperature for 2 h before being filtered through a 0.22 µm PTFE syringe filter (Whatman, Inc.).

2.2.3 PFCB coating on silicon wafers

Clean silicon wafers were coated with PFCB solutions at 25 °C using a dip coater (Mayer Feintechnik D-3400) and withdrawal speeds from 20 mm/min to 211 mm/min. The coated wafers were dried for 2 h at 80 °C and 1700 Pa pressure.

2.2.4 Surface tension measurements

Surface tension measurements were done using a contact angle goniometer (KRÜSS GmbH, Inc., DSA10-MK2). Surface tensions of polymer solutions were measured at different PFCB concentration. DSA1v1.80 Drop Shape Analysis software (KRÜSS GmbH, Inc.) was used to analyze the data using the pendant drop method. Polymer solution drops were formed inside a 10 mm × 10 mm × 47 mm quartz cuvette filled with 1 mL of the corresponding solvent to saturate the vapor space and prevent evaporation of the drop. A dispensing needle with a diameter of 1.84 mm was used to form the drop, and the cuvette was covered by a Teflon lid with a 2.00 mm hole for the needle. The approximate drop volume for chloroform solutions was 10 µl and for THF solutions was 12 µl. For every measurement, the relative position of the drop to the cuvette was the
same and the light source was stable to ensure consistent, high quality images for data collection. The limit line was positioned at the border between the needle and drop. Seven measurements were taken for each concentration. Average values are reported, and error bars represent ± 1 standard deviation.

2.2.5 Viscosity measurements

Viscosities of PFCB polymer solutions at room temperature were measured with a cup and bulb viscometer (TA Instruments, Inc.) The cup diameter was 33.8 mm, the bob diameter was 32.0 mm, the bob length was 33.5 mm and the gap was 1.0 mm. Each solution was tested at shear rates from 100 to 1000 s\(^{-1}\) in steps of 100 s\(^{-1}\). Tests at each shear rate were carried out for 60 s to ensure stable measurements. After completing the full set of measurements, the measurement at a shear rate of 500 s\(^{-1}\) was repeated to verify that any solvent evaporation that may have occurred did not affect the viscosity measurements. The measured data were analyzed by ARES V8.03.00 software. The reported viscosity and error bar values represent the average and standard deviation of data collected over the last 10 s at each shear rate.

2.2.6 Atomic force microscopy images

Atomic force microscopy was employed to observe the surface morphologies and measure surface roughnesses of PFCB polymer-coated silicon wafers. Images of thin films were obtained using a Bioscope AFM (Bruker, Inc.) with NanoScope III A controller. Samples were cleaned by nitrogen gas using a gas filter gun before analysis.
Silicon cantilevers (MikroMasch, Inc., NSC15/Si3N4/AIBS/50) were used as probes for the tapping mode measurements. AFM images were taken with 256 × 256 pixel resolution over areas of 10 × 10 µm at scan rate of 0.5 Hz. Root-mean-square (RMS) roughness values were calculated using NanoScope software version 6.12.

### 2.2.7 Contact angle measurements

Static water contact angles were measured on the surface of PFCB coated silicon wafers using a Krüss DSA10-MK2 contact angle goniometer. Deionized water was produced from distilled water that was passed through a Milli-Q water purification system (EMD-Millipore). A DI water drop (3.0 µl) was placed carefully on the sample surface. The sessile drop model was used in DSA1v1.80 Drop Shape Analysis software to determine contact angle. For consistency, measurements were taken 1 min after each water droplet was placed on the surface. Measurements were done at minimum of three locations on each sample to get an average contact angle value with standard deviation.

### 2.2.8 Ellipsometry

Dry layer PFCB film thicknesses were measured by multi-angle, single wavelength ellipsometry (Beaglehole Instruments, Picometer). The incident beam was produced by a 632.8 nm He-Ne laser source. Measurements were done at incidence angles from 56° to 80° with a step size of 4°. The reported thickness is the average of five random locations on each wafer. In this study, a PFCB-silicon dioxide-silicon substrate three layer model was applied to fit the data. PFCB thickness and refractive index based on a Cauchy model
were allowed to vary and were calculated by IgorPro Software version 4.0A.

2.3 Results and discussion

2.3.1 Modeling

Figure 2.1 illustrates the process of polymer film formation. The dip coating process forms a liquid film on the substrate. Landau and Levich [Landau and Levich, 1942] performed a force balance among the gravity force, surface tension, and viscous force about the meniscus region of the forming film to relate the attached, nonvolatile liquid layer thickness to the withdrawal speed. Equation 1 was proposed to estimate the

![Diagram of polymer film formation process: dipping, withdrawing, solvent evaporation]

**Figure 2.1** Schematic illustration of the polymer film formation process.
thickness of the liquid layer that forms during coating with a pure, nonvolatile fluid.

\[
h_L = 0.94 \cdot \frac{(\eta v)^{2/3}}{\gamma_{LV}^{1/6} \cdot (\rho g)^{1/2}}
\]  
(1)

where \( h_L \) is the thickness of the liquid layer, \( \eta \) is the viscosity of the liquid, \( v \) is the withdrawal speed, \( \gamma_{LV} \) is the surface tension of the liquid, \( \rho \) is the density of the liquid, and \( g \) is the gravitational acceleration constant.

In the case of a polymer solution with a volatile solvent, solvent evaporation must be considered as the final step in the film-forming process. Since the polymer mass is conserved during solvent evaporation, dry polymer thin film thickness can be calculated using the liquid layer thickness through Equation 2:

\[
h_P = h_L \cdot \frac{\rho_{\text{solution}}}{\rho_P} \cdot f_P
\]  
(2)

where \( h_P \) is the solid polymer layer thickness, \( \rho_P \) is the density of the polymer, \( f_P \) is the mass fraction of the polymer in solution, and \( \rho_{\text{solution}} \) is the density of the liquid solution, which was estimated by Equation 3:

\[
\frac{1}{\rho_{\text{solution}}} = \frac{f_P}{\rho_P} + \frac{f_{\text{solvent}}}{\rho_{\text{solvent}}}
\]  
(3)

where \( \rho_{\text{solvent}} \) and \( f_{\text{solvent}} \) are the density of the solvent and the mass fraction of the solvent in solution, respectively.

Combining Equations 1 and 2, we extended the Landau-Levich model to estimate dry layer polymer film thickness:

\[
h_P = 0.94 \cdot \frac{(\eta_{\text{solution}} v)^{2/3}}{\gamma_{LV, \text{solution}}^{1/6} \cdot \left(\frac{\rho_{\text{solution}}}{g}\right)^{1/2}} \cdot \frac{f_P}{\rho_P}
\]  
(4)
which can be transformed to

$$\log(h_p) = \log \left( 0.94 \cdot \frac{\eta_{\text{solvent}}^{2/3}}{\gamma_{LV \text{ solvent}}} \cdot \frac{\rho_{\text{solvent}}}{g} \cdot \frac{f_p}{\rho_p} \right) + \frac{2}{3} \log(v)$$

(5)

From Equation 5, if the properties of the solution do not depend significantly on withdrawal speed over the study range, then a log-log plot of polymer thickness versus withdrawal speed should have a slope value of 2/3.

2.3.2 PFCB solution viscosity

Intrinsic viscosities of PFCB polymer solutions were measured using an Ubbelohde viscometer at 25 °C. Measured intrinsic viscosities, [ν], of PFCB solutions were 37.9 cm³/g for PFCB/chloroform and 49.5 cm³/g for PFCB/THF. Using the accepted relationship $C^* = 0.77/[\nu]$ to define the boundary between dilute and semidilute polymer solutions [Graessley, 1980] together with solution density, overlap concentrations were estimated by Equation 6 to be 1.35 wt % and 1.75 wt % for PFCB/chloroform and PFCB/THF, respectively.

$$C^*_\text{wt} = \frac{C^*}{\rho_{\text{solution}}}$$

(6)

Thus, the coating solutions used in this study, which range in bulk concentration from 0.25 wt % to 1.00 wt %, all are considered to be dilute solutions [Sperling, 2006].

Absolute viscosities of PFCB solutions were measured using a cup and bob rheometer. PFCB/chloroform and PFCB/THF solutions exhibited slight shear thickening over the measured shear rate range (data given in Appendix A). Shear thickening
behavior of dilute polymer solutions is known to occur for dilute solutions of polymers with molecular weight higher than $1 \times 10^5$ Da in low viscosity Newtonian fluids at moderate shear rates ($100 \text{ s}^{-1}$ to $3000 \text{ s}^{-1}$) [Ebagninin et al., 2009; Rivero et al., 2012; Kamerkar et al., 2006]. It may be explained by the formation of supramolecular complexes in solution [Ballard et al., 1988]. Similar behavior has been discovered in polystyrene polymer solutions [Edwards et al., 2002]. By fitting the data with a power law, $\eta = m \cdot |\xi|^{n-1}$, where $\xi$ is the shear rate, the value for $n-1$ for all sets of data is nearly zero, as summarized in Table 2.1. Therefore, it is reasonable to use Equation 5 to model film thickness versus withdrawal speed data.
Table 2.1 Viscosity versus shear rate power law constants for PFCB/chloroform and PFCB/THF solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>m (mPa·s)</th>
<th>n-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 wt % PFCB/chloroform</td>
<td>1.10</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.50 wt % PFCB/chloroform</td>
<td>0.76</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.25 wt % PFCB/chloroform</td>
<td>0.65</td>
<td>0.0003</td>
</tr>
<tr>
<td>1.00 wt % PFCB/THF</td>
<td>0.80</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.50 wt % PFCB/THF</td>
<td>0.60</td>
<td>0.0003</td>
</tr>
<tr>
<td>0.25 wt % PFCB/THF</td>
<td>0.60</td>
<td>0.0002</td>
</tr>
</tbody>
</table>
2.3.3 Refractive index of polymer thin films

Refractive index values of PFCB thin films were measured by ellipsometry using data collected at seven different angles from 56° to 80°. The reported refractive index of PFCB BPVE [Smith et al., 2002] is 1.535 at 632.8 nm for bulk films. Figure 2.2 shows that the refractive index of a PFCB thin film increases as the film thickness decreases below about 50 nm and becomes large when the films approach about 10 nm. The polymer films were prepared by coating from a PFCB/chloroform solution at different withdrawal speeds. This phenomenon is not unique to PFCB films. Such behavior has been observed in other thin film studies [Ata et al., 2012; Ata et al., 2009; Algers et al., 2004; Kawashima, 2009; Rzodkiewicz and Panas, 2009]. Recently, for example, Ougizawa and coworkers [Ata et al., 2012] discovered increasing refractive index with decreasing film thickness for polystyrene films and attributed this behavior to polymer densification, as described by the Lorentz-Lorenz equation:

\[
\frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho} = \text{constant}
\]

They also argue that densification occurs when the concentration of precursor solution is lower than the overlapping concentration. In our case, concentrations of PFCB/chloroform and PFCB/THF solutions (0.25–1.00 wt %) are lower than their overlapping concentrations (1.35 wt % and 1.75 wt % for PFCB/chloroform and PFCB/THF, respectively), which may cause the densification in the thin film.

For film thicknesses below 50 nm, a significant difference was found between RI values measured at the two endpoint incidence angles of 56° and 80° (data given in
Figure 2.2 Refractive index of PFCB thin films measured by ellipsometry.
Appendix B). This result indicates anisotropic properties of PFCB thin films below about 50 nm. Optical anisotropy may originate from \( \pi \)-stacking among the aromatic rings in PFCB, induced by interactions among these groups and silanol groups on the treated silicon wafers [Ata et al., 2012]. This interaction would cause PFCB polymer chains to tend to be aligned in a specific orientation near the polymer-surface interface. The degree of ordering is diminished moving away from the surface into the bulk film as the interactions among aromatic rings become randomized. Thus, the effect of surface-induced ordering on measured refractive index is more significant in ultrathin films, and the data for films thicker than 50 nm do not show optical anisotropy.

To account for optical anisotropy in measured film thickness values, we used multi-angle ellipsometry and collected data at seven different incidence angles ranging from 56° to 80°. All seven points were used to fit PFCB thickness and refractive index based on a Cauchy model.

2.3.4 Effect of withdrawal speed and solution concentration on film thickness

Silicon wafers were selected as the coating substrates due to their high uniformity, high surface energy, and optical properties that enable PFCB film thickness to be measured accurately by ellipsometry. Figures 2.3 and 2.4 show that PFCB film thickness increases with increasing withdrawal speed and polymer concentration in chloroform and THF solvents, respectively. Every datum point represents the average thickness among five measurement locations on one wafer. Error bars represent \( \pm 1 \) standard deviation of thickness measured at the five locations. Dashed lines are results estimated from
Figure 2.3 Role of solution concentration and withdrawal speed (in mm/min) on PFCB film thickness (in nm). Triangles, diamonds and squares represent experimental data for 1.00 wt %, 0.50 wt % and 0.25 wt % PFCB in PFCB/chloroform solutions. Each point represents an average of five measurements, and error bars represent ± 1 standard deviation of five measurements. Lines represent model predictions from Equation 5.
Figure 2.4 Role of solution concentration and withdrawal speed (in mm/min) on PFCB film thickness (in nm). Triangles, diamonds and squares represent experimental data for 1.00 wt %, 0.50 wt % and 0.25 wt % PFCB in PFCB/THF solutions. Each point represents an average of five measurements, and error bars represent ± 1 standard deviation of five measurements. Lines represent model predictions from Equation 5.
Equation 5 (the extended Landau-Levich equation). Because PFCB/chloroform and PFCB/THF solution viscosities do not depend significantly on shear rate, it is reasonable to use the extended Landau-Levich equation to predict PFCB film thicknesses. Both study systems (PFCB/chloroform and PFCB/THF) showed behavior that was expected from the extended Landau-Levich equation at higher withdrawal speeds (>50 mm/min). But at lower withdrawal speeds (<50 mm/min), we no longer observe a decrease in thickness with decreasing withdrawal speed. This deviation from theory at low withdrawal speed may be explained by the phenomenon of surface excess.

Surface excess is defined as the deviation of the surface solute (in this case PFCB polymer) concentration from its bulk concentration. It occurs when the surface tension of the solute is less than that of the solvent [Mitropoulos, 2008]. A high polymer concentration at the air-solution interface, relative to the concentration in the bulk solution, would yield thicker films according to Equation 4. As the wafer is withdrawn from the PFCB solution, it removes solution from the interface to form a liquid film, and depletes the surface excess of polymer. PFCB chains must diffuse from the bulk solution to replenish the surface excess, driven by the Marangoni effect. At lower withdrawal
Figure 2.5 Estimated interfacial PFCB concentration in PFCB/chloroform at different withdrawal speeds. Diamonds, squares and triangles represent data for 1.00 wt %, 0.50 wt % and 0.25 wt % bulk PFCB concentration in chloroform.
speeds, more time is available for diffusion of polymer chains to the surface. The result is that the concentration of the solution removed by the silicon wafer at the air-solution interface is closer to the static (equilibrium) surface excess, which can be much higher than the bulk. At high withdrawal speed, there is less time for polymer diffusion to replenish the surface excess, and the surface concentration approaches the bulk value. Since the Landau-Levich model uses bulk concentration to estimate film thickness, it captures the experimental behavior at high enough withdrawal speeds and underestimates film thicknesses at lower withdrawal speeds. In Figures 2.3 and 2.4, reasons for the deviation between the estimations and experimental results for 0.25 wt% chloroform solution and 1.00 wt% THF solution are not clear.

Based on the thickness data in Figures 2.3 and 2.4, one can estimate a theoretical interface concentration (i.e., polymer mass fraction), $f_p'$, by Equation 8, a rearrangement of Equation 4.

$$f_p' = \frac{h_p \cdot \rho_p}{0.94} \cdot \left( \frac{\gamma_{LV \ solution}}{\eta_{solution}} \right)^{1/6} \cdot \left( \frac{g}{\rho_{solution}} \right)^{1/2}$$  

Figures 2.5 and 2.6 present the estimated interfacial concentrations versus withdrawal speed determined from Equation 8 using measured thickness values from Figures 2.3 and 2.4. As the speed increases, the surface concentration gradually reaches a constant value approaching the bulk value. The estimated surface concentrations also are higher in PFCB/THF solutions. The results are consistent with work by Bloch et al. [Bloch et al., 1985] who found that interfacial concentrations of polymer solutions could be orders of magnitude higher than the bulk concentration over an interfacial region with thickness in
Figure 2.6 Estimated interfacial PFCB concentration in PFCB/THF at different withdrawal speeds. Diamonds, squares and triangles represent data for 1.00 wt %, 0.50 wt % and 0.25 wt % bulk PFCB concentration in THF.
a range of tens to hundreds of Angstroms.

To determine if the estimated values from Equation 8 are reasonable, measurements of surface tension were made to allow direct calculations of PFCB surface concentrations. Figure 2.7 shows the relationship between surface tension and bulk PFCB concentration, presented as the molar concentration of PFCB repeat units in solutions of 0.25–10.00 wt% PFCB. The error bars represent ± 1 standard deviation among seven measurements at the same concentration. For both systems used in this study, the surface tension of the solution decreased as the concentration of PFCB increased. Ausserre et al. [Ausserre et al., 1986] stated that a decrease of surface tension in more concentrated polymer solution indicates a surface excess. The surface excess was calculated by using the measured values of surface tension and the Gibbs adsorption isotherm [Reiss, 1965], given by Equation 9, where $\Gamma$ is the surface excess, $c$ is the bulk solution PFCB concentration, $\gamma$ is the surface tension.

$$\left(\frac{\partial \gamma}{\partial \ln c}\right)_T = -RT\Gamma$$

(9)

Experimental data in Figure 2.7 were used to determine surface excess values, which have units of mole/m$^2$. To compare the results with the surface concentrations estimated in Figures 2.5 and 2.6, the surface excess needed to be converted to a wt %. The conversion was done using a layer thickness of polymer solution equal to the diameter of a PFCB repeat unit, which was estimated using Jaguar 7.7 Software (Schrödinger, LLC) at the density functional theory level. Table 2.2 summarizes other pertinent data used for the calculations.
Figure 2.7 Surface tensions of PFCB/chloroform and PFCB/THF solutions at different concentrations. Diamonds and squares represent experimental data for PFCB solutions in chloroform and THF, and curves represent polynomial fits. Each point represents an average of seven measurements, and error bars represent ± 1 standard deviation.
Table 2.2 Summary of PFCB, chloroform, and THF parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFCB density</td>
<td>1.30 g/cm³</td>
</tr>
<tr>
<td>PFCB repeat unit $M_w$</td>
<td>346 g/mole</td>
</tr>
<tr>
<td>PFCB repeat unit volume*</td>
<td>0.253 nm³</td>
</tr>
<tr>
<td>PFCB repeat unit diameter*</td>
<td>0.8 nm</td>
</tr>
<tr>
<td>Chloroform density</td>
<td>1.48 g/cm³</td>
</tr>
<tr>
<td>THF density</td>
<td>0.89 g/cm³</td>
</tr>
<tr>
<td>Chloroform viscosity</td>
<td>0.568 mPa.s</td>
</tr>
<tr>
<td>THF viscosity</td>
<td>0.480 mPa.s</td>
</tr>
<tr>
<td>Chloroform surface tension</td>
<td>27.5 mN/m</td>
</tr>
<tr>
<td>THF surface tension</td>
<td>28.0 mN/m</td>
</tr>
</tbody>
</table>

*estimated using Jaguar 7.7 Software (Schrödinger, LLC)
Figure 2.8 presents the surface concentration values in wt %. At the same bulk concentration, PFCB/THF has a higher surface excess concentration than PFCB/chloroform, which is consistent with previous estimations in Figures 2.5 and 2.6. The static (equilibrium) surface excess concentrations calculated from the Gibbs adsorption isotherm show that the surface concentrations of PFCB/chloroform and PFCB/THF solutions can be much higher than their bulk concentrations. The values also are much higher than those given in Figures 2.5 and 2.6, indicating that the values estimated from Equation 8 are physically meaningful (i.e., they fall below the equilibrium values given in Figure 2.8). It thus seems reasonable that PFCB surface excess can explain the unexpected trend in thickness versus withdrawal speed seen in Figures 2.3 and 2.4, especially at low withdrawal speeds.
**Figure 2.8** Surface excess concentrations of PFCB in PFCB/chloroform solutions (diamonds) and PFCB/THF solutions (squares) at different concentrations.
2.3.5 Typical PFCB thin film morphology characterization

Figure 2.9 presents surface morphology images by AFM of PFCB films with different thicknesses prepared from PFCB/chloroform solution. Figure 2.10 presents images of films prepared from PFCB/THF solution. Three random locations on each film were scanned to get the reported average RMS surface roughness values. Generally, these films are very smooth and uniform, with RMS roughness values around 1 nm. No major defects or dewetting phenomena were observed. Table 2.3 shows that measured water contact angles on PFCB thin films with different thicknesses are the same.
Table 2.3 Water contact angle for PFCB thin films.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.3 ± 1.5</td>
<td>96.9 ± 0.7</td>
</tr>
<tr>
<td>9.9 ± 3.9</td>
<td>98.4 ± 2.1</td>
</tr>
<tr>
<td>18.9 ± 2.6</td>
<td>96.8 ± 2.2</td>
</tr>
<tr>
<td>21.2 ± 6.1</td>
<td>99.6 ± 3.3</td>
</tr>
<tr>
<td>43.3 ± 1.2</td>
<td>96.8 ± 2.3</td>
</tr>
<tr>
<td>52.2 ± 1.0</td>
<td>96.3 ± 1.8</td>
</tr>
</tbody>
</table>
2.3.6 Polymer pattern coated from PFCB/acetone solution

Unlike films prepared using chloroform and THF solvents, films prepared using acetone were not uniform. Figure 2.11 illustrates that different film patterns appeared at different coating conditions from 1.00 wt % PFCB/acetone solution. In Figure 2.11A, the film prepared using a high withdrawal speed of 211 mm/min exhibited a rough surface with dewetted islands. Interestingly, at lower withdrawal speeds, the initial region of the silicon wafer (i.e., the first part to be coated) displayed a different film morphology than the rest of the wafer. These morphologies are shown in Figures 2.11 B and C. Figure 2.11 B shows at 131 mm/min withdrawal speed that the film on the bottom part of the wafer is very rough; whereas, Figure 2.11 C shows that the film coating the initial region of the wafer is smooth with some defects on the surface. When the film was prepared at 84 mm/min withdrawal speed, its whole surface is smooth with some defects (Figure 2.11 D).
**Figure 2.9** AFM topographical images (10 × 10 μm) of PFCB thin films on silicon substrates prepared from PFCB/chloroform solution. The z-scale is 10 nm. A: 42 nm thick film, RMS roughness = 0.4 nm; B: 26 nm thick film, RMS roughness = 1.3 nm; C: 3 nm thick film, RMS roughness = 1.8 nm.
Figure 2.10 AFM topographical images (10 × 10 μm) of PFCB thin films on silicon substrates prepared from PFCB/THF solution. The z-scale is 10 nm. A: 40 nm thick film, RMS roughness = 0.5 nm; B: 24 nm thick film, RMS roughness = 0.6 nm; C: 2 nm thick film, RMS roughness = 0.9 nm.
Figure 2.11 AFM topographical images (100 × 100 μm) of PFCB thin film on silicon substrates prepared from PFCB/acetone solution. The z-scale is 1 μm for A, 600 nm for B and 50 nm for C and D. A: dewetting pattern of PFCB prepared from 1.00 wt% solution in acetone at withdrawal speed 211 mm/min, RMS roughness = 107.0 nm; B: rough part of PFCB prepared from 1.00 wt% solution in acetone at withdrawal speed 131 mm/min, RMS roughness = 80.7 nm; C: smooth part of PFCB prepared from 1.00 wt% solution in acetone at withdrawal speed 131 mm/min, RMS roughness = 2.89 nm; D: smooth pattern of PFCB prepared from 1.00 wt% solution in acetone at withdrawal speed 84 mm/min, RMS roughness = 2.3 nm.
These different PFCB patterns might be attributed to differences in solvent-substrate interactions. Electrostatic forces, induction forces and hydrogen bonding should be considered. Treatment with Pirahna solution yields a high concentration of silanol groups on the surface of silicon wafers [Flavel et al., 2007]. Both chloroform and silanol groups are good hydrogen bond donors but poor acceptors [Ahuja and Jespersen, 2006]. It has been shown that chloroform cannot form stable hydrogen bonds with silanol groups on silicon wafers [Nadia and Allen, 2009]. As good hydrogen bond acceptors, acetone and THF do form hydrogen bonds with silanol groups. Dipole-dipole interactions and induction forces can be estimated by Equations 10 and 11 [Prausnitz et al., 1999], where $\mu$ is dipole moment, $\alpha$ is polarizibility, $\varepsilon_0$ is permittivity of a vacuum and $r$ is the intermolecular distance.

$$F_{\text{dipole-dipole}} = -\frac{4\mu_i^2\mu_j^2}{(4\pi\varepsilon_0)^2} kT r^7$$  \hspace{1cm} (10)

$$F_{\text{induction}} = -\frac{6\alpha_i\mu_j^2}{(4\pi\varepsilon_0)^2} r^7$$  \hspace{1cm} (11)

Both equations are strong functions of dipole moment. Table 2.4 summarizes the dipole moments and polarizibility values of the three solvents [Prausnitz et al., 1999; Lee et al., 2007]. The dipole moment of acetone is much larger than the values of chloroform and THF, which means acetone has much stronger dipolar and induction forces with the substrate than the other two solvents. Finally, acetone is a marginal solvent for PFCB but chloroform and THF are both good solvents. Together, these data and observations support the possibility that a depletion layer formed between silicon wafers and the
PFCB/acetone solution.

**Table 2.4** Solvent polarizabilities and dipole moments.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polarizability $\times 10^{24}$ (cm$^3$)</th>
<th>Dipole Moment (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform$^{[34]}$</td>
<td>8.50</td>
<td>1.05</td>
</tr>
<tr>
<td>THF$^{[35]}$</td>
<td>7.90</td>
<td>1.63</td>
</tr>
<tr>
<td>Acetone$^{[34]}$</td>
<td>6.42</td>
<td>2.88</td>
</tr>
</tbody>
</table>

Fondecave and Wyart [Fondecave and Wyart, 1999] discussed formation of a pure solvent depletion layer in this kind of system and proposed Equation 12 for the depletion layer thickness, e:
\[ e = a_0 \left( \frac{A}{6\pi kT} \right)^{1/3} \varphi^{-3/4} \]  \hspace{1cm} (12)

where \( a_0 \) is the molecular size, \( A \) is the Hamaker constant, \( k \) is the Boltzmann constant and \( \varphi \) is the polymer volume fraction. The Hamaker constant is usually on the order of \( 10^{-19} \) to \( 10^{-20} \) J [Ghosh, 2009]. With a PFCB concentration of 1.00 wt\% in acetone, the estimated pure acetone depletion layer could be 10 nm. A depletion layer this thick would prevent the PFCB from ‘sensing’ the underlying substrate and would lead to dewetting on the pure acetone depletion layer. After evaporation, dewetted PFCB islands would remain, as observed in Figure 2.11.

From Equation 12, a higher polymer concentration (volume fraction) would reduce the thickness of the depletion layer, which would make dewetting less likely. Based on results with chloroform and THF shown in Figures 2.5 and 2.6, lower withdrawal speed gives higher PFCB concentration in the liquid layer that coats the wafer. It is therefore reasonable to see that a smoother film surface was prepared at 84 mm/min compared to higher withdrawal speeds. The difference in surface morphologies seen on the wafer prepared at 131 mm/min (Figures 2.11 B and C) also can be explained by surface excess concentration. At the start of the coating process, the concentration of polymer being coated onto the wafer is at its highest (equilibrium) value, and the depletion layer at the silicon-solution interface is thin. The result is the formation of a relatively smooth film on the initial region of the wafer. After a transient period, the surface excess is depleted, the concentration of polymer that is coated decreases, and the thickness of the depletion layer at the silicon-solution interface increases. The result is film dewetting on the bottom part
of the wafer.

2.4 Conclusions

This study examined the roles of solvent, polymer concentration, and dip-coating withdrawal speed on biphenylvinylether-perfluorocyclobutyl polymer thin film thickness and uniformity. PFCB dip coating thickness depends on concentration and withdrawal speed, and can be estimated by an extension of the Landau-Levich equation. The accuracy of the extended Landau-Levich model for estimating layer thickness is impaired at low withdrawal speed by the surface excess of PFCB polymer. PFCB films produced from solutions in chloroform and THF are highly uniform; whereas, films prepared from solutions in acetone are rough or dewetted. This behavior could be explained by formation of a surface depletion layer resulting from strong interactions between acetone and the substrate. Therefore, when selecting solvents for dip coating, solvents that may interact strongly with the substrate are not recommended. PFCB BPVE exhibited optical anisotropy for thin films below about 50 nm thickness, likely resulting from π-stacking of aromatic groups induced by interactions among these groups and the silanol groups of the substrate. Thus, caution should be taken when using optical measurements to estimate physical properties such as density for ultrathin PFCB films on substrates that have strong interactions with aromatic groups.

This work provided guidelines for development of PFCB thin-film composite membranes. Subsequent chapters describe membrane development and testing, and the study of CO₂ plasticization and aging using long-term permeance measurements at
different CO$_2$ pressures.
2.5 References


Graessley, W.W., Polymer chain dimensions and the dependence of viscoelastic properties on concentration, molecular weight and solvent power, Polymer 21 (1980) 258–262.


CHAPTER 3

PERFLUOROCYCLOBUTYL POLYMER THIN-FILM COMPOSITE MEMBRANES FOR CO₂ SEPARATIONS

3.1 Introduction

The role of carbon emissions on global warming has fueled widespread interest in mitigation strategies. Thin-film composite membranes are a promising technology for carbon capture; however, only membranes with high and stable permeance (>1000 GPU) and moderate CO₂/N₂ selectivity (>20) potentially could be applied in flue gas treatment. In many cases, practical problems such as membrane plasticization and physical aging rule out promising new materials from commercial consideration. The present contribution is part of a larger effort to develop fundamental structure-property relationships for perfluorocyclobutyl (PFCB) polymers that provide a foundation for PFCB-based membranes with resistance to plasticization and physical aging. A focus of this part of the study was to develop procedures to fabricate PFCB thin-film composite membranes with reproducible performance characteristics. Biphenylvinylether-perfluorocyclobutyl (BPVE-PFCB) polymer (figure 1.1) was used as a model for the family of PFCB polymers. The thickness of the PFCB selective layer was controlled by changing processing conditions. Results show that uniform PFCB layers were coated successfully on support membranes to produce thin-film composites with reproducible permeance and selectivity values. Membranes prepared with the thinnest BPVE-PFCB
films yielded CO₂ permeance of 1000 GPU with CO₂/N₂ selectivity around 15. Estimated CO₂ permeance through the PFCB thin layer alone was up to 1700 GPU, with CO₂/N₂ selectivity close to the bulk film intrinsic selectivity of 20. The use of other PFCB polymers and copolymers with superior separation characteristics may be used to prepare composite membranes with improved performance.

3.2. Experimental

3.2.1. Materials

These chemicals were used as received: carbon dioxide (Industrial grade, Airgas, Inc.), chloroform (anhydrous, Acros Organics), diiodomethane (99%, Sigma-Aldrich), hydrogen peroxide (30%, Fisher Scientific), methanol (HPLC, Fisher Scientific), methyl ethyl ketone (MEK, 99%, Sigma-Aldrich), nitrogen (Industrial grade, Airgas, Inc.), sulfuric acid (96%, Sigma-Aldrich). Poly(glycidyl methacrylate) (PGMA, \( M_w = 80000 \) Da and PDI = 3.3) was received from the School of Materials Science and Engineering at Clemson. Deionized water was produced from distilled water that was passed through a Milli-Q water purification system (EMD-Millipore). Tetramer Technologies, LLC provided the biphenylvinylether-perfluorocyclobutyl (BPVE-PFCB) polymer with \( M_w = 110000 \) Da and PDI = 1.4.

PAN50 membranes were purchased from Sepro Membranes, Inc. These are composite ultrafiltration membranes comprising a poly(acrylonitrile) layer coated onto a polypropylene support. Prior to coating, the membranes were rinsed in methanol at 25 °C under gentle agitation by a shaker bath for 30 min and then dried in a vacuum oven at
room temperature and 1700 Pa. The purpose of this rinse step is to remove structural preservatives in the membrane before any other treatment.

3.2.2 Preparation of thin-film composite wafers

Silicon wafers (Silicon Quest International, Inc.) were diced into 1 cm × 3 cm sample sizes. Prior to dip coating studies, the silicon wafers were cleaned by sonication (VWR, B3500A-MTH) in distilled, deionized water for 15 min and then treated by immersion in a 3:1 v/v mixture of sulfuric acid and hydrogen peroxide for 1 h at 80 °C. (Caution: During preparation of this solution, hydrogen peroxide was poured slowly into the concentrated sulfuric acid under a hood. This solution is a very strong oxidant that may react violently if mixed with organics.)

Clean silicon wafers were coated with 1.00 wt% PGMA/MEK solution at 25 °C using a dip coater (Mayer Feintechnik D-3400) and withdrawal speed of 60 mm/min. The PGMA film was annealed for 30 min at 120 °C and 1700 Pa. PGMA-coated wafers were coated by a proprietary polymer gutter layer solution at 25 °C and withdrawal speed of 60 mm/min. The coated wafers were dried for 2 h at 120 °C and 1700 Pa pressure. Prior to PFCB deposition, these wafers were placed in a Model PDC-001 Harrick plasma chamber under 200 μmHg argon and treated with 6.8 W plasma supply for 1 min. After plasma treatment, wafers were exposed to Ar for 1 min, air for 7 h, and then soaked in water at 40 °C for 12 h to improve surface wettability. Finally, the wafers were rinsed with methanol and dried for 2 h at room temperature and 7800 Pa. PFCB thin films were coated onto gutter layer coated silicon wafers from PFCB/chloroform solutions of 0.3
wt%, 0.7 wt% and 1.4 wt%. The withdrawal speeds ranged from 50 mm/min to 220 mm/min.

3.2.3 Preparation of thin-film composite membranes

3.2.3.1 Gutter layer deposition

PAN50 membranes were cut into 6 cm × 6 cm samples and the polypropylene support side was covered by foil tape. A home-built dip coater was used to coat the poly(acrylonitrile) side of the PAN50 membrane with a thin gutter layer of a proprietary polymer characterized by CO₂ permeability >1000 Barrer and CO₂/N₂ selectivity <10. Membranes were dipped into the solution for 20 seconds, and then withdrawn at a speed of 130 mm/min. After coating, membranes were transferred immediately into an oven and dried for at least 12 h at 40 °C and 7800 Pa. Next, these gutter layer coated membranes were treated by Ar plasma following the same protocol that was used on the silicon wafers.

3.2.3.2 Selective layer coating

PFCB solutions were prepared with concentrations of 0.3–1.4 wt % in chloroform. Each PFCB solution was mixed by magnetic stirring at room temperature for 2 h before being filtered through a 0.22 µm PTFE syringe filter (Whatman, Inc.).

Gutter layer coated membranes were dip coated from 0.3 wt%, 0.7 wt% and 1.4 wt% PFCB/chloroform solution at withdrawal speeds from 50 mm/min to 220 mm/min. Membranes were air dried under 7800 Pa at room temperature for 2 h before testing.
3.2.4 Membrane Characterization

3.2.4.1 Atomic force microscopy

Atomic force microscopy was employed to observe the surface morphologies and measure surface roughness values of PAN50 membranes, gutter layer membranes, and PFCB polymer-coated wafers and composite membranes. Images were obtained using a Bioscope AFM (Bruker, Inc.) with NanoScope III A controller. Samples were cleaned by nitrogen gas using a gas filter gun before analysis. Silicon cantilevers (MikroMasch, Inc., NSC15/Si3N4/AIBS/50) were used as probes for the tapping mode measurements. AFM images were taken with 256 × 256 pixel resolution over areas of 10 × 10 µm at scan rate of 0.5 Hz. Root-mean-square (RMS) roughness values were calculated using NanoScope software version 6.12.

3.2.4.2 Ellipsometry measurements

Ellipsometry was used to measure the thicknesses of gutter layers and PFCB layers on silicon wafers (Beaglehole Instruments, Picometer). The incident beam was produced by a 632.8 nm He-Ne laser source. Measurements were done at incidence angles from 56° to 80° with a step size of 4°. The reported thickness is the average of five random locations on each wafer. In this study, a PFCB-gutter layer-silicon dioxide-silicon substrate multilayer model was applied to fit the data. PFCB thickness and refractive index based on a Cauchy model were allowed to vary and were calculated by IgorPro Software version 4.0A.
3.2.4.3 Surface tension measurements

Solid surface tensions of the gutter layer, plasma-treated gutter layer and PFCB layer were estimated by the Owens-Wendt method [Czenkiewicz, 2001] using Equations 1 and 2:

\[ \gamma_{SV} = \gamma_{SV}^P + \gamma_{SV}^D \]  
\[ \gamma_{SV} = 2\sqrt{\gamma_{LV}^D \gamma_{SV}^D} + 2\sqrt{\gamma_{LV}^P \gamma_{SV}^P} \]

where \( \gamma_{LV} \) represents the test liquid surface tension, \( \gamma_{SV} \) represents solid surface tension, and D and P represent dispersive and polar contributions. Using Equations 1 and 2, \( \gamma_{SV}^D \) and \( \gamma_{SV}^P \) were evaluated using contact angles measured with two test liquids: water and methylene iodide. Table 3.1 summarizes the surface tensions of the test liquids.

**Table 3.1 Surface tensions of test liquids used for Owens-Wendt method.**

<table>
<thead>
<tr>
<th></th>
<th>Surface Tension ( \gamma_{SL} ) (mN·m(^{-1}))</th>
<th>Dispersive ( \gamma_{SL}^D ) (mN·m(^{-1}))</th>
<th>Polar ( \gamma_{SL}^P ) (mN·m(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>22.1</td>
<td>50.7</td>
</tr>
<tr>
<td>Methylene iodide</td>
<td>50.8</td>
<td>49.5</td>
<td>1.3</td>
</tr>
</tbody>
</table>
All static contact angles were measured using a Krüss DSA10-MK2 contact angle goniometer. A liquid drop (3.0 μl) was placed carefully on the sample surface. The sessile drop model was used in DSA1v1.80 Drop Shape Analysis software to determine contact angle. For consistency, measurements were taken 1 min after each droplet was placed on the surface. Measurements were done at a minimum of three locations on each sample to get an average contact angle value with standard deviation.

3.2.4.4 Membrane performance testing

Nitrogen and CO$_2$ permeances of composite membranes were measured using a home-built, constant-pressure permeance testing apparatus. The volumetric flux was recorded by a bubble flow meter, and permeance was calculated by Equation 3, where V/t is the gas volumetric flow rate, A is the membrane area, and Δp is the transmembrane pressure.

\[
\text{Perm} = \frac{V}{At\Delta p} \quad (3)
\]

Gutter layer membranes were cut into circles with 47 mm diameter. They were placed into a 47 mm stainless steel high-pressure cell (EMD Millipore Corporation) to conduct permeance testing at room temperature and a transmembrane pressure of 20 psi. Membranes were equilibrated with the gas for 20 minutes before measurement. After testing, membranes with selectivities matching the intrinsic value of the proprietary gutter layer polymer were coated by PFCB. The back side of these membranes was covered by foil to prevent PFCB solution from filling the support membrane pores. TFC membranes were dried for 2 h at room temperature and 1700 Pa to ensure complete removal of
solvents. The dried TFC membranes were cut into 25 mm diameter circles using a punch and tested in a 25 mm stainless steel high-pressure cell (EMD Millipore Corporation) at a pressure of 2.4 bar. Measured values for the permeance of the gutter layer and the PFCB thin-film composite membrane were input to Equation 4 to calculate the permeance of the PFCB layer.

\[
\frac{1}{\text{Perm}_{i}^{\text{PFCB}}} = \frac{1}{\text{PERM}_{i}} - \frac{1}{\text{Perm}_{i}^{\text{gutterlayer}}} \tag{4}
\]

PERM\(_{i}\) is the permeance of the target penetrant through the overall membrane, while Perm\(_{i}^{\text{PFCB}}\) and Perm\(_{i}^{\text{gutterlayer}}\) are that through the PFCB layer and the gutter layer.

To provide accurate information on the permeance of PFCB thin films, all films experienced the same thermal history prior to characterization to avoid measurement artifacts due to physical aging. Time zero was set to be the time that the PFCB layer coating was finished. Performance values are reported in two ways: 1) performance of the overall TFC membranes and 2) performance of the PFCB layers. Considering aging of the thin polymer film, measurements were done at four different times within the first 24 h, and reported values represent those after 1 hour of aging, back extrapolated from permeance-time measurements using logarithmic fit.

### 3.3. Results and discussion

#### 3.3.1 Characterization of bare membranes

PAN50 membranes were washed with methanol and dried prior to use. This wash step resulted in a percentage mass loss of 11.5 ± 0.1%, likely corresponding to removal of structural preservatives. CO\(_{2}\) permeance of PAN50 was measured to be 83510 ± 1070
GPU, while its N₂ permeance was measured to be 98730 ± 790 GPU. The ideal CO₂/N₂ selectivity was therefore equal to 0.85, which is close to the characteristic CO₂/N₂ selectivity of 0.80 for Knudsen diffusion. This result suggests that the nominal pore diameter of PAN50 is close to the characteristic size for Knudsen diffusion, which is smaller than 50 nm [Dutta, 2007]. Its top surface AFM images were presented in figure 3.1. Two different scanning sizes of 5 × 5 μm and 1 × 1 μm were taken on PAN50 membranes. Three random locations on each film were scanned to get the reported average RMS surface roughness values. From the 1 × 1 μm image, one can tell the size of the pore size is around 30 nm by using the AFM image analysis software (V513r, Bruker, Inc.). The porosity of the top surface is calculated to be 50% using Image J.
Figure 3.1 a: AFM topographical images of PAN50 membranes after methanol wash: the z-scale is 30 nm. 5 × 5 um, RMS roughness = 12.3 nm; b: AFM topographical images of PAN50 membranes after methanol wash: the z-scale is 60 nm. 1 × 1 um, RMS roughness = 2.5 nm;
3.3.2 Modeling composite membrane performance

3.3.2.1 Expected composite membrane performance

For an ideal, defect-free composite membrane, a resistance in series equation describes the relationship between the gas permeance of the overall membrane and its sublayers, which are represented by superscript k in Equation 5.

\[
\frac{1}{\text{Perm}_i} = \sum_k \frac{1}{\text{Perm}^k_i} = \sum_k \frac{\delta^k}{P_i^k}
\]  

(5)

\(\delta^k\) is the thickness of the layer k polymer (PFCB layer and gutter layer), and \(P_i^k\) is the gas permeability of the layer k polymer.

In this study, the porous PAN50 support offers negligible resistance. Thus, the working relationship becomes.

\[
\frac{1}{\text{Perm}_i} = \frac{\delta^{\text{PFCB}}}{P_i^{\text{PFCB}}} + \frac{1}{\text{Perm}^{\text{gutterlayer}}_i} = \frac{1}{\text{Perm}^{\text{PFCB}}_i} + \frac{1}{\text{Perm}^{\text{gutterlayer}}_i}
\]  

(6)

Equation 6 was used 1) to predict the best possible performance of composite membranes before membranes were prepared (explained more fully in section 3.2.2) and 2) to estimate permeance and permeability of gases through the PFCB layer of the composite membranes using measured permeance values through the composite and gutter layer membranes. One also needs to know the thickness to estimate permeability, and thickness values from ellipsometry measurements were used for these estimates.

In reality, composite membranes may have pinholes that impair membrane performance, especially selectivity. Defects in the PFCB selective layer may be caused by surface dewetting, non-uniformities in the substrate, humidity, and dust particles or other impurities. Defects in the gutter layer may be caused by ineffective coating of the...
porous substrate or etching during the subsequent plasma treatment. Equation 7 is proposed to estimate membrane performance with defects in the PFCB selective layer, where $f_d$ is the area fraction of defects in that layer. Equation 8 was used to estimate ideal CO$_2$/N$_2$ selectivity $\alpha$ as it relates to the defect fraction.

$$\text{Perm}_i = \frac{1-f_d}{\text{Perm}_{\text{PFCB}}} + \frac{f_d}{\text{Perm}_{\text{gutter layer}}}$$

$$\alpha = \frac{1-f_d}{\text{Perm}_{\text{PFCB}}} + \frac{f_d}{\text{Perm}_{\text{CO}_2}}$$

$$\alpha = \frac{1-f_d}{\text{Perm}_{\text{PFCB}}} + \frac{f_d}{\text{Perm}_{\text{N}_2}}$$

3.3.2.2 Performance of ideal, defect-free composite membranes

To guide the design of composite membranes, calculations were performed using Equation 6 to model the performance of ideal, defect-free PFCB thin-film composite membranes. Figure 3.2 shows the dependence of CO$_2$ permeance and CO$_2$/N$_2$ selectivity of ideal PFCB thin-film composite membranes on PFCB film thickness and gutter layer permeance. In this figure, symbols represent data for composite membranes prepared with gutter layer thicknesses that yield CO$_2$ permeance values from 1000 to 8000 GPU. According to Equation 6, the performance of composite membranes depends on the properties of the PFCB layer and gutter layer. In cases where the PFCB layer is ‘thick’, the selective layer provides a higher resistance than the gutter layer, and composite membrane performance is dominated by the PFCB layer. From Figure 3.2, the permeance of composite membranes does not change much until the PFCB layer thickness drops
Figure 3.2 Predicted performance of ideal PFCB thin-film composite membranes with different gutter layer as a function of PFCB thickness.
below about 150 nm. The CO$_2$/N$_2$ selectivity is more sensitive to the gutter layer permeance, but also shows strong dependence on PFCB layer thickness below about 150 nm. These data illustrate that the resistance of the gutter layer only becomes significant in ultrathin-film PFCB composite membranes, and these membranes have lower CO$_2$/N$_2$ selectivity. Therefore, when the resistance of the gutter layer is non-negligible relative to the selective layer, overall CO$_2$/N$_2$ selectivity will be less than that of a bulk film of the selective layer material (assuming that the selectivity of a PFCB thin film itself is not different significantly from that of the bulk).

In Chapter 2, we have found by ellipsometry that refractive index of PFCB films coated on silicon wafers increases as film thickness decreases below about 100 nm. It is likely, therefore, that the permeability of PFCB films below about 100 nm is lower than the bulk value due to densification in these ultrathin films. Nevertheless, Figure 3.2 provides guidance on the effects that gutter layer permeance (i.e., thickness) and PFCB film thickness have on composite membrane performance. Estimated values of permeance and selectivity could be used to guide researchers on the conditions needed to prepare PFCB thin-film composite membranes with targeted performance characteristics.

### 3.3.2.3 Modeling performance of composite membranes with defects in the selective layer

Defects in the selective layer may be caused by low substrate surface tension, non-uniformities in the substrate, humidity, and dust particles or other impurities. The likelihood for defects is highest for ultrathin films. Defects in the PFCB selective layer
Figure 3.3 Estimated CO$_2$/N$_2$ selectivity and CO$_2$ permeance when defects exist. a: estimations for 60 nm PFCB thin film composite membranes; b: estimations for 200 nm PFCB thin film composite membranes. In both figures, open triangles, squares and diamonds represent estimated CO$_2$ permeance with gutter layer permeance of 6000 GPU, 4000 GPU and 2000 GPU; solid triangles, squares and diamonds represent estimated CO$_2}$/N$_2$ selectivity with gutter layer permeance of 6000 GPU, 4000 GPU and 2000 GPU.
decrease CO$_2$/N$_2$ selectivity. Calculations were made to understand the impact of such defects on the performance of PFCB thin-film composite membranes.

Figures 3.3 a and 3.3 b report model findings for membranes comprising 50 nm and 200 nm PFCB thin films on supports coated with gutter layers having different CO$_2$ permeance values. The PFCB thin films were modeled with different defect surface area fractions (0.000–0.200). Diamonds, squares and triangles represent estimates using gutter layers with 6000, 4000 and 2000 GPU CO$_2$ permeance. Open and solid symbols represent CO$_2$ permeance and CO$_2$/N$_2$ selectivity, respectively. As expected, selectivity decreases with increasing defect area, as the gutter layer has a lower CO$_2$/N$_2$ selectivity than the PFCB layer. Also apparent from the figures is that the thicker selective layer is more sensitive to the existence of surface defects. In both cases, membranes with thinner gutter layers are more sensitive to changes in the defect fraction because thinner gutter layers have higher permeance, and therefore contribute more to the overall composite membrane performance.

3.3.3 Characterization and modification of the gutter layer surface

3.3.3.1 Unmodified gutter layer membranes

An initial experiment was done to show that the PAN50 support membrane becomes fully saturated by the gutter layer solution after 20 seconds of soak time. In Figure 3.4, the relative mass of absorbed gutter layer solution (compared to the support membrane) was plotted against the soaking time of the membrane in the solution. In this experiment, dry membranes were packed into envelopes by the tape, which only has the shiny side
Figure 3.4 The mass of gutter layer polymer solution that PAN 50 absorbed over time.
exposed. Figure 3.4 described that the absorbed mass is not significantly related to the soaking time when the time is longer than 20 seconds. The slight increase in the trend is likely due to the penetration of the gutter layer solution through the epoxy of the tape. Thus, 20 seconds of soak time was used for all membrane preparations. After 20 seconds soaking, the absorbed mass of gutter layer solution is $1.7 \pm 0.1$ times the original membrane mass.

Figure 3.5 shows that CO$_2$ permeance decreases with increasing concentration of the proprietary polymer in the gutter layer solution. Since these solutions are dilute, it is reasonable to expect the volume of gutter layer solution absorbed is about the same for each concentration. The mass of gutter layer polymer deposited on the membranes after solvent evaporation therefore should be proportional to the polymer concentration in solution. Thus, we find that the permeance of the membrane is inversely proportional to the polymer concentration.

Since the ability to coat a thin film on a solid substrate depends on its surface tension, we measured the surface tension of the gutter layer coating using the Owens-Wendt method [Czenkiewicz, 2001]. Table 3.2 summarizes the measurement results. The contact angles of both water and CH$_2$I$_2$ were larger than 90°, suggesting that the gutter layer substrate before treatment is hydrophobic.
Table 3.2 Surface tensions of PFCB and gutter layer films before and after treatment.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Surface tension</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Owens-Wendt Method Values</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\gamma_D$</td>
<td>$\gamma_P$</td>
</tr>
<tr>
<td>Gutter layer before treatment</td>
<td>7.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Gutter layer 3 days after treatment with water soak</td>
<td>19.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Gutter layer 3 days after treatment without water soak</td>
<td>12.7</td>
<td>4.1</td>
</tr>
<tr>
<td>PFCB BPVE</td>
<td>28.7</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Figure 3.5 CO$_2$ permeance of untreated gutter layer membrane prepared from solutions with different concentrations (in wt%).
3.3.3.2 Plasma treated gutter layer membranes

Plasma treatment was used to facilitate uniform coating of PFCB onto the gutter layer substrate. The purpose of plasma treatment was to increase the gutter layer surface tension to prevent the PFCB coating solution from dewetting on its surface. Development of the plasma treatment protocol required special considerations. It is well known that sample materials can be etched away by oxidation [Inagaki et al., 2004] or by electrons and ions excited by plasma [Liu and Chen, 2008], which may introduce surface defects. Plasma treatment also can decrease the gas permeability of polymer films via surface crosslinking [Shao et al., 2007; Houston et al., 2002; Matsuyama et al., 1995].

Considering our specific application to gas separations, we imposed four requirements for the plasma treatment: It must (1) maintain the integrity of the gutter layer, (2) maintain high CO$_2$ permeance (> 2000 GPU), (3) increase surface tension to a value that enables uniform coating by ultrathin PFCB films, and (4) have long-term stability (to enable sufficient time for subsequent coating by the PFCB selective layer). We elected to use Ar plasma treatment, as others have found that surfaces etch more slowly with Ar plasma than O$_2$, N$_2$, and H$_2$ plasmas [Inagaki et al., 2004]. Argon also is safer to work with than O$_2$ and H$_2$. After much experimentation, the treatment conditions given in Section 2.2 were selected.

Table 3.2 reports the surface tension of the plasma-treated gutter layer substrate estimated by the Owens-Wendt method. After plasma treatment, both the dispersive and polar contributions to the surface tension increased significantly. We found
experimentally that soaking the surface in water maintains the surface properties for at least 2 weeks.

Following plasma treatment, the measured contact angle of a sessile drop of 1.4 wt% PFCB/chloroform solution on the gutter layer surface was $24 \pm 2^\circ$. Although the PFCB/chloroform solution did not exhibit complete wetting ($\theta = 0$) on the plasma-treated gutter layer substrate, it did have high wettability. Furthermore, in practice, the PFCB solutions would be deposited on the modified gutter layer surface by drawing the membrane vertically through the solution at withdrawal speeds larger than a critical value, which is called forced wetting [Matsuyama et al., 1995]. In this case, the apparent contact angle between the liquid-vapor interface and liquid-solid interface is lower than the equilibrium contact angle [Eggers, 2004]. The critical withdrawal speed for forced wetting corresponds to the critical capillary number $Ca^* = \frac{\mu v^*}{\sigma}$, where $\mu$ is the solution viscosity, $v^*$ is the critical withdrawal speed, and $\sigma$ is the solution surface tension [Eggers, 2004]. Equation 9 provides a rough scaling of this critical capillary number with the equilibrium contact angle, $\theta_e$, where $A$ is a constant [Matsuyama et al., 1995].

$$Ca^* = A \frac{3}{\theta_e}$$  

(9)

The contact angle of a sessile drop of 1.4 wt% PFCB/chloroform solution on the untreated gutter layer substrate was measured to be $57 \pm 3^\circ$. According to equation 9, the critical withdrawal speed of the untreated gutter layer substrate would be 13 times higher than that of the plasma-treated gutter layer substrate. According to the extended Landau-Levich equation described in Chapter 2, polymer film thickness is generally proportional to $v^{2/3}$. Therefore, using a withdrawal speed high enough to completely wet the untreated
gutter layer substrate would produce a PFCB film that was $13^{2/3}$ thicker than a film coated on a treated gutter layer substrate. Such a thick film would lower the gas permeance substantially.

Considering the high CO$_2$ permeance of $4180 \pm 1180$ GPU of membranes prepared using a 0.2 wt% gutter layer solution, they were selected for use in PFCB thin-film composite membrane preparation. Figures 3.6 a and 3.6 b are AFM images showing the topology of the gutter layer membranes. The open pores structure of the PAN50 membranes (see Figure 3.1) disappeared after coating with the gutter layer. Root-mean-square surface roughness also decreased following coating. The small dots that appear in Figure 3.6 a may be attributable to crosslinking of the gutter layer polymer during plasma treatment [Shao et al., 2007].

3.3.4 PFCB thin-film composite membranes

Plasma-treated gutter layer membranes with permeance ranging from 3000 GPU to 5000 GPU were coated by PFCB/chloroform solutions with concentrations of 0.3 wt%, 0.7 wt% and 1.4 wt% PFCB. The membranes were prepared by dip coating at withdrawal speeds of 50, 140 and 220 mm/min. Table 3.3 summarizes the performance of the PFCB thin-film composite membranes. Prior to all measurements, membranes were aged from 2 to 4 hours from the time that PFCB coating was finished. The testing conditions were 2.4 bar and room temperature. Uncertainties represent one standard deviation based on measurements with at least three membranes. A maximum CO$_2$/N$_2$ selectivity of 16 was achieved for membranes with CO$_2$ permeance of 1000 GPU, while that of membranes
**Figure 3.6** a: AFM topographical images of gutter layer membranes after plasma treatment: the z-scale is 15 nm. 1 × 1 μm, RMS roughness = 6.3 nm; b: AFM topographical images of gutter layer membranes after plasma treatment: the z-scale is 5 nm. 1 × 1 μm, RMS roughness = 1.5 nm
with CO₂ permeance of 270 GPU membranes was about 21. The average CO₂/N₂ selectivities are lower than expected values from Figure 3.2, likely due to a low fraction of surface defects in the PFCB layer. Performance trends are as expected: higher PFCB concentrations yielded less permeable membranes, and there was a trade-off between permeance and selectivity.

**Table 3.3** Performance of PFCB thin-film composite membranes. PFCB selective layers were deposited from PFCB/chloroform solutions. Permeance was tested at 2.4 bar and room temperature after aging for 2-4 h.

<table>
<thead>
<tr>
<th>PFCB Conc. (wt.%)</th>
<th>Withdrawal speed (mm/min)</th>
<th>220</th>
<th>140</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ permeance (GPU)</td>
<td>CO₂/N₂</td>
<td>CO₂ permeance (GPU)</td>
<td>CO₂/N₂</td>
</tr>
<tr>
<td>0.3</td>
<td>1002 ± 43</td>
<td>14.2 ± 1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>557 ± 57</td>
<td>17.9 ± 0.5</td>
<td>734 ± 115</td>
<td>16.6 ± 0.3</td>
</tr>
<tr>
<td>1.4</td>
<td>267 ± 60</td>
<td>18.9 ± 2.1</td>
<td>257 ± 5</td>
<td>17.6 ± 1.6</td>
</tr>
</tbody>
</table>
To understand the performance of the PFCB layer, one can apply Equation 6 to calculate its permeance. The permeance values of the gutter layer membranes were tested before coating. Generally, the thickness of PFCB films increases with polymer concentrations and withdrawal speed. Table 3.4 summarizes the CO₂ permeance of membranes with different estimated thicknesses. These estimated thicknesses were measured on silicon wafers by ellipsometry as mentioned in section 2.2. Since polymer thin films generally age rapidly, permeance was tracked over a period of 24 h to evaluate the impact of physical aging. The reported permeance values in Table 3.4 are for membranes aged 1 h. Overall, the CO₂/N₂ selectivities were all above 14, with uncertainties representing one standard deviation based on measurements using three membranes.

Table 3.5 gives the estimated CO₂ permeabilities. Statistically, the values of 14-17 Barrer are the same for the thin films that were investigated. Compared to the PFCB CO₂ permeability of 38 Barrer, they are much lower, likely due to thin film densification. It was observed in our previous work described in Chapter 2 that the refractive index increased as the film gets thinner, and this result can be explained by densification at the polymer-substrate interface. Selectivity values in the Table 3.5 were reported as the highest value that have been observed. No significant differences among these selectivity values were noticed. In Table 3.3 and 3.4, they both showed that permeance decreased as the withdrawal speeds increased. Table 3.5 excluded the factor of permeability. Therefore, the changing of permeance should be attributed to the fact that coated PFCB thickness strongly depended on the withdrawal speeds, which has been illustrated in Chapter 2.
Table 3.4 Permeance of PFCB selective layers and their estimated thicknesses. PFCB selective layers were deposited from PFCB/chloroform solutions.

<table>
<thead>
<tr>
<th>PFCB Conc. (wt.%)</th>
<th>Withdrawal speed (mm/min)</th>
<th>CO₂ permeance (GPU)</th>
<th>CO₂/N₂ permeance (GPU)</th>
<th>CO₂/N₂ permeance (GPU)</th>
<th>CO₂/N₂ permeance (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>220</td>
<td>141</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>1544 ± 135 (10 nm)</td>
<td>16.1 ± 2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>728 ± 70 (20 nm)</td>
<td>20.7 ± 0.3</td>
<td>1012 ± 155 (14 nm)</td>
<td>19.7 ± 0.6</td>
<td>1649 ± 169 (10 nm)</td>
</tr>
<tr>
<td>1.4</td>
<td>293 ± 61 (59 nm)</td>
<td>17.4 ± 2.6</td>
<td>316 ± 1 (46 nm)</td>
<td>18.8 ± 1.7</td>
<td>475 ± 63 (28 nm)</td>
</tr>
</tbody>
</table>
Table 3.5 Estimated permeabilities of PFCB selective layers deposited from PFCB/chloroform solutions.

<table>
<thead>
<tr>
<th>PFCB Conc. (wt.%)</th>
<th>Withdrawal speed (mm/min)</th>
<th>CO₂ permeability (Barrer)</th>
<th>CO₂/N₂ permeability (Barrer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>15.4 ± 1.4</td>
<td>19.0</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>14.5 ± 1.4</td>
<td>14.3 ± 2.1</td>
<td>21.3</td>
</tr>
<tr>
<td>1.4</td>
<td>17.3 ± 3.6</td>
<td>13.3 ± 0.1</td>
<td>20.8</td>
</tr>
</tbody>
</table>

3.3.5 Preliminary CO₂ plasticization

CO₂ plasticization usually occurred when polymeric membranes were exposed to high CO₂ pressures. The most significant characteristic is that the permeance of the membrane increases as CO₂ pressure goes up. Figure 3.7 shows the plasticization phenomena of PFCB thin films prepared using two different concentrations (0.3 wt% and 1.4 wt%) at a constant dip-coating withdrawal speed of 220 mm/min. Three membranes prepared at each concentration were tested to evaluate the reproducibility in membrane preparation. All membranes were aged in the desiccator at room temperature for 100 h after coating. These membranes are representing the thinnest and thickest membranes.
prepared in this study. For convenience, membranes prepared from 0.3 wt% and 1.4 wt% solutions were named as “thin” and “thick” membranes. Figure 3.7 a and b show the abstract and the relative CO$_2$ permeance against CO$_2$ pressure respectively. In Figure 3.7 b, the reference permeance is the one at 2.4 bar. One can tell that the plasticization pressure [Bos et al., 1999] of thin films is between 2.4 bar and 3.1 bar and that of the thick is between 4.5 bar and 6.5 bar. Considering the CO$_2$ concentration in the flue gas is 14%, it can be expected that thin and thick films will not show significant plasticization until the feed pressure is above 17 to 20 bar and 31 and 46 bar. Usually the feed pressure used for flue gas separation is much lower than these values. Merkel et al. [Merkel et al., 2010] recommended that 2 bar is the most economical feed pressure. Therefore, under these low feed pressure conditions, even the thin film will not be expected to show CO$_2$ plasticization effect. It also has been noticed that the permeance of thin membranes at 14.8 bar was 1.7 times higher than the value at 2.4 bar, whereas, the permeance of thick membranes at 14.8 bar was 1.2 times higher than that at 2.4 bar. The reason for these differences could be potentially explained by many factors, such as film thickness, solution concentration, withdrawal speeds and so on. In ongoing work, more comprehensive studies will be conducted to understand how film preparation conditions affect plasticization. In addition, membranes will be undergoing long-term testing to study CO$_2$ plasticization and physical aging effects.
Figure 3.7 CO$_2$ plasticization of thin PFCB films prepared from different concentrations of solutions: diamonds represent membranes coated from 0.3 wt% PFCB/chloroform solution; squares represent membranes coated from 1.4 wt% PFCB/chloroform solution. a: CO$_2$ permeance b: relative permeance
3.4. Conclusions

This work has provided details on the reproducible fabrication of thin-film composite gas separation membranes comprising a PAN support layer, proprietary gutter layer, and perfluorocyclobutyl polymer selective layer. Short-time treatment by argon plasma was demonstrated to be effective for improving the wettability of the gutter layer to the PFCB coating solution. Most importantly, PFCB was processed into thin films with different thickness by adjusting withdrawal speeds and solution concentration. After aging for 1 hour, these films showed a wide range of CO$_2$ permeance values between 200 GPU and 1700 GPU that depends on film thickness, with CO$_2$/N$_2$ selectivity of up to 20. Parallel measurements by ellipsometry indicate that the thinnest film, free of major defects, could be as low as 10 nm. All of these results suggest that PFCB polymers could be fabricated into composite membranes with high enough permeance to consider further for gas separation applications. Importantly, the BPVE-PFCB used in this work is a model material for fundamental research. Other PFCB polymers and copolymers with improved performance metrics are available for application to CO$_2$ separations. The fabrication process developed in this work yielded PFCB thin-film composite membranes with reproducible performance characteristics. Such reproducibility is critically important for the study of membrane aging and plasticization, which requires a large number of uniform membranes. Preliminary plasticization indicated that it is very difficult to be plasticized at low flue gas feed pressure even for the thinnest films have been prepared in this study. Plasticization and physical aging of PFCB thin-film composites will be the focus of a subsequent paper.
3.5. References


CHAPTER 4

CO₂ PLASTICIZATION AND PHYSICAL AGING OF PERFLUOROCYCLOBUTYL POLYMER SELECTIVE LAYERS

4.1 Introduction

Carbon dioxide plasticization and physical aging are two phenomena that occur in glassy polymers that limit their effectiveness as selective layers in composite gas separation membranes. These two phenomena become more significant in polymeric thin films, which presents challenges for the long-term, stable operation of thin-film composite membranes. The objective of this work was to study CO₂ plasticization and physical aging of perfluorocyclobutyl (PFCB) polymer thin film selective layers (<100 nm), which are new to the membrane art. Specifically, measurements on PFCB polymer selective layers were conducted to evaluate the influence of film processing conditions (PFCB concentration and coating speed), aging time, and heat treatments on CO₂ plasticization pressure. Findings indicate that PFCB layer thickness plays an important role on plasticization resistance when the thickness is less than 35 nm. However, when the thickness is greater than 35 nm, concentration of the coating solution also played an important role. Using concentrations above the overlap concentration yielded films with higher plasticization pressure compared to films with similar thickness prepared from dilute solution. Findings also show that films annealed at higher temperature exhibited higher plasticization pressure. Long-term CO₂ exposure studies indicated that CO₂
plasticization lessens the impact that physical aging has on permeability loss during the early stage, but at longer times, CO₂ plasticization accelerates physical aging. Overall, results presented in this work contribute new understanding of plasticization and physical aging, and may be used to guide further improvements in polymer performance for CO₂ separations.

4.2 Experimental

4.2.1 Materials

These chemicals were used as received: carbon dioxide (Industrial grade, Airgas, Inc.), chloroform (anhydrous, Acros Organics), hydrogen peroxide (30%, Fisher Scientific), methanol (HPLC, Fisher Scientific), nitrogen (Industrial grade, Airgas, Inc.), sulfuric acid (96%, Sigma-Aldrich). Deionized water was produced from distilled water that was passed through a Milli-Q water purification system (EMD-Millipore). Tetramer Technologies, LLC provided the biphenylvinylether-perfluorocyclobutyl (BPVE-PFCB) polymer with $M_w = 110000$ Da and PDI = 1.4.

PAN50 membranes were purchased from Sepro Membranes, Inc. These are composite ultrafiltration membranes comprising a poly(acrylonitrile) layer coated onto a polypropylene support. Prior to coating, the membranes were rinsed in methanol at 25 ℃ under gentle agitation by a shaker bath for 30 min and then dried in a vacuum oven at room temperature and 1700 Pa. The purpose of this rinse step is to remove structural preservatives in the membrane before any other treatment.
4.2.2. Methods

4.2.2.1 Composite membrane preparation

PAN50 membranes were cut into 6 cm × 6 cm samples and the polypropylene support side was covered by foil tape. A home-built dip coater was used to coat the poly(acrylonitrile) side of the PAN50 membrane with a thin gutter layer of a proprietary polymer characterized by CO$_2$ permeability $>$1000 Barrer and CO$_2$/N$_2$ selectivity $<$10. Membranes were dipped into the solution for 20 s, and then withdrawn at a speed of 130 mm/min. Ar Plasma treatment was conducted subsequently, using conditions reported in Chapter 3. PFCB solutions were prepared with concentrations of 0.3–1.4 wt% in chloroform. Gutter layer coated membranes were dip coated from 0.3 wt%, 0.7 wt% and 1.4 wt% PFCB/chloroform solutions at withdrawal speeds from 50 mm/min to 220 mm/min. Membranes were air dried under 7800 Pa at temperature in range from 25 °C to 90 °C for 2 h before testing. More details of the membrane preparation can be found in Chapter 3.

4.2.2.2 Membrane performance testing

N$_2$ and CO$_2$ permeance of thin-film composite (TFC) membranes were measured at room temperature using a home-built, constant-pressure permeance testing apparatus. A resistance-in-series equation was used to estimate properties of the PFCB layer, as described in Chapter 3. In this study, the coating time of TFC membranes was set to be time zero. Dry membranes were stored in the desiccator before testing. CO$_2$ plasticization studies were conducted on TFC membranes at room temperature with CO$_2$ partial
pressures ranging from 1.5 bar to 14.8 bar. Membranes were equilibrated at each CO\textsubscript{2} pressure for 15 min before a measurement was taken. This study investigated physical aging behavior at room temperature under two environments: long-term (1000 h) aging under constant CO\textsubscript{2} pressure and short-term (100 h) aging in a desiccator with air atmosphere. In the long-term studies, CO\textsubscript{2} flowed through the membranes continuously. For all membranes, CO\textsubscript{2}/N\textsubscript{2} selectivity was measured at the beginning of each run to make sure that membranes were free of major defects that would impair the results.

4.3 Results and discussion

4.3.1 Role of processing conditions on plasticization

4.3.1.1 Impact of film thickness on permeance-pressure curves

In this study, plasticization curves were measured for thin films with thicknesses of 10–60 nm that were dip-coated from solutions of different polymer concentrations using different withdrawal speeds. For data reported in Figure 4.1, membranes were prepared from 0.3, 0.7, 1.0 and 1.4 wt% PFCB/chloroform solutions using dip-coating withdrawal speeds of 50, 140, 220 and 340 mm/min. These membranes were aged for 3–4 h before testing. Data represent the average values measured using 2 or 3 membranes. Error bars represent one standard deviation. The relative CO\textsubscript{2} permeance values reported in Figure 4.1 use the permeance of each membrane at a CO\textsubscript{2} partial pressure of 2.4 bar as reference. Table 4.1 summarizes the membrane permeance values for these membranes. For convenience, these membranes will be referenced in the text using a coding system: X.X-YYY. The first two digits of the code represent the polymer solution concentration in wt%.
and the last three digits represent the withdrawal speed in mm/min. For example, membrane 1.4-140 was coated from 1.4 wt% PFCB/chloroform solution at withdrawal speed of 140 mm/min. Table 4.2 summarizes the corresponding thickness of the PFCB selective layer for all membranes, which were estimated using ellipsometry measurements [See details in Chapter 3]. Chapter 2 showed how changing PFCB solution concentration and withdrawal speed affects polymer film thickness.
Table 4.1 Permeance of PFCB selective layers deposited from PFCB/chloroform solutions.

<table>
<thead>
<tr>
<th>PFCB Conc. (wt.%)</th>
<th>Withdrawal speed (mm/min)</th>
<th>340</th>
<th>220</th>
<th>140</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ permeance (GPU)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>1544 ± 135</td>
<td>16.1 ± 2.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>-</td>
<td>728 ± 70</td>
<td>20.7 ± 0.3</td>
<td>1012 ± 155</td>
<td>19.7 ± 0.6</td>
</tr>
<tr>
<td>1.0</td>
<td>463 ± 56</td>
<td>19.3 ± 0.3</td>
<td>499 ± 43</td>
<td>17.6 ± 2.1</td>
<td>-</td>
</tr>
<tr>
<td>1.4</td>
<td>-</td>
<td>293 ± 61</td>
<td>17.4 ± 2.6</td>
<td>316 ± 1</td>
<td>18.8 ± 1.7</td>
</tr>
</tbody>
</table>
Table 4.2 Processing conditions, labeling codes, and estimated PFCB selective layer thicknesses for membranes prepared in this work.

<table>
<thead>
<tr>
<th>PFCB Conc. (wt.%)</th>
<th>Withdrawal speed mm/min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>Membrane Code (estimated thickness in nm)</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0-340 (56 ± 1.0 nm)</td>
</tr>
<tr>
<td>1.4</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.1 CO₂ relative permeance versus CO₂ pressure of films prepared at different conditions. a. Plasticization curves for all films. b. Plasticization curves for all films thicker than 35 nm. (Reference for both figures is the CO₂ permeance measured at 2.4 bar.)
Initial comparisons were done for membranes with similar PFCB selective layer thicknesses prepared from solutions with different PFCB concentrations. Membranes 1.4-140 and 1.0-220 have similar thickness, as do membranes 1.4-220 and 1.0-340. However, in both groups, membranes prepared from 1.4 wt% solution had the higher plasticization pressure. In the work of Chapter 2, we determined that the overlap concentration of PFCB/chloroform solution is 1.3 wt%. These results suggest that films prepared from solutions above the overlap concentration may be less susceptible to plasticization than ones prepared from solutions below this concentration (a.k.a., dilute solutions). The explanation is that polymer chains tend to overlap in the more concentrated solution, which leads to increased chain entanglements in the dry polymer thin film. Entanglements act like physical cross-links that inhibit polymer chain mobility. It also is noteworthy that the plasticization curve of a 20 μm bulk PFCB film is similar to the one for membrane 1.4-220. However, membrane 1.4-050, also prepared from 1.4 wt% solution but with thickness of only 28 nm, had a plasticization curve similar to films prepared from dilute PFCB solutions. It seems that thickness of the polymer films also plays an important role on plasticization pressure for ultrathin films, perhaps due to higher polymer chain mobility near free surfaces [McCaig and Paul, 2000; Cui et al. 2011; Huang and Paul, 2004].

4.3.1.2 Comparisons of physical aging of thin and thick films

CO₂ permeances of PFCB composite membranes were tracked over time. Permeance of the PFCB layer was calculated from a resistance-in-series equation using measured
values of the permeance of the overall membrane and that of the gutter layer before PFCB coating. As a control, we verified experimentally that the gutter layer does not age significantly during the first 100 hours after modification. Hence, the gutter layer permeance was constant in calculating CO$_2$ permeance of the PFCB layer in these aging experiments.

Figure 4.2 shows the CO$_2$ permeance of PFCB films over the course of 100 h of aging. These membranes were prepared at two different concentrations and the same withdrawal speed of 220 mm/min. At least 9 points were taken during the course of each experiment. All membranes were aged at room temperature in a desiccator at atmosphere pressure. Membranes with code 0.3-220 (asterisks, triangles, crosses) have estimated PFCB thicknesses of 10 ± 0.5 nm. Membranes with code 1.4-220 (squares, diamonds, circles) have estimated PFCB thicknesses of 59 ± 1.4 nm. Three samples at each concentration were tested to evaluate reproducibility. Figure 4.2a shows how the CO$_2$ permeance of the two types of membranes change with time. These data could be fitted by the function $p = a \times \ln(t) + b$, where $p$ is the CO$_2$ permeance in GPU (1 GPU = 10$^{-6}$ cm$^3$(STD)/(cm$^2$·cmHg·s)), $t$ is the aging time in hours, $a$ and $b$ are constants. The extrapolated value at 1 h aging was used as reference permeance for calculating relative permeance in Figures 4.2b and 4.2c. These figures show that membranes with thinner PFCB coatings aged faster. They showed a 45% decrease in permeance over the course of 100 h compared to a 30% decrease for the thicker PFCB films. In addition to thickness
**Figure 4.2** Comparison of PFCB thin film selective layers prepared from different solutions: aging over time. Triangles and crosses represent membranes coated from 0.3 wt% PFCB/chloroform solution. Squares, diamonds and circles represent membranes coated from 1.4 wt% PFCB/chloroform solution. a. Permeance. b. Relative permeance. c. Linear time scale. (Reference for figures b and c is the CO\(_2\) permeance measured after 1 h aging.)
differences, concentration differences may also have contributed to the differences in rate of permeation decrease described above. PFCB selective layers prepared from 0.3 wt% solution have fewer entanglements, as this concentration is well below the overlap concentration. Polymer chains in the dry layer following the rapid solvent evaporation would be expected to have fewer entanglements than those coated from solutions above the overlap concentration, and, therefore, would have higher chain mobility.

Also noteworthy from Figure 4.2c is that aging rate decreases over time. In other words, physical aging is more significant on fresh membranes.

4.3.2 Role of annealing temperature on plasticization

Thermal annealing has been adopted widely to enhance the resistance of membranes to CO₂ plasticization. Annealing processes generally are done under vacuum or an inert gas environment. Annealing temperatures can be below or above Tₑ. Higher temperatures are more effective for chemical crosslinking [Wind et al., 2003; Ismail and Lorna, 2003; Wind et al., 2003; Chen et al., 2011; Kraftschik et al., 2013; Bos et al., 1998; Shao et al., 2005]. Even though thermal annealing may increase membrane plasticization pressure, it also decreases membrane permeability (or permeance) due to polymer film densification. Methods of enhanced plasticization resistance have been discussed in literature and generally fall within three categories: chemical crosslinking, charge transfer complexes [Wind et al., 2003; Bos, 1996] and physical structure change. Crosslinking is the best defense against plasticization [Wind et al., 2003]; however, further discussion of chemical crosslinking and charge transfer complexes is beyond the scope of the presented
work. As to physical structure change, mechanisms have been attributed to distribution of the Henry’s law and Langmuir adsorption sites [Dong et al., 2011], reorientation of polymer chains [Ismail and Lorna, 2003] and crystallization [Dong et al., 2011].

Annealing temperatures usually are below \( T_g \) of the polymer [Dong et al., 2011; Ismail and Lorna, 2003; Wind et al., 2003]. Ismail and Lorna [Ismail and Lorna, 2003] suggested that annealing temperature near or above \( T_g \) is not effective at suppressing polysulfone (Udel P1700) membrane plasticization.

Vasquez [Vasquez, 2009] performed thermal gravimetric analysis on biphenylvinyl-PFCB, and measured a bulk \( T_g \) of 150 °C. Experiments in the current work focused on temperatures below this bulk \( T_g \). Figure 4.3a shows plasticization curves for membranes that were annealed at three different temperatures: 25 °C, 70 °C, and 90 °C. Membranes were heated in an oven under vacuum (0.03 bar) at these different temperatures for 2 h immediately after PFCB selective layer coating. They were equilibrated with an air environment in a desiccator for 1 h before measurement. Relative CO\(_2\) permeance values are reported, which used measured permeance at 2.4 bar as the reference. All three curves exhibited classic convex shape within the range of CO\(_2\) pressure tested. While curves for the higher annealing temperatures showed deeper well depths, PFCB layers did not differ significantly in plasticization pressure when annealed at 70 °C and 90 °C. However, plasticization pressure did increase from 5.2 bar to 10.0 bar when annealing temperature increased from 25 °C to 70 °C.

Although thermal annealing increases plasticization pressure, it also leads to a decrease in permeance. Table 4.3 shows that the CO\(_2\) permeance after thermal annealing
and 3 h aging decreased from $214 \pm 13$ GPU at 25 °C to $118 \pm 13$ GPU at 90 °C. CO$_2$/N$_2$ selectivity does not change significantly. These results showed that thermal annealing effectively enhanced the anti-plasticization behavior of the membranes at the expense of

Table 4.3 Permeance of PFCB selective layers with different thermal history.

<table>
<thead>
<tr>
<th>thermal treatment after coating</th>
<th>CO$_2$ permeance (GPU)</th>
<th>CO$_2$/N$_2$ permeance (GPU)</th>
<th>CO$_2$ permeance (GPU)</th>
<th>CO$_2$/N$_2$ permeance (GPU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>room temperature drying under vacuum for 2 h</td>
<td>214 ± 13</td>
<td>19.0 ± 2.1</td>
<td>171 ± 27</td>
<td>19.3 ± 1.3</td>
</tr>
<tr>
<td>70 °C annealing under vacuum for 2 h</td>
<td>161 ± 20</td>
<td>19.0 ± 0.8</td>
<td>115 ± 7</td>
<td>19.8 ± 1.3</td>
</tr>
<tr>
<td>90 °C annealing under vacuum for 2 h</td>
<td>118 ± 13</td>
<td>17.7 ± 1.0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Permeance reduction. Permeance decrease might be attributed to faster film aging at higher annealing temperatures. One possibility for the improved plasticization resistance by thermal treatment might be an increase in the tensile modulus of the thin film. An
increase in the chain stiffness makes it more difficult for the film to swell under the same pressure of CO₂. Future work includes measurements of the thin films tensile moduli by AFM and will be included in a subsequent publication.

During the process of thermal treatment, PFCB layers experience heating from room temperature to the designated annealing temperature, followed by cooling back to room temperature. Following the initial annealing tests, additional measurements were done to evaluate the annealing time and cooling rate. Membranes were annealed for longer time (24 h at 70 °C) and a faster cooling rate (membranes were exposed to liquid nitrogen immediately after annealing for 2 h at 70 °C). Longer annealing may hasten the approach towards an equilibrium state, while a more rapid volume reduction caused by faster cooling may also lead to polymer chain diffusion and entanglements. In both cases, we expected the resulting selective layers to have higher plasticization pressure. However, Figure 4.3b shows that longer annealing time and faster cooling rate did not change the plasticization properties of PFCB thin film selective layers. These measurements indicate that the initial heat treatment protocol is sufficient to reach the maximum enhancement in PFCB plasticization resistance.

Interestingly, the permeance values of membranes treated for longer time and a faster cooling rate were measured to be 167 ± 25 GPU and 235 ± 2 GPU, respectively,
Figure 4.3 Plasticization of PFCB thin films after thermal annealing. a. Temperature effect. b. Annealing time and cooling rate effects. (Reference for both figures is the CO\textsubscript{2} permeance measured at 2.4 bar.)
compared to that of membranes treated by the standard protocol (161 ± 20 GPU). Longer thermal annealing at 70 °C did not decrease the permeability further. Usually, $T_g$ of polymer thin films are lower than the bulk. Therefore it is reasonable that, for the ultrathin films in this study, 70 °C may be approaching $T_g$. Horn and Paul [Horn and Paul, 2011] mentioned that when the aging temperature is close to the polymer film $T_g$ the aging rate becomes slower. That may explain why there is no permeance reduction after longer time annealing. However, the increased permeance achieved by using a faster cooling rate was unexpected. One possibility is that PFCB may have a negative thermal expansion coefficient, as some polymers, such as polystyrene, do [Mukherjee et al., 2002]. The lower cooling temperature would then increase PFCB thin film free volume and its permeance.

### 4.3.3 Relationship between aging and plasticization

In this part of the work, the role of aging time on membrane plasticization was explored. Figure 4.4a compares plasticization effects of membranes aged for different times without thermal annealing. These membranes were prepared from 1.4 wt% PFCB/chloroform solution at a withdrawal speed of 220 mm/min. Membranes were stored in the desiccator at room temperature after 2 h drying as described earlier. Each datum point represents the average of three membranes. Membranes were equilibrated with CO$_2$ for 15 min before testing. The total measurement time at one pressure is 20 min. The total time needed to prepare one CO$_2$ plasticization curve was 3.6–4.3 h. Membranes aged for 3 h have higher plasticization pressure than membranes aged for
Figure 4.4 Aging effect on film plasticization. a. Aging effect on films without thermal annealing. b. Aging effect on films with thermal annealing. (Reference for both figures is the CO₂ permeance measured at 2.4 bar.)
Membranes aged for 100 h and 400 h exhibit similar plasticization trends. At a CO$_2$ partial pressure of 14.8 bar, the relative permeance for membranes aged for 3 h is 1.05; whereas, for membranes aged for 100 h and 400 h, the relative permeance is 1.28.

Horn and Paul [Horn and Paul, 2012] proposed that competition exists between plasticization and physical aging during the early the stages of plasticization testing. During plasticization measurements for membranes that were initially aged for only 3 h, one may be concerned with artifacts in the plasticization curve brought about by physical aging during the actual measurements, which themselves lasted up to 4.3 h. One can calculate the aging rate from Figure 4.2b. Since the times were recorded for each measurement reported in Figure 4.4, one can adjust the permeance at each testing pressure due to physical aging. The curve made of circles in Figure 4.4a shows the adjusted values, excluding the effect of physical aging during the time needed for measurements. Clearly, the adjusted and original curves match closely. Thus, the impact of physical aging during plasticization curve measurements is negligible in this case.

A similar comparison was conducted on membranes annealed at 70 °C as in Figure 4.4 b. Plasticization pressure decreased as time increased. In work done by Paul and coworkers [Horn and Paul, 2011; Xia et al., 2012], plasticization curves were measured at CO$_2$ pressure up to 40 atm. Horn and Paul also noticed plasticization pressure of Matrimid thin films decreased with time. Xia et al. pointed out that permeability of Extem thin film aged for 100 h increased much more than one aged for 400 h at 40 atm CO$_2$. However, the data below 15 atm (identical to 15.2 bar CO$_2$) are similar to each
other. These variances seen at different partial pressures suggest that higher CO₂ pressure should be tested in future research to obtain more information.

Table 4.3 and Figure 4.5 present data that illustrate the performance change of PFCB selective layers over time. They compare the physical aging with and without thermal treatment. While thermal treatment improved plasticization resistance, the aging behavior of these two different types of PFCB layers is similar, particularly at long operation times.
Figure 4.5 Comparison of physical aging of PFCB thin layers with different thermal history. a. CO₂ permeance. b. Relative CO₂ permeance. (Reference for both figures is the CO₂ permeance measured at 2.4 bar.)
4.3.4 Long-term permeance measurements

Paul and colleagues have studied the effects of long-term CO$_2$ exposure on PSF, PPO, Matrimid [Horn and Paul, 2011; Horn and Paul, 2012] and polyetherimide [Xia et al., 2012]. They have compared aging rates of these polymer thin films at identical thickness (150-190 nm) under CO$_2$ pressures below and above than their plasticization pressure. These films were aged at 35 °C for 200 h before testing. The permeance versus time curve of membranes under long-term CO$_2$ exposure comprises the combined effects of CO$_2$ plasticization and physical aging. At early exposure times, CO$_2$ permeance increased to a maximum and then decreased. At later times, it appears that physical aging became dominant. Horn and Paul [Horn and Paul, 2012] suggested that the time needed to reach the maximum permeance is inversely related to the CO$_2$ solubility within the polymer film. However, Xia et al. [Xia et al., 2012] discovered that Extem did not conform to this relationship; rather, Extem has a lower CO$_2$ solubility than the other polymers that were studied and required a shorter time to reach the maximum.

Figure 4.6a shows permeance data measured during the long-term CO$_2$ exposure of thin PFCB films under pressures below and above the plasticization pressure. The plasticization pressure of membranes aged for 3 h is around 5.2 bar; thus, data collected at 7.9 bar and 14.8 bar are above the plasticization pressure and those at 2.4 bar are below the plasticization pressure. In these studies, time zero is defined as the time that membranes were first contacted with CO$_2$. Permeance of the first measurement (around 30 min) was used as reference permeance. In the first 50 h (to the left of the vertical blue line), the permeance of PFCB at 2.4 bar decreases monotonically. This result was
expected, since the pressure is much lower than its plasticization pressure, and physical aging is the dominant factor affecting the performance. Permeance of PFCB increased slightly to a maximum under 7.9 bar CO$_2$, and remained almost constant under 14.8 bar CO$_2$. The later behavior was unexpected, because plasticization should be observed at 14.8 bar CO$_2$. However, the first permeance measurement around 30 min after contacting the membrane with 14.8 bar CO$_2$ is 15% higher than the value measured at 2.4 bar. Thus, the swelling process at 14.8 bar may occur very fast, and the permeance may have reached a peak value before the first measurement.

After the first 50 h (to the right of the vertical blue line), the decreasing slopes of all three curves are in the order from high to low: 14.8 bar > 7.9 bar > 2.4 bar. Membrane permeance decreased faster under higher CO$_2$ pressures, because CO$_2$ molecules can act like lubricants and enable polymer chains to move with less resistance. Plasticization involves polymer swelling, whereas physical aging leads to layer compaction. These two phenomena have opposite effects on film structure. Even though physical aging becomes the dominant factor at long exposure times, CO$_2$ plasticization still occurs and affects physical aging. That is, plasticization and physical aging occur throughout the measurement period, but they show different relationships at different stages. A similar discovery has been made in the work by Paul and his coworkers [Horn and Paul, 2011; Xia et al., 2012]. For PSF, PPO, Matrimid and polyetherimide, they have shown faster aging after the maximum permeance value has been achieved at higher CO$_2$ pressure. Xia et al. summarized the idea in saying that “There is some reason to believe from these long
term exposure experiments that higher pressures of CO$_2$ may accelerate the physical aging process.”

Results of a control experiment are shown in Figure 4.6b. In this experiment, the membrane was exposed to N$_2$ (instead of CO$_2$) at 14.8 bar under continuous flow. It was exposed to 14.8 bar CO$_2$ only to measure its permeance at different times. The result is that the rate of permeance decline is slower for the non-plasticizing gas and is different
Figure 4.6 a. Relative CO₂ permeance of films under different flow conditions.
(Reference for figures a and b is the first CO₂ permeance measured 30 min after exposure to CO₂.) b. Results of control experiment with non-plasticizing gas. c. Plasticization curves for films after 1000 h exposure to CO₂ under flow conditions. (Reference for figure c is the CO₂ permeance measured at 2.4 bar.)
from the results obtained by aging under continuous flow at 2.4 bar CO$_2$. From this result, we conclude that the faster rate of permeance decline at higher CO$_2$ pressure is not attributed to physical compaction by force alone.

Figure 4.6c compares membranes after 1000 h aging under continuous flow at 2.4 bar CO$_2$ and 14.8 bar CO$_2$, which are below and above the membrane plasticization pressure. Interestingly, the plasticization curve of the membrane aged under 2.4 bar CO$_2$ differed markedly from that for the membrane aged under 14.8 bar CO$_2$, which itself showed a similar plasticization curve to the one aged for 3 h in air. It appears that exposure to high pressure CO$_2$ (above the plasticization pressure) has a similar effect as thermal annealing.

### 4.3.5 Correlation of plasticization pressure to polymer properties

CO$_2$ plasticization appears to start at the pressure when the total mass/volume of absorbed CO$_2$ reaches a critical value. Bos et al. [Bos et al., 1999] summarized 11 different polymers and found that plasticization was initiated when the polymers absorbed around $37 \pm 7$ cm$^3$ STP/cm$^3$. Wind et al. [Wind et al., 2003] reported the critical concentration to be $29 \pm 2$ cm$^3$/mol. Simons et al. [Simons et al., 2010] reported this value to be $25.3$ cm$^3$/mol, while Horn and Paul [Horn and Paul, 2012] reported it to be $23$ cm$^3$/mol. However, the actual situation may be more complicated. In this part of the study, a new correlation is proposed to relate plasticization pressure to polymer properties.

Swelling is a process that can be described by four steps: 1) CO$_2$ penetrants diffuse into the polymer. 2) CO$_2$ weakens the polymer-polymer interactions. 3) Polymer chain mobility increases. 4) Additional free volume is created. Therefore, CO$_2$ absorbance is
the driving force for polymer swelling, while tensile modulus resists the polymer deformation. Polymer swelling, therefore, should be proportional to the quotient of CO\textsubscript{2} solubility (S) to tensile modulus (E). Inversely, plasticization pressure (resistance to swelling) should be proportional to the quotient of E to S.

Table 4.4 summarizes properties of eight different polymers. These properties include polymer free volume, solubility coefficient at the plasticization pressure, plasticization pressure and tensile modulus. Figure 4.7 shows that there is a significant correlation between plasticization pressure and the quotient of tensile modulus and solubility coefficient. It suggests that one can increase material modulus and/or lower solubility coefficient to enhance plasticization pressure. However, to maintain high selectivity by the thin film selective layer, increasing tensile modulus would be preferred. Indeed, standard practice is to use cross-linking as a mitigation strategy for plasticization and physical aging. Further work should be conducted to validate this correlation.
Table 4.4 Polymer plasticization pressure and physical property data.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Solubility coefficient ((\text{cm}^3/\text{cm}^2/\text{s/bar}))</th>
<th>Tensile modulus (MPa)</th>
<th>Plasticization pressure (bar)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF (Udel P3500)</td>
<td>1.4(^a)</td>
<td>2480(^b)</td>
<td>34(^a)</td>
<td>a: Bos et al.; b: Solvay</td>
</tr>
<tr>
<td>Polyethersulfone (Ultrason E 6010P)</td>
<td>1.6(^a)</td>
<td>2600(^b)</td>
<td>27(^a)</td>
<td>a: Bos et al.; b: BASF</td>
</tr>
<tr>
<td>PEI (ULTEM 1000)</td>
<td>1.3(^a)</td>
<td>3300(^b)</td>
<td>28(^a)</td>
<td>a: Bos et al.; b: GE Plastics</td>
</tr>
<tr>
<td>Bisphenol A polycarbonate</td>
<td>1.1(^a)</td>
<td>2300(^b)</td>
<td>31(^a)</td>
<td>a: Bos et al.; b: Gallina</td>
</tr>
<tr>
<td>Matrimid® 5218</td>
<td>3.9(^a)</td>
<td>2896(^b)</td>
<td>12(^a)</td>
<td>a: Bos et al.; b: Ciba</td>
</tr>
<tr>
<td>P84</td>
<td>2.2(^a)</td>
<td>3581(^b)</td>
<td>22(^a)</td>
<td>a: Bos et al.; b: Evonic</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>2.8(^a)</td>
<td>1378(^b)</td>
<td>11(^a)</td>
<td>a: Bos et al.; b: Rotuba</td>
</tr>
</tbody>
</table>
Figure 4.7 Relationship between plasticization pressure and the quotient of polymer tensile modulus to solubility coefficient for CO₂ at the plasticization pressure. Each point represents a commercial polymer, with properties summarized in Table 4.4.
4.4 Conclusions

In this work, PFCB thin film selective layers were prepared from PFCB/chloroform solutions with concentrations below and above the overlap concentration. When film thickness is below about 35 nm, all films exhibited low plasticization pressure and high degree of plasticization. For thicker films, the plasticization behavior was found to depend on the solution PFCB concentration, with films prepared above the overlap concentration exhibiting higher plasticization pressures likely due to enhanced chain entanglements. This result offers a strategy for improving the resistance to plasticization by adjusting solution concentration above the overlap concentration.

Plasticization curves of films annealed at different temperature and aged for different periods of time were compared. Higher annealing temperatures yielded higher plasticization pressure, but reduced permeance. Plasticization pressure decreased and degree of plasticization increased for membranes aged longer.

During long-term permeance measurements, physical aging and plasticization showed different relationships at different stages. Plasticization competes with physical aging at earlier stages of operation. At later stages, plasticization accelerates physical aging.

Finally, a relation was proposed to correlate plasticization pressure to the quotient of tensile modulus and solubility coefficient. Data from eight polymers indicate a strong linear correlation. This correlation provides insight on how one might approach the design/modification of polymer thin films that have improved resistance to plasticization and physical aging.
4.5 References


Bos, A., High pressure CO2/CH4 separation with glassy polymer membranes-aspects of CO2 – induced plasticization, Ph.D. Dissertation, University of Twente, Netherlands, 1996.


Vasquez, E. S., Rheological, thermal and processing studies of perfluorocyclobutyl (PFCB) polymers, M.S. Thesis, Clemson University, United States, 2009.


5.1 Conclusions

Perfluorocyclobutyl (PFCB) polymers are a new class of materials. These polymers have shown promise for CO$_2$/N$_2$, CO$_2$/methane, and O$_2$/N$_2$ separation applications. The overall work described in this dissertation is based on a collaborative project with Tetramer Technologies to develop fundamental structure-property relationships for PFCB polymers that provide a foundation for PFCB based membranes with better resistance to plasticization and physical aging. Specifically, this project started with thin film preparation and characterization on silicon wafers. Thereafter, tremendous efforts were put into the fabrication of PFCB thin-film composite (TFC) membranes. Ascribed to the good reproducibility and high quality of membranes produced using procedures I developed, plasticization and aging studies could be conducted on PFCB TFC membranes prepared from different conditions and exposed to different thermal history. At the end of the work, an observed correlation was found between the CO$_2$ plasticization pressure and polymer properties.

PFCB coating studies on silicon wafers, described in Chapter 2, guided the subsequent investigations. In this part of the work, PFCB thin films were formed on silicon wafers by dip coating. Viscosities, surface tensions, and overlap concentrations of PFCB/chloroform and PFCB/THF were characterized. Thickness, refractive index and
surface patterns of PFCB thin films were controlled through the variation of polymer solution concentration, withdrawal speeds and the solvent type. Generally, polymer solutions of higher concentration produced thicker films. When the withdrawal speeds were higher than 50 mm/min, film thicknesses were close to predicted values from the extended Landau-Levitch equation, and film thickness increased with increasing withdrawal speeds. However, when the withdrawal speeds were lower than 50 mm/min, film thickness decreased with withdrawal speeds. The deviations were attributed to the surface excess phenomena in the polymer solutions. Apparent surface concentrations of the wet layer on silicon wafers during withdrawal from solution were estimated from the extended Landau-Levitch equation by knowing the film thickness, withdrawal speeds, and solution properties. The highest concentration in the wet layer was determined to be twice the concentration in the bulk solution. Static surface excess values were estimated from surface tension measurements. These measurements showed that the surface concentration could be up to 28 times higher than the bulk concentration. Refractive index measurements of the PFCB coated silicon wafers showed the anisotropic properties of films below 50 nm, likely caused by π-stacking of aromatic groups induced by interactions among these groups and the silanol groups of the substrate. It also was discovered that films produced from PFCB/acetone solution showed dewetted patterns of films. A depletion layer of acetone was proposed to explain such phenomena.

Work described in Chapter 3 utilized the knowledge about PFCB thin film formation on silicon wafers to prepare composite membranes for CO₂ separations. Theoretical calculations helped to guide membrane preparation. On the one hand, these calculations
set an upper bound on the best performance that could be achieved by the composite membranes. On the other hand, they highlighted the importance that surface defects play on performance, especially on the membrane separation factor. Another challenge came from the preparation and modification of the gutter layer. Since the major cause of surface defects was from PFCB dewetting during the coating process, preparing a TFC membrane that was free of major defects required the gutter layer itself to be defect free and also to have sufficiently high surface energy. Theories of forced wetting provided fundaments to guide the surface modification. Argon plasma with low power (6.8 W) and short time (1 min) treatment was applied to the gutter layer. Subsequent testing of PFCB TFC membrane transport properties gave CO$_2$/N$_2$ selectivity values close to the intrinsic value of the bulk PFCB film, indicating successful gutter layer modification and PFCB coating. Finally, a series of PFCB TFC membranes were characterized. These membranes were prepared from three different concentrations of PFCB/chloroform: 0.3, 0.7 and 1.4 wt%. For each solution, withdrawal speeds were controlled in the range 50–220 mm/min. Thickness of the PFCB layer was estimated to be between 10 and 59 nm. A resistance in series equation was used to estimate the initial permeance through the PFCB layer, which was reported for films aged for 1 h. The highest permeance among these films was 1700 GPU. Small membrane-to-membrane deviations in permeance and CO$_2$/N$_2$ values validated the good reproducibility and high quality of the membranes, which enabled the plasticization and physical aging studies.

Transport properties of polymer thin films generally are highly sensitive to time and thermal history. Chapter 4 focused on the roles that these factors played on the properties
of the PFCB selective layer in TFC membranes. Plasticization curves were compared for PFCB films prepared with different processing conditions and aged for 3 h. Findings suggested that thickness was the most important factor affecting plasticization on films with thickness below about 35 nm. When the thickness was higher, films prepared from solutions above the overlap concentration were more resistant to plasticization. Effects of thermal treatment and physical aging on PFCB TFC membranes also were explored. I discovered that films annealed at 70 °C and 90 °C for 2 h had a plasticization pressure of up to 10.0 bar; whereas, films aged at room temperature in the desiccator had a much lower plasticization pressure of 5.2 bar) and significantly higher degree of plasticization. Long-term (1000 h) flux testing under CO₂ was conducted to observe physical aging of PFCB films. CO₂ pressures below and above the PFCB plasticization pressure were selected. Results showed a complicated relationship between physical aging and CO₂ plasticization. At the early stage of exposure to CO₂, plasticization and physical aging showed competing effects on permeance; whereas, at longer times, plasticization appeared to accelerate physical aging. The competition results from the fact that the physical aging involves chain packing, while the nature of plasticization is polymer swelling. Absorbed CO₂ also can act like a lubricant in the film, increasing chain mobility and allowing the film to relax toward an equilibrium state. Macroscopically, films age faster under CO₂ plasticization. Finally, I proposed a correlation between plasticization pressure and properties of polymer films. This correlation provides a method to estimate polymer plasticization pressure from physical property data that often is available in the literature or from polymer manufacturers. It also suggests a strategy to increase
plasticization pressure, namely, seek ways to increase polymer tensile modulus (e.g., crosslinking) that do not significantly impair CO$_2$ solubility in the polymer.

In all, my scientific and engineering contributions to the project involved 1) coating process development and understanding; 2) thin film characterization method and protocol development; 3) thin-film composite membrane characterization and fabrication procedure development; 4) design and construction of transport property testing apparatus; 5) method development for plasticization and physical aging studies; 6) proposed correlation to guide further research. Based on experiments and theories, findings from my PhD research contribute my understanding and suggestion to plasticization and physical aging effects on polymer thin films.

5.2 Recommendations

Plasticization and physical aging are classic problems that hinder the use of polymeric membranes for gas separations. To understand these phenomena better and design polymers with enhanced resistance to plasticization and physical aging, based on my previous studies, I suggest the following for subsequent researchers.

5.2.1 Recommendations for polymer film thickness measurements

Since SEM measurement of the nanothin selective layer in PFCB TFC membranes is difficult, PFCB thicknesses on the composite membranes reported in the chapter 3 were estimated from ellipsometry measurements on silicon wafers. I do not expect significant discrepancy between the estimated values and the true values; however, I recommend
developing a strategy to measure the film thickness directly. I suggest depositing sparsely dispersed, uniform metal nanoparticles on the surface of the gutter layer before PFCB coating. One could use AFM to characterize the distance between the top of the nanoparticles and the surrounding substrate before and after coating. The change of this distance could be used to determine the coated thin film thickness. The sizes of the nanoparticles would depend on the target PFCB layer thickness. For the 10 to 60 nm PFCB layer, 20 to 100 nm diameter nanoparticles are suggested. As a starting point, gold nanoparticles are suggested.

5.2.2 Recommendations for polymer film coating

In my PhD work, I have demonstrated that dip coating can be used to prepare TFC membranes, which has the potential to scale up using existing membrane manufacturing principles. However, for lab scale research, the underside of the support membranes must be sealed off using tape/glue. Efforts were made to use adhesive materials that were not soluble in the coating solution; however, it is possible that the solution becomes contaminated over multiple coating experiments. I would strongly recommend exploring the possibility of using spin coating to prepare thin films.

We have also built a roller based coating device, but it did not work very well. I suggest modifying it in two ways: 1) change the motor to a step motor that can produce stable and controllable movement and 2) change the roller to a smaller one that can make the lab scale production easier.
5.2.3 Recommendations for plasticization studies

Plasticization data of films were collected from 1.4 bar to 14.8 bar. As I mentioned in chapter 4, the degree of plasticization may be different at higher CO$_2$ pressures. Here, 42.4 bar CO$_2$ is recommended for study. However, one should first experimentally check whether swelling occurs in the gutter layer at pressures higher than 14.8 bar.

We have started PFCB thin film swelling studies by ellipsometry. Previous efforts were invested on high-pressure cell design (see details in Appendix C), experimental protocol development, instrument adjustment and calibration, and pilot experiments. Even though no reliable data were collected during pilot experiments, largely as a result of equipment malfunction, I highly recommend continuing this study. Because of the anisotropic properties of PFCB thin films, I would recommend that PFCB sample films should be at least 80 nm for initial work. The thermal and aging history of the films in this study should be well controlled and tracked. Considering the possible difference between films coated on a silicon wafer and the gutter layer, it is strongly recommended to compare swelling behavior on these two different substrates. Due to the birefringence of the sapphire windows in the cell, the experimental setup must be very stable. Small vibrations of the stainless steel 1/8 inch tube connecting the cell and the gas cylinder or the wafer during pressurization may cause artifacts in the result.

During our pilot experiments, we observed some irregular phenomena showing that film thickness increased and decreased. However, we also discovered that the ellipsometer birefringence modulator controller and photomultiplier HV controller were malfunctioning, which may have caused artifacts in these data. I suggest refining the
experimental set up and making it more stable. Furthermore, these experiments run longer than 10 h and produce a large amount of data. Due to the sensitivity and stability of the whole testing system, data vibrations are expected. To avoid artifacts brought by these vibrations, it is expected to produce a thickness or refractive index versus time curve with almost every datum points measured. However, the current calculation software performs only a single calculation at one input. A more efficient calculator which can calculate multiple inputs at the same time is necessary and can be purchased (e.g., from the SemiconSoft Inc.) or programmed (e.g., using Python).

Finally, a control experiment on a special sample needs to be conducted to determine the type B measurement uncertainty of the whole system. The sample could be an 80 nm silicon dioxide layer deposited on a silicon wafer. This control experiment is quite important, because, for example, if the system measurement uncertainty is 1 nm, then one should not expect to observe 1 nm change of the film caused by either plasticization or physical aging.

5.2.4 Recommendations for physical aging studies

Physical aging is a complicated process and more could be done to further our understanding of this phenomenon. Once the ellipsometry system has been improved and measurement uncertainty has been determined, it can be a powerful tool to analyze the free volume change of thin films during physical aging.

Permeance tracking of TFC membranes over time after thermal annealing should be done. One of my pilot experiments suggested that the physical aging rate did not change
over the course of a 100 h aging experiment after annealing. If it is true, it would be very interesting to see how the thermal annealing made different impacts on physical aging and plasticization.

Since physical aging is universal to glassy polymers, I strongly recommend creating a database of polymers whose physical aging properties have been reported in the literature. Perhaps writing a review article on this topic would be highly informative and would help us to see the bigger picture.

5.2.5 Recommendations for mixed gas separations

From the feedback of our paper reviewers and current literature articles, mixed gas separation experiments are becoming a standard practice to characterize novel membranes. During the real separation, if plasticization occurred, CO₂/N₂ selectivity would decrease. But the decrease of selectivity can also be caused by a well-known phenomenon called competitive sorption has not been studied yet for PFCB TFC membranes. Competitive sorption occurs when another gas like methane or nitrogen is introduced to the feed gas. Sometimes, even a small amount of impurities will decrease the CO₂ permeance significantly, especially at high CO₂ partial pressure.

5.2.6 Recommendations for the testing apparatus

The current gas transport testing apparatus in our lab falls under the category of a constant pressure setup. I strongly recommend building up a constant volume setup, which is also called a “time lag” system. This system can be used to determine diffusivity
and solubility coefficient of bulk polymer films. Observance of how these two parameters vary by aging time, selective layer thickness, and thermal history should provide a more in-depth understanding of how physical aging and thermal treatments affect film transport properties.

For the “time lag” system, I suggest setting the working pressure from 0 to 40 bar, building a special thermal insulation box for the system, adding a temperature control system (20 to 60 °C), and connecting a gas chromatography (GC) unit to enable measurements for both pure and mix gas separations.

Two obstacles that I can foresee now include 1) system requires ultralow pressure (< 10 millitorr); 2) leak rate must be insignificant. I would suggest finding expertise from Swagelok and applying long-time vacuum (24 h) before testing.

For mixed gas measurements, we need to install a thermal conductivity detector (TCD) for our GC and install a vent on the separation cell to make sure that gas composition is constant during the separation. In addition, a mass controller needs to be connected to the vent to control the stage cut above 100 (stage cut = flow rate of the vent/flow rate of the permeate).

5.2.7 Recommendations for validating the correlation between plasticization pressure and polymer properties

This idea comes from the literature data analysis. Literature data that we have found so far yield a strong, linear correlation between plasticization pressure and the quotient of tensile modulus to solubility. Results are very encouraging; however, more needs to be
done to validate the correlation. I have two suggestions: 1) One can generate additional data by measuring the z direction tensile modulus of thin films with different thermal history by AFM, combined with measurements of the plasticization pressure. 2) Explore an idea offered by our collaborator, Adam T. Haldeman from Tetramer Technologies, in which biphenyl derivative (monomer of BPVE-PFCB) is mixed into bulk PFCB films with different fractions. This monomer has an identical solubility coefficient as the PFCB. Then one would measure the bulk film tensile moduli and solubility coefficients for this set of films. A cautionary note is that, if the mixture becomes rubbery, then this correlation may not apply, as it was developed using data for glassy polymers only.

5.2.8 Recommendations for polymer film design

Currently, the most common method to improve polymer resistance to plasticization is using crosslinking. But crosslinking also causes diminished free volume and lower permeance. From our swelling studies, I have found that polymer films swell significantly after exposure to 35.5 bar CO$_2$ and remain swollen after being brought back to atmospheric pressure conditions. When annealed at a temperature higher than the bulk $T_g$, the film thickness decreases again. I strongly recommend designing a novel polymer that can be crosslinked by UV light at low temperature. One can swell the polymer at high CO$_2$ pressure to create a film with a high free volume and then crosslink it by UV light exposure to make it more resistant to high pressure CO$_2$ and less resistant to thermal annealing, while retaining the high permeance. It is likely that the pressure used to swell the film will need to be optimized to produce TFC membranes will the desired balance
between permeance and selectivity.
APPENDICES
Appendix A

Viscosity measurement of PFCB/chloroform and PFCB/THF solutions at different concentrations and shear rates.

Figure A-1. Viscosity measurements for PFCB/chloroform solutions. Triangles, squares and diamonds represent 1.00 wt %, 0.50 wt % and 0.25 wt % bulk PFCB concentrations.
Figure A-2. Viscosity measurements for PFCB/THF solutions. Triangles, squares and diamonds represent 1.00 wt %, 0.50 wt % and 0.25 wt % bulk PFCB concentrations, respectively.

Note: Figures A1 and A2 show absolute viscosities of PFCB solutions measured using a cup and bob rheometer. PFCB/chloroform and PFCB/THF solutions exhibited slight shear thickening over the measured shear rate range.
Appendix B

Refractive index values of PFCB thin films at two different testing angles

Figure B-1. Refractive index of PFCB thin films measured by ellipsometry at 80° (squares) and 56° (diamonds).

Note: Figure B-1 shows refractive index values for PFCB thin films that vary in film thickness. A significant difference was found between RI values measured at the two
endpoint incidence angles of 56° and 80°, indicates anisotropic properties of PFCB thin films below about 50 nm
Appendix C

Design of high pressure cell for swelling study

(The following CAD drawings were prepared by Dr. Christopher L. Kitchens)