FABRICATION OF POSS NANO-COMPOSITE MEMBRANES
USING PLASMA TECHNOLOGY FOR SOLVENT SEPARATION

By

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Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

At Deakin University

Institute for Frontier Materials

March 2019, Geelong – Victoria, Australia
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General Abstract

The development of thin film membranes for solvent purification, recovery, and recycling is critical to tackle issues related to traditional distillation. The separation performance of membrane materials is largely affected by its properties which may be further enhanced by smart addition of nano-scale texture or fillers across the supporting membrane matrix.

Thin film nano-composite membranes provide controllable chemical structure and properties towards the performance of the separation as permeability and selectivity. Amongst potential nano-fillers, octamethyl polyhedral oligomeric silsesquioxane (octamethyl POSS) offers a symmetric cubic structure with 8 corner functional groups and may act as bridges with organic and inorganic materials to yield hybrid nano-composite materials of controlled free volume distributions and densities. However, current challenges related to nano-composite design from POSS nano-particles included lengthy processes, aggregations of nano-particles, and toxic wastes in wet chemical route. Thus, incorporation of POSS nano-particles with the polymeric matrix has encouraged to develop alternative pathways such as environmental friendly plasma technologies. The interaction between nano-particles and polymeric matrix can be tuned through ionization by controllable plasma conditions as to achieve designable nano-composite for membrane purpose. Therefore, aim in this Thesis is developing a simple strategy by plasma to fabricate a POSS nano-composite thin film membrane to address the solvent separation such as ethanol/water system.

Firstly, to control the degree of crosslinking in the nano-composite matrix by tuning the functional groups on POSS nano-particles, gas plasma was used to produce the functionalized octamethyl POSS nano-particles to bridge the network with
polymers. The requirement for a simple functionalization without costly route was always the target for production. Physical plasma functionalization can be one of the pathways for processing octamethyl POSS nano-particles. Hence, it is critical to investigate the efficiency of the functionalization on POSS to access the number of functionalized sites for bonding in the polymeric matrix and form cross-linked structure.

A low-pressure plasma treatment using N$_2$/H$_2$ gas mixture was studied to produce amine groups for covalent bonding with polymers. Plasma generation was controlled by plasma power and duration to carefully tune the methyl groups on the POSS nano-particle without degrading the POSS cage-like structure. Characterizations of composition with FTIR and XPS suggested successfully introduction of nitrogen-containing groups without losing cage-like structure and the number of primary amine groups was defined by TFBA derivatization.

To improve the number of functional groups on POSS nano-particles, a stirring system with the low-pressure environment was developed by O$_2$ plasma. Carboxylic groups were determined by characterization with an enhanced yielding of POSS nano-particles compared to the previous system towards the feasible synthesis of functionalized POSS nano-composite. However, limited functionalized sites on POSS nano-particles was produced due to limited vacuum condition and difficulty on uniform dispersing under a solid state in the stirring system. Therefore, functionalization by plasma is requiring better preparation of solid nano-particles for increasing number of functional groups.

Secondly, to develop the fabrication of POSS nano-composite thin film by plasma with homogenous distribution of nano-particles in the matrix, an atmospheric pressure plasma deposition with aerosol-assisted method was investigated.
Hexamethyldisiloxane (HMDSO) monomer was used for polymerizing ethanol selected layer on the commercial ultrafiltration (UF) poly (sulfone) (PSf) membrane. Thin film nano-composites were demonstrated by plasma with a lateral configuration and a series of different octamethyl POSS concentration in the deposition as well as a series of deposition thickness. The homogeneity of POSS nano-particles in the polymerized matrix was led by the aerosol generation and an increasing amount of network structure was characterized by composition, profilometry, and wettability. Ethanol selected membrane performance was examined by dead-end filtration of pure ethanol and water as a selectivity of 6.5 for the ethanol against water.

To further improve the effective area for deposition on the substrate for membrane application, an X-Y moving stage was applied to a plasma configuration of precursor through the electrodes at atmospheric pressure.
Acknowledgment

Firstly, I would like to thank my principal supervisor Dr. Ludovic Dumée for his knowledge and constant guidance as well as kindly support during my whole PhD life. I really thank him for helping review my work and plan as well as providing me with opportunities to further develop my research skills.

I would like to thank my co-supervisors Dr. Zhiqiang Chen for his constant support on plasma field throughout my studies and Dr. Kevin Magniez for his support and initiate on the knowledge of POSS nano-particle application. I would also thank my co-supervisor A/Prof. Johan du Plessis for the support of XPS characterization and facility access in RMIT. I am particularly grateful for the kind support by my retired co-supervisor Dr. Xiujuan J. Dai and her husband Dr. Peter R. Lamb with their knowledge on the plasma. I am also particularly presenting my deepest sympathy to the loss of my co-supervisor Prof. Riccardo D’Agostino for his great support on plasma deposition of monomer and assistance given for my visit at University of Bari (Italy).

I would like to express my gratitude to Dr. Fabio Palumbo, Ms. Chiara Lo Porto, and Prof. Favia Pietro for the work on plasma deposition of POSS nano-composite thin film for membrane purpose and their support at University of Bari (Italy). I would like to also acknowledge technicians for their experimental support at University of Bari (Italy).

I would like to thank Dr. Matthew Field and Dr. Edwin Mayes for helping access the XPS facility and performing XPS characterization at RMIT University. I would like to express my gratitude to Dr. Anders Barlow for helping composition characterization with XPS at Latrobe University.
I send my gratitude to Ms. Debra Hamilton for helping access the Malvern DLS system at CSIRO. I would also like to thank Mr. Craig Noble from Emgrid Australia for the training on Olympus laser microscope. I would also like to acknowledge the grant M10645 from the Australian Synchrotron for the SAXS / WAXS measurements.

I would like particularly thank Mrs. Helen Woodall, Dr. Daniel Fabijanic, and Dr. Luke O'Dell for their support on my Thesis progress.

I would like to sincerely grateful all the members of Institute for Frontier Materials including staff, students, and technicians for their support throughout my whole PhD study especially all the members of plasma group and micro-nano group.

I would like to specifically thank Dr. David R. de Celis, Dr. Gayathri D. Rajmohan, Dr. Sri B. Ponraj, Dr. Arun T. Ambujakshan, Dr. Mohammad Maniruzzaman, Dr. François-Marie Alliouix, Mr. Andrea Merenda, Dr. Zhifeng Yi, Dr. Bao Lin, Mr Riyadh AL-Attabi, Mr. James Wainaina Maina, Mr. Erwan Castanet, Ms. Elise des Ligneris, Ms. Jingshi Wang, and Ms. Marion L. Wright for their friendship and kindly support in the lab.

I would like to acknowledge Deakin University for providing opportunities to enable my PhD study and Institute for Frontier Materials for supporting me for the visit to University of Bari (Italy) via the IFM Travel Award.

Finally, I would like to send my deepest gratitude to my entire family especially my parents whom always support me with their love and keep me moving forward during my PhD life. I would like to express the gratitude to Dr. Shirley Shen and Prof. Yibing Cheng for their kind support throughout my stay in Australia.
Publications, award during candidature

Journal publications published:


Conference proceedings:


- **Oral presentation**: “Thin film formation from aerosol-assisted plasma deposition for solvent separation application”, 9th International Membrane and Science Technology Conference, 05 – 08 Dec. 2017, Adelaide, South Australia, Australia.

- **Poster**: “POSS contained thin film composite deposition using aerosol-assisted atmospheric plasma for solvent separation”, International Conference on Nanoscience and Nanotechnology, 29 Jan. – 02 Feb. 2018, University of Wollongong, New South Wales, Australia.

Awards:

- **Travel award**: IFM Travel Award, May 2016. Visit study at University of Bari, Italy (2 months).
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Chapter 1 Introduction

Separation processes have been widely used in the liquid and gas recycling and recovery applications due to the challenges of both environmental deterioration from the intensive waste generation and limited global energy resources [1, 2]. Membrane separation has gained increased recognition over the past 30 years for the low operating and capital costs allowing for high selectivity and performance. Membrane materials were developed as cost-effective technologies compared to traditional distillation separations which have been used in water treatment, gas permeation, catalysis, energy generation, and solvent separation [3, 4]. Solvent separation is one of the important technologies to produce pure solvents from mixed organic solvents for chemical [5], petrochemical [6], and pharmaceutical industries [7, 8]. Membranes have supported the water purification sector but also to the mixed solvent with less production of waste and cost.

Membrane separation has been particularly successful for the purification of bio-fuels over the past 10 years, specifically as a result of low-cost alternatives to distillation, separate water mixed with oils and solvents in solvent separation, and a hybrid thermal-molecular sieve separation system [9-12]. Membrane technologies typically rely on the formation of a selective layer to control the mass or charge transfer across the layer and therefore results in selectivity of passing component. However, trade-off behaviour of permeability and selectivity in membrane processes has limited their industrialization as well as the short lifetime cycles in harsh environments [9, 11, 12]. Uptake of solvent, through chemically or physically sorption as well as interactions with primarily organic contaminants in the solution, were shown to lead to plasticization and long-term performance loss to the polymeric membrane material.
Hence, more stable and nano-structured materials are required whereby both bulk and surface interactions can be finely tuned to specific effluent treatment applications [12].

Nanofiltration (NF) and pervaporation (PV) are technologies whereby either a pressure difference or a partial vapour pressure differences across a dense membrane material are used for separating mixed solvents [9, 12]. It has been demonstrated for the separation of azeotropic mixtures such as ethanol/water systems because of the low energy consumption and environmental footprint which used in bio-fuel generation [13-15]. NF process basically depends on the steric mechanism for neutral solutes which bases on the size exclusion effects but/and also in the Donnan effects for ionizable components during the filtration. Performance of membranes in pervaporation systems is typically dominated by the degree of free volume across the matrix and the surface energy of the material [11]. For both applications, however, the free volume represents the non-physical pores which statistically locate across polymeric macro-molecular chains, therefore solvents may selectively diffuse by either molecular sieve mechanisms or partial pressure evaporation [9, 10, 12]. The surface energy of the material is the other critical factor which determines the material surface and bulks preferential wettability to the different solvents in the system [10]. The selectivity of one solvent against the other, referred to the separation factor of a system, is therefore unique to one membrane material and mixed solvent condition-reflecting the large array of liquid waste materials awaiting recovery and purification.

Recently, the development of advanced crosslinking agents for enhancing the performance of membrane materials has been studied for the preparation of membranes from low-cost polymers such as poly (dimethyl siloxane) (PDMS), poly (benzimidazole) (PBI) and poly (amide) (PA) [16-18]. However, depending on the intrinsic nature of macromolecular networks, crosslinking control technique, and the
remaining of crosslinking agents in the polymeric matrix, membrane performance for separation would drop down the permeability or selectivity [12]. Thus, a composite membrane using nanomaterials as fillers incorporated across an otherwise impermeable polymer matrix have been investigated as a potential strategy to improve diffusion by providing low resistance networks across the macromolecular chains of the polymer. The promising outputs of such nano-composite membranes, delivering highly enhanced permeation rates without loss of selectivity led to the investigation of a number of potential nano-fillers with their chemistries and morphologies [19-21]. However few challenges limit their performance such as the control of agglomeration from the nano-fillers and their homogeneous incorporation across the polymeric matrix due to their large aspect ratio and the specific interactions with the macromolecular chains [12]. Thus, strategies to control the interactions between nano-fillers and macro-molecular chains across thin film membranes, as well as smarter routes to fabricate membranes for solvent separation specifically tuned for precise effluents and applications are urgently required.

Polyhedral oligomeric silsesquioxane (POSS) materials are one class of silicon-based cage-like nano-structured materials which act as highly crystalline, 3 – dimensional building blocks for creating a controllable structural advanced composite [22-24]. The small size of the cage (1 - 3 nm) let POSS nano-particles work as nano-fillers while the shape and chemistry of corner or bridging bonds to tune the reactivity and the surface energy of the compounds [22, 25]. Currently, POSS nano-composite materials have been used for a wide range of scientific and industrial applications, primarily for optical use with electronic devices, thermal resisted composite, and bio-compatible implants [22]. It has been shown that the thermal, and mechanical properties of polymers, while also their free volume and degree of crosslinking may
be significantly altered by covalently attaching POSS nano-cages to the backbone of the polymer. The build-up structure opens opportunities in the design of crystalline hybrid polymer-silicon networks [22]. Thus, POSS materials have been incorporated into polymeric materials to enhance membranes properties and control surface interactions with contaminants critical to producing high-performance materials with low fouling tendencies [26].

In order to covalently attach the POSS to the polymer backbone, POSS nanoparticles have to bear reactive functional groups to bind with groups across the polymer chains. However, the large majority of POSS feedstock derived from common synthesis have limited functional groups and are extremely expensive [27] due to the cost of the solution based synthesis methods used for their preparation. Direct synthesis of target POSS or wet chemical functionalization of non-functional POSS has been reported for the development of POSS nano-particles bearing reactive functional groups, thus extending their function into a wider range of applications [22]. However, the commercial functionalization of POSS nano-particles requires some costly toxic and hazardous chemicals as well as consuming duration of reaction to achieve the production [22-24, 28]. New possibilities are therefore required to modify and functionalize POSS materials and adapt them to their incorporation into membranes towards enhanced performance separation materials.

The current proposal focuses on providing an innovative approach to the fabrication of ultra-selective, fast permeation rate, durable and versatile POSS nano-composite membranes through plasma treatment and plasma polymerization. Hence, the motivation of this project begins with investigating of the functionalization of non-functional POSS materials by physical plasma as a more environmentally friendly method. The fabrication of nano-composite thin films with controlled densities and
thicknesses of functionalized POSS is evaluated through one-pot synthesis routes. The main purpose of the project is developing a homogenous hybrid membrane of POSS/polymer using plasma with the aerosol-assisted method as a simple, fast, and environmentally friendly process. Permeability and selectivity are studied for the impact of the functionality and structure of the POSS nano-nanoparticles on the membrane performance. If the control of the interaction is achieved, plasma fabrication for nano-composite thin film membrane could become an alternative strategy than traditional solution casting method to provide high performance membrane. Also, the study of the interaction between POSS nano-fillers and polymeric matrix during plasma would empower the industrialization of plasma nano-fabrication.

The discussion of the membrane material with POSS incorporation and the technology of plasma are presented in Chapter 2. The understanding of solvent separation membrane including NF and PV, as well as the use of POSS nano-particles for membrane design will be presented along with their main advantages and limitations. Fundamental information on plasma processes are then discussed and their capacity to yield reactive functional groups across nano-materials and to form membranes. The research questions have been developed from the gaps identified in the literature review in order to design the research plan for producing the solvent separated membrane.

The materials and methodologies are introduced in Chapter 3. The chosen POSS, monomer and polymer for hybrid membrane are presented as well as properties of the solvents used for testing. Both functionalization routes for the POSS and that of the polymerization of POSS nano-composite membranes are described. Then, the
general characterization techniques for determining the properties and structure of the material are detailed as well as the testing of membrane performance.

The modification of the POSS nano-particles with plasma strategies to generate functional POSS nano-particles is evaluated in **Chapter 4**. Plasma treatment is performed with composition and structural characterization to determine the degree of functionalization. Potential scale-up methods for higher functional POSS yielding are presented using a stirring plasma based method.

In **Chapter 5**, the fabrication of the thin film POSS nano-composite is discussed. The two different plasma systems (at Bari University and Deakin University) studied, based on aerosol-assisted deposition and the characterization of the produced materials, have been used to assess applicability and feasibility for membrane separation applications. Permeability and selectivity are discussed by the pure solvents filtration through dead-end testing driven of pressure. The separation performance is discussed and the limitation of the current systems processed at Bari University and Deakin University presented.

In the end, **Chapter 6** summarises the experimental results, limitations, and provides the future study on the directions towards the development of plasma processes as cost-effective alternatives to generate thin film membranes.
Chapter 2 Literature review

The fundamentals of the design of nano-composite membranes for mixed aqueous-organic solvent separation will be first reviewed in this section. The potential of POSS materials to act as fillers for nano-composites design will then be discussed and linked to the latest development for application in membrane technologies. Routes to modify or functionalize POSS material and to incorporate them into otherwise dense polymeric matrix will be presented. The impact of the microstructure of the membranes and chemistry of the POSS will be particularly discussed in light of flux and selectivity results. The advantages and drawbacks of these strategies will be critically discussed to extract this PhD thesis research questions.

2.1 Introduction

2.1.1 General introduction on membrane separation processes

Membrane materials are thin film materials used for selective separation of contaminants or resources from gases or liquids. A feed stream is typically circulated across the surface of the membrane and a permeate stream, generated by specific or selective transfer across the membrane, may be collected. Membrane materials present varied geometries, chemistries, and microstructure based on their end-application and may be found for instance as dense or porous, homogeneous or heterogeneous, isotropic or anisotropic, as bulk or very thin films [3]. The driving force for each membrane process is critical to the selectivity and performance of the system. There are four main driving forces including physical pressure, chemical activity, temperature, and electrical potential difference [29].
Generally, membrane processes for wastewater treatment and desalination include microfiltration (MF), ultrafiltration (UF), NF, and reverse osmosis (RO) technologies with size sieving to select permeable components across the membranes driven by pressure [29]. Gas separation and PV processes are driven by chemical potential or concentration differences across membranes thus letting specific moieties diffuse by solution-diffusion type behaviours [4, 12]. Membrane distillation is driven by a temperature difference across the membrane material which allows adjusting a vapour pressure differential to selectively evaporate compounds from a mixture used for solvent separation [29]. Commercial membranes are typically made of the plain polymer due to the lower cost of both raw materials and manufacturing processes compared to polymer composite and ceramic-based membranes. In order to improve the performance of polymeric membrane materials, strategies involving the design of nano-composite membranes have been extensively investigated [4, 30]. In such an approach, filler materials are incorporated into the membrane material to generate active and controlled interfaces with their surrounding matrix and enhance separation performance [30].

Currently, separation membrane processes play an important role in the chemical, petrochemical and pharmaceutical industries due to the cheap cost of material and operation [29]. Separation and reclamation of organic solvents and their mixtures are of interest due to their high-added value and environmental synthesis footprint. The purification of solvent mixtures is rendered more difficult than that of pure solvents due to the miscibility and the typically close size and surface energy of the solvents in the system. In order to deal with such solvents separation, reclamation and disposal advanced membrane materials must be developed to render processes economically viable [29].
2.1.2 Solvent separation

2.1.2.1 Introduction

Solvent separation is a critical area to reclaim contaminated or mixed solvents from the petrochemical, pharmaceutical, food or waste recycling industries where ~70% of the costs are attributed to operating conditions [31]. Liquid-liquid extraction processes were used for separating organic solvents due to the simple concept. However, liquid-liquid solvent extraction usually requires a large amount of the solvent materials which must be eventually regenerated, is time-consuming, and not environmental friendly [31]. With the development of membrane technology, membrane separation became a more conventional process with lower cost compared to traditional extraction methods.

Filtration is usually based on four factors for applying the target separation, i) driving force; ii) size of the selected solute and the pore size of the membrane; iii) the molecular weight cut-off (MWCO); iv) the mechanism of the filtration [31, 32]. Due to the size of the solvent usually being very small, the non-porous membrane needs to be used to perform the selectivity with smaller free volume compare with ultrafiltration and microfiltration processes. Therefore, NF and reverse osmosis were considered to have an effective selection of the solvent separation due to their high selectivity from non-porous membrane material and is referred to as Solvent Resistant Nano-Filtration (SRNF) [31].

Since SRNF belongs to the pressure-driven the process, components transport across the membrane will follow combined sieving from the pore exclusion mechanisms and the solution/diffusion mechanism due to high density and sub-nanometer scale of the pores across the membrane. The first application on non-aqueous liquid separation was published in 1964 for separating hydrocarbon solvents
using a cellulose acetate [32]. In the 1980’s, the increase of the interests on SRNF led to the development of a number of the new materials and processes to tackle challenges related to solvent regeneration and low molecular weight organic compounds separation in the petroleum industries, while the first commercial membranes were produced in the mid-1990’s [32]. Compared to other non-membrane based solvent separations, such as distillation, pressure driven process provide nonthermal separation pathways thus less likely to lead to damage or degradation of the valuable components. Energy consumption and waste materials or waste generation were also reduced due to the more streamlined and lower footprint process. SRNF processes may be designed either as continuous processes for separation and setup with other existing technologies to yield hybrid separation systems to upscale reclamation or separation of mixed solvent production [32].

The membranes used for solvent separation mainly face challenges related to the trade-off behaviour of permeability and selectivity, fouling issues from organic compounds, and to the nature of the azeotropic behaviour from such solvent mixtures. The success of the large-scale process is still limited nowadays due to long-term operation stability affected by the lack of membrane materials robustness, the harsh conditions of such reactive environments leading to chemical instabilities, membrane fouling and concentration polarization across the surface of the membrane materials over operation [33, 34]. Another technology for solving solvent separation mainly based on non-aqueous or mixed solvent systems is PV. Membranes for PV are also dense, non-porous materials, whereby diffusion is driven by chemical affinity from mixture components across the materials [11].

The chemical potential difference across the membrane, generated by mild energy gradient and concentration differences, leads to a semi-selective transport by
diffusion/solution mechanisms across the free volumes of the material [10, 12]. The feed stream during the PV process will evaporate from liquid to vapour phase during the diffusion across the membrane and then condense to liquid phase again upon reaching the permeate stream. The permeate stream is generally collected by flowing a sweeping gas, working in a vacuum, or using a cold stream to reach the target partial pressure or temperature difference [11, 35].

A phase change from liquid to vapour therefore occurs during PV. The latent heat of the system, and therefore the energy consumption, is directly related to the ratio of the different solvents separation as well as the presence of contaminants in the feed [10]. Membranes used in PV usually offer separation factors 100 times higher than that of direct distillation, which makes of the technique a perfect route to produce ultra-pure solvents [10]. These features support PV as the most-effective liquid separation technology to date [12]. Furthermore, because of the mild operating conditions, PV does not require excessive flow pressure, as opposed to reverse osmosis, or heat, as opposed to membrane distillation [12]. However, the permeation is typically low due to the effective selectivity required in the process, induced by the narrow and low density of free volume in the layer [29]. Therefore, the design of higher free volume materials offers the opportunity to improve selectivity and permeation across the active membrane layer.

Recent hybrid processes involve combining solvent separation membranes with other separation techniques [36] to optimize the latent heat of the feed reaching the membranes. There are three main areas currently for solvent separation membranes. The first is dehydration of organic solvents such as alcohols, ethers, esters, and acids under PV [29]. Dehydration is the most developed applications for solvents where water is easy to travel across the hydrophilic membrane with its small molecular size...
compared to other solvents [12]. The second relates to the removal of dilute organic compounds from aqueous solutions, which includes volatile organic compounds separation, and biofuels generated from fermentation broths [29]. When SRNF or PV is used for removing trace small organic solvents from water, the efficiency is limited which is due to the similar size of water and the size of the organic molecule in the dilute solution and the azeotropic nature of most of such systems [37]. However, when the selected organic solvent concentration is up to 90 wt.% in the mixed solvent, adsorption diffusion dominant the transportation of the solvent from feed to permeate and the continuous process brings large benefits compare with traditional methods [12]. The third and last application is related to organic-organic mixtures separation, which may include methyl tert-butyl ether (MTBE)/methanol, or recently dimethyl carbonate (DMC)/methanol separations [12]. The separation of mixtures from organic solvents are the most challenging applications for SRNF or PV and yet the most interesting area from the industrial point of view due to the high added value of the resources to recover [19]. In the case of PV, only some polar/non-polar pair of solvents were successfully separated including methanol/MTBE, benzene/n-hexane, and p-xylene, m-xylene, and o-xylene [12].

The challenges and opportunities of solvent separation membranes will be discussed in the following sections to design more efficient membrane materials in terms of selectivity and permeability. The mechanisms of diffusion across membranes will also be discussed to correlate Hansen solubility and kinetic diameter to a relation to separation factor and quantify the rate of permeation [12].
2.1.2.2 Hansen solubility parameter and kinetic diameter for solvent separation

The influence of the Hansen parameter is critical during the solvent diffusion process. The Hansen solubility parameter is a factor which refers to the density of cohesive energy within a solution [38]. Three components of solubility parameter were split into $\delta_h$ as the contribution of the hydrogen bonding interaction, $\delta_p$ as the contribution of the polar interaction, and $\delta_d$ as the contribution of the dispersion interaction. The solubility parameter is therefore referred to as a vector in a three-dimensional structure of a membrane.

In a binary system, the components from the mixture have a distance between ends of two components which are shown as vectors of one component to the other and is referred to as an index of dis-similarity [38]. Thus, over 50 solubility parameters of solvents were collected for SRNF or PV system to develop a theoretical design for the separation process of mixed solvents [12, 38]. The polar interaction is always lower than dispersion interaction except water in Figure 2-1a [12]. The contribution of hydrogen bonding and dispersion interactions within the solvents allows for the classification of the solvents into characteristic groups related to their chemical structures or functionalities which are represented in Figure 2-1b [12]. For instance, between water and most organic solvents, the larger impact of hydrogen bonding interactions for water supports the dehydration of organic solvents and the separation of water from mixed organics such as hydrocarbons from water is thermodynamically preferential. The successful polar/non-polar mixture separation of methanol and MTBE by Sultzer Chemtech are also been justified from the difference between methanol and MTBE in Figure 2-1b [36].
Therefore, the hydrogen bonding and the dispersion interaction of organics are critical to control the selectivity through the difference between solvents and water which towards the dehydration of organic solvents and removal of organics such as hydrocarbons from water. However, the difference in dispersive interactions cannot
fully explain selectivity for chemicals when organics in the same groups such as benzene/cyclohexane (e.g. dispersion interaction 1.6 (MPa)$^{0.5}$). Thus, liquids with similar dispersion interactions are hard to use the thermodynamic discriminating capability of the membrane to design the separation process. Hence, an approach to evaluate similar dispersion interactions in a binary system based on the kinetic response of the membrane to the different sizes and shapes of the solvent molecules has been developed [39]. Some liquid pairs with challenging dispersion interaction differences are presented in Figure 2-2. The kinetic diameter is used in the Figure to highlight substantial size differences for separating the solvents. With same carbon number groups of 6 and 8, there is a 0.95 Å difference between p-xylene and m-xylene, and a 1.5 Å difference between n-hexane and benzene respectively. Therefore, the design of high-performance SRNF and PV membrane has been developed through Hansen solubility parameter and kinetic parameter including highly selective nano-composite membrane and advanced ceramic membrane materials [12].

![Figure 2-2 The kinetic diameters of several organic solvents and water [12]](image)
2.1.2.3 Solution-diffusion theory for solvent separation membrane

Solution-diffusion theory

In general, the mass transport mechanisms across a dense membrane is ruled by the solution-diffusion theory, established by Graham [40], and based on the dusty gas permeation model through homogeneous membranes. There are three basic processes during mass transport, including (i) the adsorption and solubilization of molecules on the feed side, (ii) the diffusion of the dissolved species through the membrane matrix across the free volume, and (iii) the desorption of the dissolved species on the permeate side. SRNF and PV processes are ruled by the same mechanisms [41] which were shown in Figure 2-3. Therefore, when the liquid feed stream contacts with the membrane, a thermodynamic equilibrium will reach the interface between the membrane and feed stream instantly [40, 41], which translates into:

\[ \frac{C_m}{C_{feed}} = K \] (2.1)

Where \( C_m \) represents the concentration of a species across the membrane surface in the feed and \( C_{feed} \) represents the concentration of species in the feed. \( K \) is the partition coefficient of species between the membrane surface and bulk feed. The partition coefficient can be a characteristic parameter to evaluate the interactions between molecules and the membrane material. Since membrane operations are a rate-controlled process, these diffusions can be related to the Fick’s first law [40] and by introducing the partition coefficient \( K \) at membrane/feed, and the membrane/permeate interfaces, be used to evaluate the permeation rate for the species such as:

\[ N = DK \frac{\Delta C}{\delta} = \frac{DK}{\delta} \Delta C \] (2.2)
Where $N$ is the flux of species, $D$ is the diffusion coefficient of species in the membrane, and $\delta$ is the position variable (thickness). The model can be extended to mixtures of $n$ components to evaluate the contribution of each species to the permeation rate:

$$
\alpha_j^i = \frac{P_i}{P_j} = \frac{D_i}{D_j} \frac{K_i}{K_j} = (\alpha_j^i)_D (\alpha_j^i)_K
$$

Where $i$ and $j$ correspond to 2 different components here as an example. SRNF and PV developments were therefore based on a strict material selection to maximize the diffusion coefficient $D$, the partition coefficient $K$, and the permeability $P$ across a membrane material. Thus, the experimental permeation flux and separation factor are obtained by:

$$
N = \frac{Q}{A \Delta t}
$$

$$
(\alpha_j^i)_{permselectivity} = \frac{(Y_i/Y_j)}{(X_i/X_j)}
$$

Where $Q$ is the quantity in gram or mole of permeate in a time interval $\Delta t$, $A$ is the effective membrane area, and $X$, $Y$ are the fractions of components in the feed and permeate, respectively.

Therefore, the performance of the membrane is depending on the free volume of the membrane material and the surface energy of the material. This classical theory is only applied to the non-swollen membranes such as dilute organics from water [42, 43]. When membrane swelling occurs during the dehydration or organic-organic separation, both partition and diffusion coefficient would be decided by the concentration of the components which the modification of theory will be required.
Modified Solution-diffusion theories

Typically, after swelling or plasticizing, the increase of free volume across a membrane is due to reduced interactions between polymer chains and leads an increase of the diffusion coefficient, as developed by Vrentas and Duda [44]. The fractional free volume (FFV) of polymers [45] is typically defined as:

\[
FFV = \frac{\text{specific free volume}}{\text{polymer specific volume}} \quad (2.6)
\]

Thus in a ternary system which includes the membrane material and two species to separate, the diffusion coefficient becomes:

\[
D = D_0 e^{\left(-\frac{E_a}{RT}\right)} \times \exp\left[\frac{\gamma(\omega_1 V_1^* + \omega_2 V_2^*)}{V_{FH}}\right] \quad (2.7)
\]
With \[ V_{FH} = \omega_1 K_{11} (K_{21} - T_{g1} + T) + \omega_2 K_{12} (K_{22} - T_{g2} + T) \] (2.8)

Where \( D_0 \) is diffusion coefficient at infinite dilution, \( E_a \) is the diffusion activation energy, \( \tilde{V}_i \) is the specific critical hole free volume required for diffusion of a component I, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( \gamma \) is an overlap factor, \( \omega_i \) is the weight fraction of component i, \( \xi \) is the ratio of critical the volume of solvent per mole to that of the polymer, \( V_{FH} \) is the specific hole free volume of the polymer-solvent system, \( K_{1i} \) and \( K_{2i} \) are the free volume parameters, and \( T_{g_i} \) is the glass transition temperature of component i.

Therefore, the diffusion coefficient of species i can be expressed as [46]:

\[ D_i = D_{i0} \exp(\alpha_{ii} C_i + \beta_{ij} C_j) \] (2.9)

Where \( D_{i0} \) represents the diffusion coefficient of species i at infinite dilution, \( C_i \) and \( C_j \) are the local concentrations of species i and j, and \( \alpha \) and \( \beta \) are interpreted as plasticization coefficients of the two species across the membrane. Thus, the flux \( N \) becomes:

\[ N_i = -D_{i0} \exp(\alpha_{ii} C_i + \beta_{ij} C_j) \frac{dC_i}{d\delta} \] (2.10)

\[ N_j = -D_{j0} \exp(\alpha_{ij} C_i + \beta_{jj} C_j) \frac{dC_j}{d\delta} \] (2.11)

Depending on the permeation rate, the permeate selectivity is then expressed by introducing the expression of the concentration of species \( C_{Si} = K C_T X_i \) in the equation, where \( C_{Si} \) is the species concentrations on the feed side of the membrane, \( K \) is the partition coefficient of species i between the feed and the membrane. \( C_T \) is the total concentration of feed, and \( X_i \) is the percentage of species i in the feed. Therefore, the separation factor becomes:
\[
(a)^{\text{perm.}} = (a)^{\text{corp.}} \frac{D_{i0}}{D_{j0}} \left\{ 1 + \frac{(a_{ii} - a_{ij}) K C_T}{2!} X_i + \frac{[(a_{ii} - a_{ij}) K C_T]^2}{3!} X_i^2 + \ldots \right\} 
\]

So that the diffusion selectivity can be generalized to become:

\[
(a)^{\text{diff.}} = \frac{D_{i0}}{D_{j0}} \left\{ 1 + \frac{(a_{ii} - a_{ij}) K C_T}{2!} X_i + \frac{[(a_{ii} - a_{ij}) K C_T]^2}{3!} X_i^2 + \ldots \right\} 
\]

2.1.2.4 Challenges and opportunities of solvent separation

**Organic solvent dehydration for PV**

PV has been largely developed for the dehydration of organic solvents such as alcohols, ethers, acids, and ketones [47], which were first separated using natural polymer-based membranes, such as cellulose derivatives [10]. Specifically for separation of ethanol-based mixtures applications, synthetic polymers [48] such as poly(acrylic acid) (PAA) and poly(vinyl alcohol) (PVA) were shown to be more stable and efficient. In the 1980’s, the breakthrough was achieved by Gesellschaft fur Trenntechnik Co. (GFT) to improve the performance of the PV, leading to the first PV plant in 1988 in France of 15 m³ capacity per day [36]. From the success of GFT, the membrane fabrication based on cross-linked systems were developed leading to improved membrane strength and chemical stability by using glutaraldehyde as a cross-linker or thermal treatments to generate more crosslinking reactions [49]. Since crosslinking limits the mobility of the polymer chains, membrane swelling is controlled by preventing high brittleness and therefore premature failure of the membranes.

Blending polymers have also been used to modify the membrane materials properties. Cellulose cuoxam blended with alginate led to a higher density of hydrogen bonding interactions, between the hydroxyl groups of two components, which
increases the mechanical properties and stability of the membranes in aqueous liquids [50]. Similarly, Chitosan/PVA blended membranes achieved better separation performance than purely cross-linked PVA for dehydration applications with up to 25,000 increases in separation factor [51, 52]. The high hydrophilicity of chitosan, naturally unstable in aqueous solution, was compensated by the strong electrostatic interactions generated between the polyanion from poly(acrylic) and polycation across the chitosan [51, 53]. Shieh and Huang blended chitosan solution with poly(acrylic) acid to forming such polyanion-polycation interactions in the membrane, which results in polyelectrolyte linkages acting as ionic cross-linked networks across the membrane [53]. Therefore, the resultant membranes exhibit stable and improve performance in PV process compared to pure poly(acrylic) systems [12]. Hence, membrane properties can be modified by control of crosslinking, such as cross-linker agent selection, density characterization, and solution chemistry tuning.

**Dilute organics removal from water**

The separation of organics from water is a hot topic in environmental protection. Both adsorption and solvent separation technologies includes NF and PV. Since the membrane process is a continuous process which can offer a more convenient operation than otherwise intermittent adsorption processes, SRNF and PV have become increasingly popular along with novel materials developments. In the case of organics removal from water, membranes are based on hydrophobic or hydrophilic polymers to extract organics or water from mixture feed [42]. Hence, the design of membrane chemistry is aimed at attracting organic molecules to the membrane surface to allow for their transfer across the membrane. Poly(dimethylsiloxane) (PDMS) membranes with cross-linked structures are widely
used in the organics removal due to their hydrophobicity, high stability and simple fabrication such as toluene, methylene chloride, and benzene as shown in Table 2-1 [54]. The high affinity and low transport resistance with stable operation under stream for organics provide it as a good material to generate membranes which can operate with high total organic carbon contents. Table 2-1 highlights rubbery materials properties and relevant selectivity for several corresponding organics which at least 2,500 [12].
Table 2-1 Several membrane materials and their selectivity of organic against water [12].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Organics</th>
<th>Selectivity (organic/water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>Chloroform</td>
<td>6,800</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>25,000</td>
</tr>
<tr>
<td></td>
<td>Methylene chloride</td>
<td>19,000</td>
</tr>
<tr>
<td></td>
<td>Trichloroethane</td>
<td>5,000</td>
</tr>
<tr>
<td></td>
<td>Benzene</td>
<td>11,000</td>
</tr>
<tr>
<td></td>
<td>Styrene</td>
<td>13,000</td>
</tr>
<tr>
<td></td>
<td>Cyclohexane</td>
<td>9,300</td>
</tr>
<tr>
<td>Poly(urethane)</td>
<td>Toluene</td>
<td>10,000</td>
</tr>
<tr>
<td></td>
<td>Trichloroethane</td>
<td>2,600</td>
</tr>
<tr>
<td>Poly(ether-block-amide)</td>
<td>Trichloroethane</td>
<td>4,300</td>
</tr>
<tr>
<td></td>
<td>Methylene chloride</td>
<td>6,000</td>
</tr>
<tr>
<td>Nitrile-butadiene rubber</td>
<td>Chloroform</td>
<td>18,000</td>
</tr>
<tr>
<td>Styrene-butadiene rubber</td>
<td>Chloroform</td>
<td>17,000</td>
</tr>
</tbody>
</table>

The presence of highly concentrated organics may lead to surface concentration polarization. Concentration polarization is an important phenomenon during SRNF and PV operation due to the high selectivity of the membranes and this boundary layer effect is shown in Scheme 2-1. Based on the difference of permeation of the different components across the membrane during the process, the retention of slow diffusion components will drive them towards the membrane surface generating a cake layer. On the other hand, fast diffusion components, although initially favoured in diffusion, will need to cross the newly formed cake layer formed across the membrane surface and their permeation will be slowed down. For rubbery membranes
able to separate organics from water, and for which high flux and selectivity are obtained, organics in the feed will be exhausted quickly and a water-rich concentration-polarized layer containing less hydrophobic compounds will be formed beside the membrane surface [12]. In this case, the concentration polarization will decrease the selectivity and the permeation of hydrophobic organics, and therefore the overall process performance.

Scheme 2-1 Scheme for boundary layer effect which is concentration polarization [37].

Hence, challenges for solvent separation membranes are not only relate to the material selection to maintain high selectivity and high flux but also to the effect of
concentration polarization in order to maximize the separation properties of the available membranes.

**Organic-organic separation**

Organic-organic separation is another field of application of solvent separation membranes and relevant to the pharmaceutical, oil and petrochemical industries, historically relying on thermal separation systems [12]. Industrial mixed solvents such as benzene/hexane, toluene/heptane, ethylbenzene/xylene, have similar physicochemical properties, making them difficult to separate based on the solubility theory. Several methods have been therefore developed to tackle this issue.

Copolymer membranes made of poly(amide) (PI) are candidates for the separation of organic mixtures such as aromatics/saturated hydrocarbon mixtures [55], by presenting a macro-organized structure made of soft and hard segments. Soft segments offer higher selectivity to the organics while hard segments provide mechanical integrity for the membrane. Polymer blending is another method previously used for benzene/cyclohexane separation [9, 56]. The polymer blending with crosslinking results in the optimization of the polymer chain architectures whereby chain entanglement and intermolecular interactions are tuned to achieve a good balance between permeation and selectivity. Also, nano-particles have been incorporated to favour high flow pathways across the membranes at the interface with the polymer matrix [12].

Another unique class of materials used for the synthesis of solvent separation membranes is based on zeolitic frameworks. Zeolitic membranes are stable inorganic materials, with high crystallinity and sharp molecular-sized pore structures [57].
Ferrierite zeolite membranes represent a selectivity of 100 for benzene against p-xylene, and a benzene flux of 12 g.m\textsuperscript{-2}.h\textsuperscript{-1} at 303 K [58]. Although the performance is comparable to other materials such as poly(vinyl acetate) (PVAc)/poly(vinyl alcohol) (PVA) these membranes offer longer chemical stability [12]. However, these membranes are extremely brittle making them sensitive to shocks and rendering module design more complicated.

2.1.2.5 Concluding remarks

The materials selection and free volume distributions are critical factors to develop the next generation of SRNF and PV membranes. Routes such as the addition of nano-particles into membranes have shown improvement in membrane performance by providing faster pathways across the membrane for diffusion. However, issues related to membrane formation and structure control need to be tackled through specific site coordination and crosslinking with the polymer matrix. In addition, the micro-structure of the membrane material shall be tuned to the specific contaminants or solvent to be separated given the preeminent role of molecule size and solubility on the separation.

2.1.3 Nano-composite membrane materials

Nano-composite materials have usually been defined as the composite with fillers at least less than 100 nm to reinforce the properties of the pristine material due to the high surface area of nano-fillers in the interaction of the matrix [59]. Hence, membranes made from nano-composite materials usually provide promising performance compared with traditional membranes due to the better control of the
interfacial bonding and structure. This enhancement is due to the nanoscale fillers inside the polymeric matrix which adjust the structure of the composite materials through interaction bonding between fillers and matrix [30].

Typically, in composite materials, interactions include van der Waals force, electrostatic attractions, chemical covalent bonding, molecular entanglement and mechanical interlocking [59]. Therefore, the interaction causes the linking structure between fillers and matrix and generate a network with either higher interspacing or denser spacing called free volume compare with pristine to meet suitable applications. The control of interfaces also benefits the surface charge due to the influence of chemical structure modification on membrane surface which uses for design high selective membrane [59]. The change in free volume, surface charge, and other properties by fillers addition may lead to more selective membranes compared to the plain polymeric membrane. Thus, the enhancement of the pristine polymeric materials can be achieved with different nanomaterials including nanotubes, nano-particles, and nanosheets [30, 60].

As per the examples of thin film nano-composite membranes presented in Table 2-2, acid-modified multi-walled carbon nanotubes (MWNTs) were introduced to a polysulfone support layer for improving salt rejection performance. A 5.0 wt.% of MWNTs addition across poly(sulfone) support led an increased salt rejection up to 88 % NaCl and 94 % Na2SO4 compared to nearly no rejection from an equivalent bare poly(sulfone) support without MWNTs [61]. However, to improve the selectivity of the membrane, the water permeance dropped from 69.2 to 2.22 L.m⁻².h⁻¹.bar⁻¹ due to the cross-linked structure which reduced the free volume for the rejected component [61]. Selective dense thin films were prepared with 10 wt.% nanosilver (nAg) in the 1,3-phenylenediamine (MPD) which led to a rise of 15.4 % of permeance compared.
to MWNTs only films due to an increase in free volume [61]. Therefore, nanomaterials addition provides increased pathways for selected component to diffuse across the membranes without necessarily losing selectivity from the polymeric matrix upon controlling the interactions between filler and matrix.

The design of nano-composite membranes requires mixing of nanomaterial with appropriate polymeric precursors, solvents and adjuvants to prevent their agglomeration which may be both costly and represent a waste of high-value chemicals. Nanomaterials may indeed require pre-functionalization to avoid aggregation during the dispersion in the polymer matrix. Compared to non-modified MWCNTs, the oxidized MWCNTs provided a salt rejection 400 % higher than the bare poly(ether sulfone) (PES) membranes while the permeance was also 51.8 % higher than that of the pristine materials [62]. Due to the selectivity increase from the cross-linked structure, the pathway for selecting components also becomes complex and may lead to a sharp decrease in permeance. Metal-organic framework (MOF) nano-particles, including ZIF-8 and MIL-101(Cr), were added into poly(amide) (PA) for rejection of styrene oligomers, and provided an increase of permeance for methanol (MeOH) and tetrahydrofluran (THF) with 160 % and 488 % compared to pristine polymers respectively [63]. However, the rejection of styrene oligomers decreased by 2 % for MOF nano-composite as 96.3 % in methanol and 94.1 % in THF compared to pristine resulted from loosen of the interfacial structure which led more path for styrene oligomers pass the membrane [63]. Additionally, amine functionalized POSS nano-particles were incorporated across PA to enhance the permeance by 16.5 % while salt rejection (NaCl) also increased from 95.83 to 98.65 % [64]. Hence, with the controllable interfacial structure between nano-particles and matrix, the nano-composite membrane would solve the trade-off effect of permeability and selectivity.
An organo-clay sodium dodecyl sulfate (SDS) was dispersed across a PA membrane to make a hybrid nano-composite which led to an increase in selectivity of alcohol against water, but a decrease in permeance due to higher level of crosslinking [65]. The reported selectivity from PA-SDS membrane was found to be 117 % higher than that of pure PA membrane with a 23.1 % drop in flux under the same condition [65]. Nano-composite membranes made from MWCNTs wrapped with chitosan offered a 456 % higher selectivity for benzene removal, as well as 225 % higher flux than the neat membranes for benzene/cyclohexane (50 wt.%) mixtures during PV testing [66].

The 20 wt.% mesoporous molecular sieve (MCM-41) filled NaAlg nano-composite showed a dehydration selectivity up to 30,000 for 10 % water in isopropanol which was 45 times higher than plain NaAlg membranes [67]. The water flux of the MCM-41 nano-composite membranes also increased with 64.2 % to 0.11 kg.m⁻².h⁻¹ compared to the plain NaAlg membrane [67]. The pore size of the MCM-41 nanoparticle (2 - 3 nm) increased the free volume which would prefer smaller water molecules (0.28 nm) than isopropanol (0.42 nm) molecules to pass through the membrane and enhance the flux and water selectivity [67]. Furthermore, the filler-matrix interaction from hydrogen bonding between water molecules and hydrophilic MCM-41 nano-particles with NaAlg membrane also increased both the flux and selectivity of water compared to the pristine NaAlg membrane [67]. Nano-composite membranes based on chitosan with Preyssler type heteropolyacid (H₁₄-P₅) nanoparticles also provided a small increase in flux, but again a large increase of separation factor [68]. Regarding the separation of 90 wt.% ethanol/water solution at 30°C, the nano-composite membranes led to selectivity as high as 2,725 of water from ethanol compared to 8 from pure CS membrane while only affecting positively permeation by 22 % [68].
Nanomaterials may therefore offer great opportunities to increase control over the membrane microstructure, chemical functionalities of the interfaces generated through specific modification processes and intrinsic properties, supporting solubility/diffusion separation processes.
Table 2-2 Some nano-composite membranes for separation applications and their performance

<table>
<thead>
<tr>
<th>Materials</th>
<th>Target applications</th>
<th>Separation conditions</th>
<th>Separation performance</th>
<th>Permeance (L.m⁻².h⁻¹.bar⁻¹)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf</td>
<td>Salt rejection</td>
<td>Room temperature (23 ± 1.0 °C), 2000 ppm, 4.48 bar</td>
<td>Not recorded</td>
<td>69.2</td>
<td>[61]</td>
</tr>
<tr>
<td>Acid modified MWNTs on PSf support</td>
<td>Salt rejection</td>
<td>Room temperature (23 ± 1.0 °C), 2000 ppm, 20.7 bar</td>
<td>88.4 % NaCl, 94.7 % Na₂SO₄ rejections</td>
<td>2.22</td>
<td>[61]</td>
</tr>
<tr>
<td>Nanosilver in 1,3-phenylenediamine (MPD)</td>
<td>Salt rejection</td>
<td>Room temperature (23 ± 1.0 °C), 2000 ppm, 20.7 bar</td>
<td>88.1 % NaCl, 95.6 % Na₂SO₄ rejections</td>
<td>2.42</td>
<td>[61]</td>
</tr>
<tr>
<td>PES NF</td>
<td>25 ± 1 °C, 200 ppm Na₂SO₄, 4 bar</td>
<td>20 % Na₂SO₄ rejection</td>
<td>5.4</td>
<td>[62]</td>
<td></td>
</tr>
<tr>
<td>Oxidized MWCNTs with PES</td>
<td>NF</td>
<td>25 ± 1 °C, 200 ppm Na₂SO₄, 4 bar</td>
<td>80 % Na₂SO₄ rejection</td>
<td>8.2</td>
<td>[62]</td>
</tr>
<tr>
<td>Material</td>
<td>NF of methanol and tetrahydrofluran (THF), rejection of PS for THF, 30 bar</td>
<td>98 % rejection in methanol, 94.7 % (Meth)/styrene oligomers rejection in THF (PS) and 1.7 THF/PS</td>
<td>1.5 methanol</td>
<td>[63]</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------------------</td>
<td>-----------------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td><strong>DuraMem DM150-TFC</strong></td>
<td>30°C, 232 g.mol⁻¹ MWCO for methanol, 295 g.mol⁻¹ MWCO for THF, 30 bar</td>
<td>96.3 % rejection in methanol, 94.1 % (Meth)/styrene oligomers rejection in THF (PS) and THF/PS</td>
<td>3.9 and 10 for methanol (Meth)/styrene oligomers</td>
<td>[63]</td>
<td></td>
</tr>
<tr>
<td>MOF in PA thin film</td>
<td>30°C, 232 g.mol⁻¹ MWCO for methanol, 295 g.mol⁻¹ MWCO for THF, 30 bar</td>
<td>98.65 % NaCl rejection 2.75</td>
<td>2.36</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>Salt rejection, Room temperature 25°C, 2000 ppm, 20.7 bar rejection</td>
<td>95.83 % NaCl rejection 2.36</td>
<td>95.83</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>PA-Amine functionalized</td>
<td>Salt rejection, Room temperature 25°C, 2000 ppm, 20.7 bar rejection</td>
<td>98.65 % NaCl rejection 2.75</td>
<td>98.65</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>POSS</td>
<td></td>
<td>2.75</td>
<td>2.75</td>
<td>[64]</td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>Separation of alcohol and water, PV 25°C, 90 wt.% ethanol/water solution, 0.133 mbar permeate</td>
<td>12 EtOH/H₂O 3,477</td>
<td>12 EtOH/H₂O 3,477</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td>Organo-clay sodium dodecyl sulfate with PA</td>
<td>Separation of alcohol and water, PV 25°C, 90 wt.% ethanol/water solution, 0.133 mbar permeate</td>
<td>26 EtOH/H₂O 2,633</td>
<td>26 EtOH/H₂O 2,633</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>PV for 49.85°C, benzene/cyclohexane (50/50, w/w), 0.01 bar benzene/cyclohexane</td>
<td>9.6 2 kg.m⁻².h⁻¹.bar⁻¹</td>
<td>9.6 2 kg.m⁻².h⁻¹.bar⁻¹</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>PV Process</td>
<td>Conditions</td>
<td>Properties</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>---------------------------</td>
<td>-----------------------------------------</td>
<td>--------------------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>Chitosan-wrapped MWNT with PVA</td>
<td>PV for benzene/cyclohexane</td>
<td>49.85°C, benzene/cyclohexane (50/50, w/w), 0.01 bar</td>
<td>benzene/cyclohexane</td>
<td>6.6 kg.m².h⁻¹.bar⁻¹</td>
<td>[66]</td>
</tr>
<tr>
<td>Plain NaAlg</td>
<td>PV for dehydrating isopropanol</td>
<td>30°C, feed 10 wt.% water, 0.0133 bar</td>
<td>/isopropanol separation factor</td>
<td>6.24</td>
<td>[67]</td>
</tr>
<tr>
<td>Mesoporous molecular sieve (MCM-41) filled NaAlg nano-composite</td>
<td>PV for dehydrating isopropanol</td>
<td>30°C, feed 10 wt.% water, 0.0133 bar</td>
<td>/isopropanol separation factor</td>
<td>10.25</td>
<td>[67]</td>
</tr>
<tr>
<td>CS</td>
<td>Water ethanol separation</td>
<td>30°C, 10 wt.% feed water mixture, 0.005 bar permeate</td>
<td>8 H₂O/EtOH</td>
<td>21.97</td>
<td>[68]</td>
</tr>
<tr>
<td>Preyssler type heteropolyacid with chitosan nano-composite</td>
<td>Water ethanol separation</td>
<td>30°C, 10 wt.% feed water mixture, 0.005 bar permeate</td>
<td>2,725 H₂O/EtOH</td>
<td>26.85</td>
<td>[68]</td>
</tr>
</tbody>
</table>
2.2 POSS hybrid membranes for separation applications

Recently, promising approaches through the design of mixed matrix, hybrid, and nano-composite membranes have been studied for the generation of high flux and high selectivity membrane materials. It was shown that while inorganic membranes show superior separation characteristics over polymeric membranes, they are however more fragile, complex and costly. Therefore, the interest to combine organic and inorganic materials is growing up to form hybrid membranes to benefit from organic and inorganic materials while maintaining selectivity and improving both permeation and physical-chemical strength of the material.

The main challenges for the incorporation of nano-particles in a polymeric matrix are related to agglomerate formation leading to the inhomogeneous distribution of nano-particles and thus to poor interfaces and defects across the membranes. The other challenge in the nano-composite membrane is related to the intrinsic solubility of the nano-particle. The membrane materials and nano-fillers must also be non-soluble and stable in the target solvents and feed stream. Therefore, functionalization treatments of the nano-particles must be carried out to support their incorporation and crosslinking to generate stable chemical structures. Novel synthesis methods for directly structure have therefore been developed to control the homogeneous distribution of nano-fillers [26].

Such nano-fillers include zeolite, silica, and metal oxide provide superior properties on mechanical strength, stable structure, high selectivity, and improved flux amount when they incorporated in the composite [60]. One of such nano-particles called polyhedral oligomeric silsesquioxane (POSS) offers a unique inorganic-organic hybrid cage structure as building blocks for composite such as electronic and catalytic
applications since the 1940s [69]. With its flexible functionality, the incorporation of POSS across membrane materials has been investigated.

The flexibility of the POSS nano-particle depends on the functional groups present across the corners of the POSS molecules. These may be tailored with amine, alcohol, carboxylic or other groups through arrange of functionalization routes. The small size of the POSS nano-particles (~ 1-3 nm) makes them the smallest occurring semi-crystalline silica nano-particles. POSS is a highly suitable for bridging inorganic and organic material together within a nano-composite due to their versatile chemistries and structures [28]. Therefore, the incorporation of POSS nano-particles into membrane has been found to enhance properties of the nano-composite membranes with great potential for gas separation and PV [70, 71].

The structure and properties of the POSS nano-composite have reviewed in following sections to investigate their advantages and limitations for different membrane applications.

2.2.1 POSS structure and properties

The development of silsesquioxane has led to breakthroughs in the electronics, energy and bio-implants applications due to their bridging properties between organic and inorganic materials [22]. Silsesquioxane materials mainly include two categories based on their structure, which is either non-caged or caged. POSS nano-particles, which are caged silsesquioxane, are generated from the condensation reaction from RSiX₃ monomers and water [72]. Thus, POSS particles have an inorganic core cage structure with Si-O-Si bonding which is connected to corner functional groups, such as organic groups -R. Hence, the general chemical formula of POSS materials is
(RSiO_{1.5})_n$, where organic group R can be hydrocarbons (non-functional) or an organic functional group (such as, but not limited to, alcohol, amine or acrylate) [28]. POSS nano-particles offer a stable 3-dimensional architecture with highly symmetric molecules for building up composite materials.

Hence several forms of silsesquioxane including a random, ladder, cage or incomplete condensed structures in the form of partial cage structures are shown in Figure 2-4. The cage-like POSS contains one silicon atoms linked with three oxygen atoms at the corner which was referring as “T”. Hence, with 8 corner cage like POSS, it can be represented as T8 [27] is the structure R_8Si_8O_{12} where n refer as the number of silicon atoms and been represented as T8 [22, 23].
Due to the bridging properties of the POSS derivatives, the incorporation in the composite provides enhance of strength, modulus, glass transition temperature, dielectric conductivity from structural crosslinking.

In a dental composite from 2,2’-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA)/tri-(ethylene glycol) dimethacrylate (TEG DMA), the effect of methacrylate-POSS (MA-POSS) could increase 20 % flexural strength and 35 % modulus with less than 10 wt.% [73]. The glass transition was reduced by 10 °C upon adding 2 mol.% of POSS in poly(vinyl pyrrolidone) (PVP) compared to pure PVP,
while the glass transition increased by 18°C when the POSS content was increased above 3.0 mol.% (Figure 2-5) [74]. Furthermore, in microelectronic applications, the low dielectric constant can be obtained from POSS in the PI nano-composite which from 3.4 to 3.09 upon only adding 25 mol.% of POSS in the bare material [75].

![Figure 2-5 Differential scanning calorimetry thermograms of PVP-POSS [74].](image)

However, due to the small size and high density of functional groups on the POSS nano-materials, POSS agglomeration and integration with the matrix represent challenges. Functional POSS nano-particles are better than non-functional POSS (octamethyl for instance) at bridging and bonding with polymeric matrixes through either covalent or electrostatic interactions [23]. Such functionalization is typically achieved either during the POSS synthesis or through post-synthesis chemical reactions. The hydrolysis and condensation methods for producing POSS with wet chemical functionalization of are therefore discussed in the next section.
2.2.2 Synthesis and functionalization of cubic POSS

There are several routes for introducing the required functional group R on the cage of silsesquioxane for selected applications. The most direct pathway, as well as the most traditional route, is the hydrolysis and condensation of RSiX₃ in the presence of a catalyst which was developed over 60 years ago. The general reaction formula is presented in the following for the synthesis of cubic (i.e. T₈) structures [23].

\[ nRSiX_3 + 1.5nH_2O \rightarrow (RSiO_{1.5})_n + 3nHX \]

Chemically stable groups R including methyl, phenyl, or vinyl, while the group X is a highly reactive functional group including Cl, OH or OR may be used to replace with oxygen atoms and form cage structure. However, the process not only can form cage-like structure, but may also produce linear, cyclic, or polycyclic siloxanes from this reaction [24]. It was reported that the occurrence of the low yield of targeted T₈ POSS from condensation reaction due to a result of the bi-products of T₁₀ and T₁₂ oligomers [23]. The most common synthesis of T₈H₈ POSS using hydrolysis of HSiCl₃ and a partially hydrated FeCl₃ catalyst in a biphasic system. Yields reached of only 17.5 % for T₈ POSS from hydrolysis reactions were obtained due to the production of T₁₀ POSS derivatives [76]. Furthermore, amine containing POSS [(CH₂)₃NH₂]₈ are produced using acid-catalyzed hydrolysis of H₂N(CH₂)₃Si(OEt)₃ to the yield of 35 % only even after six weeks of reaction time [77-79]. Therefore, the traditional simple process still maintains bi-products while the time for process may take several months depending on the required functionality making their synthesis extremely costly [23].

A general list of the common POSS nano-particles with simple functionalities synthesized using condensation methods is presented in Table 2-3. Relative low yields from 7 to 37 % for most of the CₓHᵧ groups except the C₆H₅ used benzene and
PhCH₂(CH₃)₃NOH were reported. The reaction usually under the acidic environment with different solvents to activate the POSS production. Therefore, the not only the low yielding of the POSS from the reaction but also the waste production from acid and solvent could lead a high cost of the POSS fabrication. Hence, new routes were suggested towards the functionalization of raw POSS nano-particles must be investigated.

Table 2-3 Typical syntheses of relative simple polyhedral oligomeric silsesquioxane (POSS), (RSiO₁.₅)ₙ, by condensations of RSiX₃ precursors [24]

<table>
<thead>
<tr>
<th>R</th>
<th>N</th>
<th>X</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>8</td>
<td>OCH₃</td>
<td>Cyclohexane</td>
<td>HCl + CH₃COOH</td>
<td>13</td>
</tr>
<tr>
<td>H</td>
<td>10, 12, 14, 16</td>
<td>Cl</td>
<td>Benzene</td>
<td>H₂SO₄ + SO₃</td>
<td>15-35</td>
</tr>
<tr>
<td>CH₃</td>
<td>6</td>
<td>OC₂H₅</td>
<td>Benzene</td>
<td>HCl</td>
<td>–</td>
</tr>
<tr>
<td>CH₃</td>
<td>8</td>
<td>Cl</td>
<td>Methanol</td>
<td>HCl</td>
<td>37</td>
</tr>
<tr>
<td>CH₃</td>
<td>10, 12</td>
<td>OC₂H₅</td>
<td>Benzene</td>
<td>KOH</td>
<td>–</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>6</td>
<td>OC₂H₅</td>
<td>Benzene</td>
<td>HCl</td>
<td>–</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>8</td>
<td>Cl</td>
<td>Methanol</td>
<td>HCl</td>
<td>37</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>10</td>
<td>Cl</td>
<td>Butanol</td>
<td>HCl</td>
<td>16</td>
</tr>
<tr>
<td>C₆H₁₁</td>
<td>6</td>
<td>Cl</td>
<td>Acetone</td>
<td>HCl</td>
<td>7</td>
</tr>
<tr>
<td>C₆H₁₁</td>
<td>8</td>
<td>OCH₃</td>
<td>Nitrobenzene</td>
<td>OH</td>
<td>–</td>
</tr>
<tr>
<td>CH=CH₂</td>
<td>8</td>
<td>OCH₃</td>
<td>Methanol</td>
<td>HCl</td>
<td>20</td>
</tr>
<tr>
<td>CH=CH₂</td>
<td>10</td>
<td>OCH₃</td>
<td>Butanol</td>
<td>HCl</td>
<td>–</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>8</td>
<td>OCH₃</td>
<td>Benzene</td>
<td>PhCH₂(CH₃)₃NOH</td>
<td>88</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>10</td>
<td>OC₂H₅</td>
<td>Tetrahydrofuran</td>
<td>Me₄NOH</td>
<td>–</td>
</tr>
<tr>
<td>C₆H₅</td>
<td>12, 22, 24</td>
<td>OC₂H₅</td>
<td>Tetrahydrofuran</td>
<td>Me₄NOH</td>
<td>–</td>
</tr>
</tbody>
</table>
Several processes other than direct synthesis for creating targeted POSS functionality are presented in Scheme 2-2 including addition reaction for a partially condensed silsesquioxane, substitution at silicon atoms or functionalization of substituents [24].

Scheme 2-2 Four synthesis methods of the cubic T₈ POSS molecules include direct hydrolysis and condensation reaction, addition reaction from incomplete caged silsesquioxane, and substitution reaction on either silicon atom or substituents [23]

The degree of functionality of the corner groups can be altered from the functionalization including methacrylate, acrylate, styrene, norbornene, amine, epoxides, alcohol, or phenol moieties to incorporate with the polymeric matrix [28]. The synthesis of high purity functionalized POSS nano-particles in large amounts is
still a challenge primarily due to the synthesis steps complexity and the duration required for the synthesis reaction [22, 23, 25].

Therefore, due to the cost of raw material and complexity of the processes, the market price of functionalized POSS with primary amine on phenyl groups may be as high as a few thousands of US dollars per kg while the cost of pristine POSS is on the order of US$ 500 per kg [25, 27].

Direct substitution reactions were achieved using several chemical methods such as nucleophilic substitution [80-82], Heck reactions [83-85], Suzuki reactions [86-89] and Sonogashira reactions [83, 90]. Besides, the non-directed substitution methods of an aromatic ring such as T₈Ph₈ POSS were also reported with less cost [72]. The bromination of octa-phenyl POSS was reported by several methods with the mono-brominated POSS products being predominantly 3-, and 4- substituted phenyl rings [91]. Sulphonation substitution reactions have also been reported involving octaphenyl POSS in the chlorosulfonic acid in order to obtain the sulfonic acid POSS [92, 93]. Besides the direct substitution, the indirect method which contains more than two steps to have desired POSS has also been discussed. The mono-nitration of phenyl rings in octa-phenyl POSS (ONPS) followed by a reduction of the nitro groups to amine groups was achieved (OAPS) (see Scheme 2-3). The process using fuming nitric acid to forming nitro groups on the phenyl ring, and formic acid and triethylamine with catalyst Pd/C to reduce the nitro group into amine group [94].
Scheme 2-3 Synthesis of octanitro-phenyl POSS (ONPS) and octaamino-phenyl (OAPS) [94]

The procedures described in Scheme 2-3 presents a yield around 82 % while the functionalization method have been investigated by other researchers [94]. The amine functionalization for octa-phenyl POSS in Scheme 2-4 replaces the Pd/C catalysts with hydrazine hydrate as the reducing agent which offers a more cost-effective solution and increased yield by up to 86 % [95]. Amine groups are used as anchoring points for developing a library of functional POSS material as shown in Scheme 2-5 [94-96]. A 3-dimensional built imide nano-composite has been formed from the result octaphthalimide (OPIPS) and the corresponding maleimide (OMIPS) has been generated using self-polymerization or Michael addition reactions with dithiols or diamines [97, 98]. The high reactivity of primary amine groups again offers excellent precursors for binding with corresponded polymeric matrix this enhancing the nano-composite properties, including free volume desired in dense membrane application.
Due to the reaction of OAPS with diepoxides or dianhydrides, nano-composites contained a highly cross-linked structure with thermal stability, improved tensile and compressive strength used for diverse applications [99] presented in Scheme 2-5. As well as in the photoelectronic application, fluorene derivative (OFPS) has been used in light emitting diodes with the reaction of bromofluorene with Pd-catalysing [100, 101]. Furthermore, the Schiff Base Derivative (OSPS) has been also used to generate a green light emitting diode-system under UV illumination [102-104].
Furthermore, an alternative method proposes by the author of this thesis, using plasma for functionalization, is established for successfully introduced amines on the octamethyl POSS powder with potentially 7.1 % efficiency (N/Si) opening the route to the development of an environmentally friendly method for functionalizing octamethyl POSS nano-particles [105].

The incorporation of POSS in nano-composites may be achieved with three main methods as shown in Figure 2-6 including (i) physical blending of POSS with non-reactive groups in polymeric matrix, (ii) mono-functional POSS grafting across polymer backbones to form pendant structure, and (iii) multi-functional POSS crosslinking with the surrounding polymeric matrix to generate a 3D network [23].
Non-covalent bonding across mixed matrix composite with nano-scaled POSS has been used to support the enhancement of mechanical and thermal properties [23]. Poly(methyl methacrylate) with octakis(3-hydroxypropyl(dimethyl)siloxy)octasilsesquioxane (OHPS) and OAPS polymers have been presented simultaneously increase the glass transition temperature while the nano-cages were well dispersed in the matrix as shown in Figure 2-7 [106]. Viscoelastic properties of polymers have been depended on the relaxation of molecular chains by connection of the POSS and matrix which up to eight chemical linkages in the $T_s$ POSS [23, 107-109]. The microstructure of a polymer, such as poly(ethylene terephthalate) [110] has been altered after the
introduction of amine-POSS-aminopropyl isoctyl (AM-POSS-2) particles, resulting in an increased glass transition temperature ($T_g$) approximately 30°C due to the motions restrictions within the nano-composite matrix [23, 111, 112]. In addition, the viscosity of HDPE-POSS nano-composite decreased compared with raw material by 100 Pa.s when minute amounts (0.5 wt.%) of POSS were added across the matrix. When the POSS content increased beyond 1 wt.%, the viscosity raised by more than 100 Pa.s above that of the raw material even in a higher temperature environment (e.g. 10 wt.% POSS at 180°C and $\omega = 10.0$ rad.s$^{-1}$) [23, 113].

Figure 2-7 DSC curves for PMMA polymers and OAPS or OHPS incorporated in PMMA nano-composite [106]

Covalently bonded polymer/POSS nano-composite systems have also been found to enhance strength, glass transition temperature of the corresponding nano-composites. Propyl methacrylate functionalized POSS has been widely used for nano-composite poly (methyl methacrylate) polymers due to a tough, highly transparent
system corresponding to the crosslinking from the POSS particles [114, 115]. High resolution and sensitivity lithography resist devices have been produced using a combination of methacrylate-functionalized POSS with other acrylate-based polymers [23, 116-118]. Amine-functionalized POSS materials were found to improve the glass transition temperature and mechanical properties of thermoset resins [78]. The amino-propyl isobutyl POSS and octaamino-phenyl POSS derivatives can crosslinking with dianhydrides resins systems (PMDA or ODPA) to form POSS-based hyperbranched PI with increased stability of temperature up to 500°C which is 25 % higher compared with classic Kapton PI [96, 119, 120]. The glass transition temperature has also been shown to be modified based on the loading of POSS, while for 3-glycidyloxypropyl-POSS (G-POSS) in the bisphenol-A epoxy resin/3-methyl-tetrahydrophthalic anhydride (BPAER/MeTHPA) presents the 5°C increase with 10 wt.% POSS and 14.2°C decrease with 40 wt.% POSS [108, 121].

Last, POSS have been used as cross-linkers to enhance the chemical stability but have been found to decrease the packing density of polymer matrixes due to their bulky form, which resulted in an increase of free volume across the polymeric matrix [18].

The incorporation of POSS materials, therefore, affects fundamental properties relevant to diffusion, as assigned by the solution-diffusion theory, and particularly to free volume distribution generation, which plays a major role in SRNF and PV membranes performance. Therefore, the beneficial properties from the incorporation of POSS across polymeric nano-composite materials as hybrid membranes were investigated and will be discussed in the following section.
2.3 POSS nano-composite membranes

POSS nano-composite has been evaluated for several membrane separation processes including gas separation, liquid separation, desalination, fuel cell application and solvent separation [122]. POSS nano-particles can act as cross-linkers, may improve permeability and provide anti-fouling properties of membrane materials. The following section will discuss the POSS-containing membrane for particle filtration, desalination, mixed solvent separation, gas separation, and proton exchange in a fuel cell.

2.3.1 Pressure-driven liquid filtration

Commercial filtration materials, including microfiltration (MF), ultrafiltration (UF) and NF membranes, are made from polymeric materials with different pore size or free volume to selectively reject different components from a feed. MF and UF on the one hand are used for the separation of large organics components, including proteins, enzymes, and colloids, or for particulate matter, due to the large pore size of the membrane materials (20 nm to several microns) [123]. NF on the other hand presents sub-nanoscale pores which are used for separation of salts or small molecular weight molecules including solvents. Commercial NF membrane from PA usually provides a salt rejection of MgSO\textsubscript{4} as high as 98 to > 99 % with the permeance of 10 to 20 L.m\textsuperscript{-2}.h\textsuperscript{-1}.bar\textsuperscript{-1} [123]. Fouling of the membranes, and the balance between flux and selectivity are recurrent issues for the membrane fabrication and operation and limit long-term degradation and replacement of the materials. A number of POSS mixed matrix membranes strategies have been developed for improving permeability and selectivity as well as antifouling in the ultrafiltration and NF applications.
The incorporation of POSS nano-particles across polymeric matrixes with covalent bonding or indirect bonding, may support the control of nano-scale pores and alter the performance of the membrane. As an example, Q-POSS (quaternary-ammonium-functionalized POSS) may work as cross-linkers in the Q-POSS-PDMS system. Q-POSS led to the lower extent of quaternization which provided more freedom for alkyl groups to extend and penetrate the shell of microbial organisms thereby neutralizing the micro-organisms up to contact and resulting in the bio-antifouling property for UF application [16]. In Table 2-4, cellulose acetate (CA) anchored nano-particle additives (CA-POSS) have been added to CA membranes and exhibited flux 278 % higher than the pristine CA [124]. However, the rejection of the NaCl was reduced from 39 % to 20 % which is related to pore-enlargement from the impact of the particles onto the phase separation process used for the membranes synthesis [124]. PA membranes were incorporated with POSS nano-particles to improve the permeability and/or the selectivity of the materials compared to pristine PA membrane [125]. PEG functionalized POSS nano-particles provided more interspacing to support the selective diffusion of components across the membranes. This incorporation increased permeance by 91.6 % and only reduced Na$_2$SO$_4$ rejection by 3 % [126]. The incorporation of different functional groups across POSS nano-particles also led to performance variations, highlighting the impact of surface energy and surface charge generated from these groups. PA membranes with non-reactive phenyl groups present a 19.6 % higher permeance than NH$_3$Cl or PEG-POSS compared to pristine PA membrane due to increased free volume. Mg$_2$Cl and NaCl rejection were found to be 7.85 % and 24.04 % respectively, which was lower than that of the pristine PA membrane due to less degree of crosslinking which lose the selectivity of the membrane [127]. NF has been used for heavy metal ions removal,
and POSS nano-composite PA membranes also provided higher permeance and rejection due to controllable cross-linked structure [127]. The removal of selenium and arsenic ions was improved compared to octaammonium POSS nano-composite PA membranes, as shown in Table 2-4. The pure water permeance increased by 35 % and 50 % while the rejection of SeO\textsubscript{4}\textsuperscript{2-} increased by 7.8 % and that of HAsO\textsubscript{4}\textsuperscript{2-} decreased by 1.6 % compared to commercial NF and modified hollow fiber membranes respectively [127].

Furthermore, bovine serum albumin (BSA) removal and improvement in antifouling properties have been also observed for POSS nano-composite membrane. The addition of 1.0 wt.% ethylene glycol functionalized POSS (EG-POSS) across a poly(vinylidene fluoride) (PVDF) matrix, led to anti-fouling properties and to a halved BSA adsorption capacity, from 5.76 mg.g\textsuperscript{-1} to the 2.61 mg.g\textsuperscript{-1} [128]. The pure water flux for the PVDF-POSS composite membrane was also found to be a 15 kg.m\textsuperscript{-2}.h\textsuperscript{-1} higher compared to pure PVDF with only 0.5 wt.% of POSS incorporation across the UF membranes [128]. Such an improvement has also been reported for coatings with a hydrophilic monomer, poly (ethylene glycol methacrylate) (PEGM), across PSf membrane supports using methacryl-POSS as cross-linkers [129]. The produced nano-porous POSS-PEGM films exhibited 82.3 % higher water permeance compared with bare PSf membrane as a NF membrane [129]. The rejection for BSA was increased to 97.5 % compared with ~ 0 % from bare PSf membrane been observed [129]. Due to the high rejection ratio of BSA, the fouling of the membrane will be largely reduced as only small amounts of BSA were able to diffuse across the membranes [130].

Amphiphilic organic/inorganic hybrid star-shaped polymers (SPP) coated PSf membrane has showed improved bio- and oil-fouling resistance. The water flux decline ratios (DR) was reduced from 77 % to 30 % while the oil flux-decline ratios
were also reduced from around 51% to 21% [131]. The enrichment of hydrophilic and hydrophobic segments across the membrane surface decreased the interactions of the membrane surface and proteins and oils, resulting in enhanced fouling resistance and flux-recovery ability [131]. In the case of oil-water separation, epoxy POSS nano-composite materials (ePOSS) were prepared by epoxidation of octavinyl POSS and then introduced across graphene oxide (GO) films to benefit from their super-hydrophobicity [132]. The water contact angle in air of the ePOSS across the GO was 145° which is 600% higher than hydrophilic neat GO film. A mixture of 50 vol.% CH₂Cl₂/H₂O was filtered using suction filtration which resulted in a less than 2 ppm concentration of water remaining in the collected CH₂Cl₂ phase. Hence, depending on the functional groups present across the POSS nano-particles, the covalent bonding between GO and ePOSS would largely affect the surface charge of the membrane to effective repulse water but facilitate oil diffusion across the membrane material [132].
Table 2-4 Result performance of the POSS nano-composite membrane for ultrafiltration and NF

<table>
<thead>
<tr>
<th>Materials</th>
<th>Separation conditions</th>
<th>Permeance (L.m⁻²h⁻¹.bar⁻¹)</th>
<th>Separation performance</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA</td>
<td>2000 ppm NaCl , 10 bar, 25°C</td>
<td>0.18</td>
<td>39% NaCl rejection</td>
<td>[124]</td>
</tr>
<tr>
<td>CA-POSS (1 wt.%)</td>
<td>2000 ppm NaCl ,10 bar, 25°C</td>
<td>0.68</td>
<td>20% NaCl rejection</td>
<td>[124]</td>
</tr>
<tr>
<td>PA-NF</td>
<td>Industrial scale</td>
<td>10 – 20</td>
<td>&gt; 99 – 98 % MgSO₄ rejection</td>
<td>[123]</td>
</tr>
<tr>
<td>PA-NF</td>
<td>1000 ppm Na₂SO₄, 2 bar; 25°C</td>
<td>10.1</td>
<td>90 % Na₂SO₄ rejection</td>
<td>[126]</td>
</tr>
<tr>
<td>PA with PEG-POSS</td>
<td>1000 ppm Na₂SO₄, 2 bar; 25°C</td>
<td>19.35</td>
<td>87.1 - 91.6 % Na₂SO₄</td>
<td>[126]</td>
</tr>
<tr>
<td>PA-POSS-8phenyl (0.5 wt.%)</td>
<td>1000 ppm Mg₂Cl or NaCl, 10 bar, room temperature</td>
<td>6.1 ± 0.4</td>
<td>84.5 ± 1.2 % Mg₂Cl, 23.7 ± 1.5 % NaCl rejection</td>
<td>[127]</td>
</tr>
<tr>
<td>PA-POSS-8NH₃Cl (0.5 wt.%)</td>
<td>1000 ppm Mg₂Cl or NaCl, 10 bar, room temperature</td>
<td>5.5 ± 0.2</td>
<td>91.7 ± 0.8 % Mg₂Cl, 29.8 ± 1.1 % NaCl rejection</td>
<td>[127]</td>
</tr>
<tr>
<td>Material</td>
<td>Condition</td>
<td>Rejection</td>
<td>BSA Retention</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------------------</td>
<td>-----------</td>
<td>---------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PA-POSS-8PEG</td>
<td>1000 ppm Mg\textsubscript{2}Cl or NaCl, 10 bar, room temperature</td>
<td>5.1 ± 0.1</td>
<td>88.9 ± 0.7 % Mg\textsubscript{2}Cl, 31.2 ± 0.7 % NaCl</td>
<td>[127]</td>
</tr>
<tr>
<td>0.5 wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF 90</td>
<td>20 ppm, 10 bar, room temperature</td>
<td>4</td>
<td>89.5 ± 1.9 % SeO\textsubscript{4}\textsuperscript{2-}, 94.1 ± 1.9 % As(V)</td>
<td>[133]</td>
</tr>
<tr>
<td>PAMAM-grafted</td>
<td>1000 ppm, 10 bar, room temperature</td>
<td>3.5</td>
<td>&gt; 99 % HAsO\textsubscript{4}\textsuperscript{2-}</td>
<td>[134]</td>
</tr>
<tr>
<td>hollow fiber</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA-OAS POSS (1 wt.%)</td>
<td>1000 ppm, 10 bar, room temperature</td>
<td>5.4 ± 0.3</td>
<td>93.9 ± 0.6 % SeO\textsubscript{4}\textsuperscript{2-}, 96.5 ± 1.1 % SeO\textsubscript{4}\textsuperscript{2-}, 97.4 ± 1.9 % HAsO\textsubscript{4}\textsuperscript{2-}</td>
<td>[127]</td>
</tr>
<tr>
<td>PVDF-UF</td>
<td>Industrial scale</td>
<td></td>
<td></td>
<td>[135]</td>
</tr>
<tr>
<td>PVDF bare</td>
<td>BSA retention: 500 ppm; BSA adsorption: 2000 ppm; Water flux: 1 bar, room temperature</td>
<td>76</td>
<td>92.5 % retention, 2.61 mg.g\textsuperscript{-1} BSA sorption</td>
<td>[128]</td>
</tr>
<tr>
<td>EG-POSS in PVDF</td>
<td>BSA retention: 500 ppm; BSA adsorption: 2000 ppm; Water flux: 1 bar, room temperature</td>
<td>90</td>
<td>67.5 % BSA retention, 5.76 mg.g\textsuperscript{-1} BSA sorption</td>
<td>[128]</td>
</tr>
<tr>
<td>Coating</td>
<td>BSA Concentration</td>
<td>Buffer Conditions</td>
<td>BSA Rejection</td>
<td>Reference</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-------------------</td>
<td>----------------------------------------------------------</td>
<td>---------------</td>
<td>-----------</td>
</tr>
<tr>
<td>PSF uncoated</td>
<td>1000 ppm</td>
<td>0.1 M phosphate buffer (pH 7.4), 25°C, 2.07 bar</td>
<td>19.32</td>
<td>0%</td>
</tr>
<tr>
<td>POSS-PEGM A50D</td>
<td>1000 ppm</td>
<td>0.1 M phosphate buffer (pH 7.4), 25°C, 2.07 bar</td>
<td>36.23</td>
<td>97.5%</td>
</tr>
<tr>
<td>PEGM with methacryl POSS</td>
<td>1000 ppm</td>
<td>0.1 M phosphate buffer (pH 7.4), 25°C, 2.07 bar</td>
<td>28.5</td>
<td>97%</td>
</tr>
<tr>
<td>SPP on PSF membrane</td>
<td>0.9 g L⁻¹</td>
<td>for oil, room temperature, 1 bar</td>
<td>Water flux decline ratio reduce to 30% from 77%; Flux recovery ratio increased from 38% to 86% after 180 min; Oil flux decline ratio reduced to 21% from 51%</td>
<td>[131]</td>
</tr>
<tr>
<td>Epoxy POSS in graphene film</td>
<td>CH₂Cl₂/H₂O (1:1, v/v) and petroleum/H₂O (1:1, v/v)</td>
<td>CH₂Cl₂ in water less than 2 ppm collected side; cannot separate petroleum/water</td>
<td></td>
<td>[132]</td>
</tr>
</tbody>
</table>
2.3.2 Desalination

Desalination is an important application to generate pure water from the salted stream and has been achieved with membrane technologies including reverse osmosis (RO), forward osmosis (FO), and pressure retarded osmosis (PRO). Currently developed commercial RO membranes for industrial-scale desalination are made from PA and can reach >99.8 % of NaCl rejection. Their permeance is however low on the order of 10-20 L.m⁻².h⁻¹.bar⁻¹ due to the effective free volume size on the order of 0.4 – 0.6 nm, leading to semi-permeable materials [123].

Nano-composite membranes based on POSS have been reported to provide a higher water flux with uniform incorporation in the PA membranes promoting diffusion of water and tuning the charge on the surface of the membrane [18, 136]. The performance of octatrimethyl ammonium (TMA) POSS/PA nano-composite membranes prepared via aqueous solution casting showed an increased flux from 33.71 to 44.57 L.m⁻².h⁻¹ compared to pure PA film [125]. The salt rejection of the POSS-PA membrane was maintained at 99.62 % compared to the 99.0 % from pristine membranes [136]. Amine functionalized POSS (A-POSS) with 0.05 % (w/v) were incorporated across PA films, leading to a 34.3 % increase in water flux at 20.7 bar and at room temperature while the rejection of NaCl was increased by 2.82 % [64]. An increase of the POSS loading above 0.05 % (w/v) reduced the salt rejection by 3 % due to surface charge modified but a continued increase of water flux by 15.5 % when POSS loading reached 0.1 % (w/v) compared to 0.05 % (w/v) [64]. Octaphenyl POSS (P-8Phenyl), octaaminonium POSS (P-8NH₃Cl), octaaminophenyl POSS (P-8NH₂) and aminopropylisobutyl POSS (P-1NH₂) were added across PA thin-film nano-composite (TFN) membranes for RO application [18]. The extra addition of the triethylamine (TEA) with POSS nano-particles across TFN film increased the water
flux from 20 to 33 L.m$^{-2}$.h$^{-1}$ while the salt rejection was maintained around 98 % except for the P-1NH TFN due to more hydrophobic surface, at 15.5 bar and 23°C, as shown in Table 2-5 [18].

Since POSS nano-particles are hydrophobic materials, higher surface POSS loading should lead to enhanced hydrophobicity and decreased water flux [18]. Adjusting the number of corner groups therefore offers routes to control the location of the crosslinking across the polymeric chains and thickness of the material. 8-site NH$_2$-POSS would therefore likely act as a stronger bulk cross-linker than 1-site NH$_2$-POSS [18]. The 7 pendant phenyl groups with 1 NH$_2$ group would let POSS located across the surface of films and increase the material hydrophobicity due to hydrophobic phenyl groups and likely reduced pure water flux [18].

In forward osmosis (FO) and pressure retarded osmosis (PRO) applications, octa (3-hydroxy-3-methylbutyldimethylsiloxy) POSS have been used to generate dual-layer hollow fiber membranes to achieve a high salt rejection capability for desalination [17]. Dual-layer hollow fiber membranes based on poly(benzimidazole) (PBI)/POSS poly(acrylonitrile) and (PAN)/PVP materials were synthesized [17, 137, 138]. The salt rejection of MgCl$_2$ and NaCl from POSS nano-composite dual-layer hollow fibers increased from 87.2 % to 92.3 % and from 40 % to 81.6 % respectively compared to normal dual layer fiber as shown in Table 2-5 [17, 139]. The rejection difference of MgCl$_2$ from the POSS nano-composite dual layer PBI membranes was only 0.2 % compared to cross-linked PBI. However, due to the free volume created by interactions between POSS and matrix, water flux has found with more than 30 % higher than cross-linked membrane [137, 140]. However, due to the higher crosslinking the permeance of PBI-POSS membrane reduced from 1.74 L.m$^{-2}$.h$^{-1}$.bar$^{-1}$ to 0.58 L.m$^{-2}$.h$^{-1}$.bar$^{-1}$ compared to the bare PBI [137, 139]. The POSS-hollow fiber
(dimension outside diameter/inside diameter: 1.00/0.65 mm) also offered enhanced mechanical strength, modulus, and elongation by 193, 12.7, and 400 % respectively compared to the bare PBI-PAN membrane (dimension outside diameter/inside diameter: 0.95/0.58 mm) [137]. The improvement is largely depending on the loading of POSS content across the nano-composites due to a higher degree of crosslinking than the plain PBI-PAN membrane [137]. Hence, the flux from the FO and PRO measurements for the 0.5 wt.% POSS membranes offered a 57 % higher performance compared to the bare PBI dual layer membranes as presented as shown in Table 2-5 [137, 138]. Larger amounts of the POSS enhanced the formation of defects at the polymer/nano-particle interface which resulted in an increase of water and salt permeability. Near total loss of selectivity was found for loadings of POSS above 0.5 wt.% [17]. Therefore, in order to effectively improve membrane performance, the loading of POSS is also an important parameter to tune the degree of crosslinking other than functionality to reach enhanced permeation and selectivity. A fine balance between free volume formation, nano-particles agglomeration and distribution control must be achieved to tune the chemical structure of the polymeric matrix.
Table 2-5 RO performance, water flux and salt rejection of the POSS nano-composite membrane

<table>
<thead>
<tr>
<th>Materials</th>
<th>Separation conditions</th>
<th>Flux (L.m⁻².h⁻¹)</th>
<th>Rejection (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PA-RO</td>
<td>Industrial scale</td>
<td>10 – 20</td>
<td>99 to &gt; 99.8 % NaCl</td>
<td>[123]</td>
</tr>
<tr>
<td>PA</td>
<td>32000 ppm NaCl at pH 6.5, 55 bar, 25 °C</td>
<td>33.71</td>
<td>99 % NaCl</td>
<td>[125]</td>
</tr>
<tr>
<td>PA-TMA-POSS</td>
<td>32000 ppm NaCl at pH 6.5, 55 bar, 25 °C</td>
<td>44.57</td>
<td>99.62 % NaCl</td>
<td>[125]</td>
</tr>
<tr>
<td>PA</td>
<td>2000 ppm NaCl feed, 20.7 bar, room temperature</td>
<td>48.9</td>
<td>95.83 % NaCl</td>
<td>[64]</td>
</tr>
<tr>
<td>PA/A-POSS (0.05 %, w/v)</td>
<td>2000 ppm NaCl feed, 20.7 bar, room temperature</td>
<td>56.9</td>
<td>98.65 % NaCl</td>
<td>[64]</td>
</tr>
<tr>
<td>PA/A-POSS (0.1 % w/v)</td>
<td>2000 ppm NaCl feed, 20.7 bar, room temperature</td>
<td>65.7</td>
<td>95.76 % NaCl</td>
<td>[64]</td>
</tr>
<tr>
<td>Pristine PA</td>
<td>2000 ppm NaCl feed; 15.5 bar; 23 °C,</td>
<td>20.0 ± 0.5</td>
<td>98.0 ± 0.2 % NaCl</td>
<td>[18]</td>
</tr>
<tr>
<td>PA/P-8Phenyl</td>
<td>2000 ppm NaCl feed; 15.5 bar; 23 °C,</td>
<td>33.0 ± 3.0</td>
<td>98.2 ± 0.3 % NaCl</td>
<td>[18]</td>
</tr>
<tr>
<td>PA/P-8NH₃Cl</td>
<td>2000 ppm NaCl feed; 15.5 bar; 23 °C,</td>
<td>27.1 ± 1.1</td>
<td>98.9 ± 0.2 % NaCl</td>
<td>[18]</td>
</tr>
<tr>
<td>PA/P-8NH₂</td>
<td>2000 ppm NaCl feed; 15.5 bar; 23 °C,</td>
<td>33.4 ± 1.1</td>
<td>98.6 ± 0.3 % NaCl</td>
<td>[18]</td>
</tr>
<tr>
<td>PA/P-1NH₂</td>
<td>2000 ppm NaCl feed; 15.5 bar; 23 °C,</td>
<td>3.2 ± 0.7</td>
<td>95.9 ± 0.6 % NaCl</td>
<td>[18]</td>
</tr>
<tr>
<td><strong>PBI dual-layer</strong></td>
<td>200 ppm NaCl and MgCl₂ solutions, 1.0 bar, 25 °C</td>
<td>1.74 Pure water permeance (PWP, L.m⁻².h⁻¹.bar⁻¹); 20.0 Flux (L.m⁻².h⁻¹)</td>
<td>87.2 % MgCl₂; 40.0 % NaCl</td>
<td>[137, 139]</td>
</tr>
<tr>
<td><strong>PBI cross-linked</strong></td>
<td>200 ppm NaCl and MgCl₂ solutions, 1.0 bar, 25 °C</td>
<td>1.25 Pure water permeance (PWP, L.m⁻².h⁻¹.bar⁻¹); 5.0 Flux (L.m⁻².h⁻¹)</td>
<td>92.5 % MgCl₂; 61.0 % NaCl</td>
<td>[137, 140]</td>
</tr>
<tr>
<td><strong>PBI dual-layer (PBI-PAN-P0.5, POSS contained)</strong></td>
<td>200 ppm NaCl and MgCl₂ solutions, 1.0 bar, 25 °C</td>
<td>0.58 Pure water permeance (PWP, L.m⁻².h⁻¹.bar⁻¹); 31.37 Flux (L.m⁻².h⁻¹)</td>
<td>92.3 % MgCl₂; 81.6 % NaCl</td>
<td>[137]</td>
</tr>
</tbody>
</table>
2.3.3 Solvent separation

Solvent separation membranes based on NF and PV have been prepared from POSS nano-composite materials. POSS nano-particles usually acted as fillers and crosslinking agents to build up a three-dimensional (3D) structures at the nanoscale to enhance the native material in the performance of membrane separation. The cage-like POSS structure with 8 sites functionalities suggests a range of interactions across the polymeric matrix and provides more crosslinking control compared with the base polymeric material [26].

Nano-composites from PDMS matrix with trimethylsilanol hydrophobized silica (TMS-H-silica) for alcohol recovery, nano-composite provided an increase of 115 % separation factor compared to pure PDMS at 30°C (Table 2-6) [141]. The decrease in flux from 0.306 to 0.117 kg.m⁻².h⁻¹ indicateing a higher degree of crosslinking and thus a reduced free volume distribution across the membrane [141]. Polyether-block-amide (PEBAX)/POSS hybrid membranes have been used for ethanol recovery at different octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS (AL0136) loadings [21]. An improvement in membrane performance was achieved with 2 wt.% of POSS (AL0136) loading which led to a 113 % higher flux than neat PEBAX membrane at room temperature, up to 0.184 kg.m⁻².h⁻¹ [21]. The separation factor of the POSS/PEBAX nano-composite membranes for ethanol against water increased by 91.7 % to 4.6 for the 5 wt.% ethanol/water mixture separation compared to the pristine [21]. Hence, both increased permeability and selectivity from 2.0 wt.% POSS nano-composite resulted from raised free volume between POSS nano-particles and matrix and preferential sorption maintained for ethanol respectively. However, a decrease of both flux and separation factor is found beyond 2.0 wt.% POSS loading due to the larger size of the pathway created by POSS across the membrane which larger
molecules also started easy to pass [21]. Therefore, to modify the performance of the solvent separation ability of the membranes, only minute amounts of POSS should be used to affect the degree of crosslinking.

For the dehydration of ethanol solution, octaaminophenyl POSS-containing Chitosan (CS) with 5 wt.% loadings were reported with selectivities (H₂O/EtOH) up to 373 compared to 65 from neat CS membranes at 29.85 °C with a 10 wt.% water feed solution [71]. The pure solvent flux dropped however by nearly 50 % from 0.05 to 0.03 kg.m⁻².h⁻¹ [71]. The performance for ethanol dehydration was also found to be affected by the loading of POSS which reduced the selectivity but increased the flux as shown for PEBAX/POSS membrane [21, 71].

In Table 2-6, copoly(1, 5-naphthalene/3, 5-benzoic acid-2,2'-bis (3, 4-dicarboxyphenyl) hexafluoropropanedimide (6FDA-NDA/DABA)/POSS/Ultem® dual-layer hollow fibers were also studied for ethanol dehydration by PV [142]. In Figure 2-8, the flux across the POSS nano-composite membranes increased until 2.0 wt.% POSS loading to reach a maximum of 1.9 kg.m⁻².h⁻¹ prior to decrease with increasing separation factor [142]. The separation factor of the POSS nano-composite membranes was 166 (H₂O/EtOH) for the 2.0 wt.% POSS nano-composites, which was 51 % higher than membranes without POSS [142]. Therefore, an interesting multilayer structure was achieved by controlling the deposition conditions and the diffusive incorporation of POSS nano-particles across the structures [142]. A further increase in separation factor to 237 (H₂O/EtOH) was observed from Polyimide/Ultem® with sulfonation and POSS modification with only 0.1 kg.m⁻².h⁻¹ increase under the same condition [143]. The PI/SPI/Ultem®/POSS membranes showed an increase of hydrophilicity thanks to the sulfonic groups which led to better selectivity [143]. Pegylated (PEG) POSS across the alginate matrix provided a high selectivity as 1077
(H₂O/EtOH) towards dehydration of ethanol solution which was increased by 65 % compared to plain alginate membrane at 76.85°C from a 10 wt.% water feed [144]. At high loading of POSS (30 wt.%) across the membrane the flux of the solution increased by 38.1 % up to 2.5 kg.m⁻².h⁻¹ compared to the plain alginate membranes [144].

Figure 2-8 Membrane performance involving flux and separation factor for ethanol dehydration from an 85 wt.% aqueous ethanol solution at different temperatures with the effect of POSS loading [142]

PDMS/POSS (octamethyl POSS) membranes were investigated for separating thiophene/n-heptane, toluene/n-heptane and benzene/n-heptane mixtures for desulfurization as shown in Table 2-6[20]. The 2.0 wt.% POSS-containing membranes led to an increase in enrichment factor of thiophene of 75 % compared to the neat PDMS membranes at 70°C and with 0.52 wt.% thiophene, 0.58 wt.% benzene, 0.61 wt.% toluene feed solutions [20]. 10 wt.% glycidyl-POSS dispersed across the 6FDA-4MPD/6FDA-DABA (49:1) hybrid membranes (PI) were used for removing sulphur
aromatics from benzothiophene and n-dodecane mixtures [26]. When the temperature reached 100°C, the selectivity of POSS nano-composite increased by 22 % as 2.41 compared to bare membranes which presented a high temperature environment suited application [26]. The flux presented a 51 % drop when compared to the pristine membranes [26]. Therefore, the highly cross-linked structure may offer enhanced separation for selected components but may reduce diffusion pathways, thus reducing flux across the membranes [26].

The incorporation of the POSS nano-particles improved the thermal stability of the membrane structures which open routes for operations at relatively high environment temperatures compared to bare polymeric membranes. POSS nanoparticles have been used as organic solvent NF membranes to improve the rejection of dyes during solvent filtration, as shown in Table 2-6 [145]. The pristine PI membranes only rejected 10 % of Rose Bengal (RB) dye from ethanol solvent and offered flux up to 233.2 kg.m⁻².h⁻¹ [145]. After incorporation of octaammonium (OMA) POSS, the PI nano-composite membranes rejection increased to 99 % while the flux dropped by 98 % compared to the bare PI membranes [145].

POSS materials have generally been used as crosslinking agents to strengthen bare polymeric structures and provide more free volume for increased permeation. However, the free volume density largely depends on the POSS loading a level of interactions or crosslinking density. Such crosslinking structures may enhance the composite properties allowing the membranes to operate in a larger range of conditions compared with pristine membranes. Therefore, the incorporation of the POSS nanoparticles across membrane materials requires loading and functionality control to achieve the desired cross-linked structure towards the performance for the target separation.
Table 2-6 Performance of POSS nano-composite membranes for solvent separation mainly PV and NF

<table>
<thead>
<tr>
<th>Type</th>
<th>Materials</th>
<th>Purpose</th>
<th>Conditions</th>
<th>Selectivity</th>
<th>Flux (kg.m$^{-2}$.h$^{-1}$)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV</td>
<td>PDMS</td>
<td>Recovery of alcohol</td>
<td>30°C, 4 wt.% ethanol feed, 1 mbar downstream</td>
<td>13 for EtOH/H$_2$O</td>
<td>0.306</td>
<td>[141]</td>
</tr>
<tr>
<td>PV</td>
<td>PDMS with TMS-H silica</td>
<td>Recovery of alcohol</td>
<td>30°C, 4 wt.% ethanol feed, 1 mbar downstream</td>
<td>28 for EtOH/H$_2$O</td>
<td>0.117</td>
<td>[141]</td>
</tr>
<tr>
<td>PV</td>
<td>PEBAX 2533</td>
<td>Ethanol recovery</td>
<td>25°C, 5 wt.% ethanol feed, pressure close to 0 at downstream</td>
<td>2.4 EtOH/H$_2$O</td>
<td>0.08</td>
<td>[21]</td>
</tr>
<tr>
<td>PV</td>
<td>AL0136 Poss with PEBAX 2533</td>
<td>Ethanol recovery</td>
<td>25°C, 5 wt.% ethanol feed, pressure close to 0 at downstream</td>
<td>4.6 EtOH/H$_2$O</td>
<td>0.184</td>
<td>[21]</td>
</tr>
<tr>
<td>PV</td>
<td>Neat CS</td>
<td>Ethanol dehydration</td>
<td>29.85°C, 10 wt.% water feed, 10 mbar</td>
<td>65.2 H$_2$O/EtOH</td>
<td>0.05</td>
<td>[71]</td>
</tr>
<tr>
<td>PV</td>
<td>Material</td>
<td>Temperature, Water Feed</td>
<td>Ethanol Dehydration</td>
<td>Permeate Side Pressure</td>
<td>H2O/EtOH Ratio</td>
<td>Reference</td>
</tr>
<tr>
<td>----</td>
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<td>------------------------</td>
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</tr>
<tr>
<td>Octaaminophenyl POSS</td>
<td>29.85°C, 10 wt.% water feed, 10 mbar</td>
<td>373 H2O/EtOH</td>
<td>0.03</td>
<td>[51]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanoldehydration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>across CS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6FDA-NDA/DAB A/Ultim® (PI)</td>
<td>60°C, 15 wt.% water feed, 1 mbar permeate side</td>
<td>110 H2O/EtOH</td>
<td>1.2</td>
<td>[142]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanoldehydration</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6FDA-NDA/DAB A/POSS/Ultim® (PI-POSS)</td>
<td>60°C, 15 wt.% water feed, 1 mbar permeate side</td>
<td>166 H2O/EtOH</td>
<td>1.9</td>
<td>[142]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PI/SPI/Ulte POSS modification</td>
<td>60°C, 15 wt.% water feed, 1 mbar permeate side</td>
<td>237 H2O/EtOH</td>
<td>2</td>
<td>[143]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pristine SA</td>
<td>76.85°C, 10 wt.% water feed, 3 mbar</td>
<td>653 H2O/EtOH</td>
<td>1.81</td>
<td>[144]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>Sodium alginate dehydration with PEG-POSS</td>
<td>76.85 °C, 10 wt.% water feed, 3 mbar</td>
<td>1077 H₂O/EtOH</td>
<td>2.5</td>
<td>[144]</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>PDMS Desulfurization</td>
<td>70 °C, 0.52 wt.% thiophene, 0.58 wt.% benzene, 0.61 wt.% toluene feeds, 10 mbar, cross flow 90 L.h⁻¹</td>
<td>(Sulphur enrichment factor) 3.2 thiophene/n-heptane; 2 benzene/n-heptane; 2 toluene/n-heptane</td>
<td>5.6 thiophene/n-heptane</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>Octamethyl POSS Desulfurization</td>
<td>70 °C, 0.52 wt.% thiophene, 0.58 wt.% benzene, 0.61 wt.% toluene feeds, 10 mbar, cross flow 90 L.h⁻¹</td>
<td>(Sulphur enrichment factor) 4.0 thiophene/n-heptane; 2 benzene/n-heptane; 2 toluene/n-heptane</td>
<td>6.1 thiophene/n-heptane</td>
<td>[20]</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>Native 6FDA-4MPD/6FDA-DABA (49:1) Removal of sulphur aromatics</td>
<td>100 °C, benzothiophene/n-dodecane (3/97 wt.%) at, 19 – 30 mbar permeate side</td>
<td>1.98 benzothiophene/n-dodecane</td>
<td>2.42</td>
<td>[26]</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>6FDA-4MPD/6FD A-DABA Glycidyl-POSS (10 wt.%)</td>
<td>Removal of sulphur aromatics 100°C benzothiophene/n-dodecane (3/97 wt.%) at 19 – 30 mbar permeate side</td>
<td>2.41 benzothiophene/n-dodecane</td>
<td>1.48 [26]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>---------------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>PI</td>
<td>NF for rejecting solutes from ethanol Room temperature, 35 μmol.L(^{-1}) solute feed concentration, 5 bar 10 % rejection Rose Bengal (RB)</td>
<td>233.2 [145]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>Catechol/O AM-POSS/PI</td>
<td>NF for rejecting solutes from ethanol Room temperature, 35 μmol.L(^{-1}) solute feed concentration, 5 bar 99 % rejection Rose Bengal (RB)</td>
<td>4.88 [145]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.3.4 Gas separation

Membrane technologies have also been studied for gas separation applications due to their low capital and operating costs, processability and attractive properties. As for previous applications, POSS nano-particles are amongst the most promising materials in gas separation membrane for its small crystal size and tuneable functionality for better dispersion across the polymeric matrix [146].

POSS nano-composite membranes were developed to adjust the permeability and selectivity for gases as shown in Table 2-7. Poly(styrene) (PS) was used to generate nano-composite membranes with styrylisobutyl POSS for separation of oxygen and nitrogen [70]. Compared to pure PS, the nano-composite membranes provided 72.4 % higher permeability without losing selectivity at 35°C and 2.03 bar [70]. To improve the performance of the gas transport properties, PI with aminoethylaminopropylisobutyl POSS showed an O₂ permeability increase of 34 % to 15.61 Barrer and a CO₂ permeability increase of 18.9 % to 53.86 Barrer compared to pure PI at a feed pressure of 3.55 bar [147]. Additionally, PI-POSS membrane suggested no loss of selectivities of O₂/N₂ and CO₂/CH₄ compared to pristine PI membrane in the same conditions [147]. Matrimid polymeric membranes provided better performance for gas separation than the previous example but exhibited lower permeability such as 8.4 Barrer for CO₂ compared to 53.86 Barrer from PI-POSS membrane at a feed pressure of 10.1 bar and at the same temperature [148]. Matrimid hybrid with POSS® octa amic acid with Zn²⁺ have been developed to achieve higher degree of crosslinking and control of surface charge and exhibited a maximum selectivities of 9 for O₂/N₂ and 62.8 for CO₂/CH₄ while losing 52.2 % O₂ and 63.3 % N₂ permeability compared to the bare membranes [148]. In order to enhance the permeability of gases for industrial scale applications, glycidyl-POSS nano-particles
were used to crosslink with poly(ether amine) (PEA) polymer [149]. The PEA-POSS (50:50 w/w) membrane led to a permeability of 380 Barrer at 35°C and 1 bar. The separation ratios have of 39.1 for CO2/N2 and 7.0 for CO2/H2 were obtained which was attributed to the enhanced interaction of PEA and the gas thanks to the nanohybrid micro-structure [149].

POSS nano-particles have been used across hollow fiber membranes to enhance the CO2 separation, with amine functionalized POSS nano-particles by impregnation on Torlon supports [150]. The modification of the hollow fibers increased the CO2 separation selectivity performance up to 16.7 compared to 1 for the bare support (no selectivity) [150]. Poly (ethylene glycol) (PEG) functionalized POSS nano-particles were added to the poly(ether block amide) PEBAX® to alter the free volume of the membrane. The CO2 permeability was shown to reach 152 Barrer after 30 wt.% of POSS addition compared to 73 Barrer for the neat membrane, while the CO2 selectivities against N2, O2, CH4, and H2 gases were maintained at the level of the pristine membranes in a 30°C environment [151, 152]. POSS nano-particles such as POSS-OH and octa amic acid POSS have been incorporated across PEBAX® matrix, and the loading optimised to control intrinsic cavity distributions. Highest permeability of CO2 as 136 Barrer at 8.11 bar and 35°C with a selectivity of CO2/H2 52.3 have been achieved by POSS across the PEBAX® membrane [153]. The study found that polymeric chains packing was disrupted at low loading of POSS nano-particles, which led to the rigidification of the materials at high POSS loading [148, 154]. PA-POSS nano-composite membranes were reported for gas transport at 30°C and 1 bar to optimize the interactions of the PA matrix with heptacyclopentyl tricycloheptasiloxanetriol functional POSS nano-particles [155]. Results from POSS across PA membranes showed a maximum drop of 43.5 % in permeability for all tested
gases but selectivity increased by 19.2 % and 28.1 % in the O$_2$/N$_2$ and CO$_2$/N$_2$ respectively compared to bare PA membranes [155]. Furthermore, polymers with intrinsic microporosity (PIM) have been incorporated with phenethyl POSS (PhE-POSS) to prevent the physical aging and improve gas transport properties [156]. The POSS nano-composite PIM membranes reached a high 4,917 Barrer permeability which was 340 % higher than the pristine PIM-1 without loss of selectivity [156].

POSS nano-particles affect local free volume and generate regions across the membrane structures which favour solubility and diffusion thus increasing the overall separation efficiency [70, 147]. The loading of POSS nano-particles within the polymeric matrix must be controlled to effectively reinforce the membrane structure and to increase performance.
### Table 2-7 Performance of POSS nano-composite for gas separation

<table>
<thead>
<tr>
<th>Materials</th>
<th>Conditions</th>
<th>Permeability (Barrer)</th>
<th>Selectivity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>35°C and 2.03 bar</td>
<td>O₂, 2.9</td>
<td>5.6 O₂/N₂</td>
<td>[70]</td>
</tr>
<tr>
<td>PS with 10 wt% POSS</td>
<td>35°C and 2.03 bar</td>
<td>O₂, 5.0</td>
<td>5.2 O₂/N₂</td>
<td>[70]</td>
</tr>
<tr>
<td>PI</td>
<td>35°C and 3.55 bar</td>
<td>O₂, 11.65; N₂, 1.78; CH₄, 1.68; CO₂, 45.31</td>
<td>6.6 O₂/N₂; 27.0 CO₂/CH₄</td>
<td></td>
</tr>
<tr>
<td>PI with POSS</td>
<td>35°C and 3.55 bar</td>
<td>O₂, 15.61; N₂, 2.37; CH₄, 1.98; CO₂, 53.86</td>
<td>6.6 O₂/N₂; 27.2 CO₂/CH₄</td>
<td></td>
</tr>
<tr>
<td>Pure Matrimid</td>
<td>35°C and 10.1 bar</td>
<td>O₂, 2.07; N₂, 0.3; CH₄, 0.23; CO₂, 8.4</td>
<td>6.9 O₂/N₂; 36.4 CO₂/CH₄</td>
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</tr>
<tr>
<td>Matrimid with POSS - 20 wt.%</td>
<td>35°C and 10.1 bar</td>
<td>O₂, 1.33; N₂, 0.19; CH₄, 0.141; CO₂, 5.3</td>
<td>6.9 O₂/N₂; 37.2 CO₂/CH₄</td>
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<tr>
<td>Matrimid with POSS - 20 wt.% with 0.3 M ZnCl₂</td>
<td>35°C and 10.1 bar</td>
<td>O₂, 0.99; N₂, 0.11; CH₄, 3.4; CO₂, 9.0</td>
<td>6.9 O₂/N₂; 62.8 CO₂/CH₄</td>
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<td>Glycidyl-POSS with PEA</td>
<td>35°C and 1 bar</td>
<td>H₂, 54.2; N₂, 9.7; CO₂, 380</td>
<td>7.0 CO₂/H₂, 39.1 CO₂/N₂</td>
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</tr>
<tr>
<td>Torlon hollow fiber support</td>
<td>35°C and 3.45 bar</td>
<td>CO₂, 50,000; N₂, 54,000</td>
<td>0.9 CO₂/N₂</td>
<td>[150]</td>
</tr>
<tr>
<td>Material</td>
<td>Temperature</td>
<td>Pressure</td>
<td>CO₂</td>
<td>N₂</td>
</tr>
<tr>
<td>------------------------</td>
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</tr>
<tr>
<td>PEBAX ® MH 1657</td>
<td>30 °C and 1 bar</td>
<td>1 bar</td>
<td>CO₂, 73; H₂, 8.1; CH₄, 4.1; O₂, 3.6</td>
<td>N₂, 1.4</td>
</tr>
<tr>
<td>PEBAX ® 2533</td>
<td>30 °C, 1 bar</td>
<td>1 bar</td>
<td>CO₂, 225; H₂, 43; CH₄, 30.7; O₂, 23.3: N₂, 8.8</td>
<td>CO₂/CH₄; 5 CO₂/H₂</td>
</tr>
<tr>
<td>PEG-POSS across PEBAX ® MH1657</td>
<td>30 °C, 1 bar</td>
<td>1 bar</td>
<td>CO₂, 152; H₂, 14.1; CH₄, 10; O₂, 6.9</td>
<td>CO₂/CH₄; 10.9 CO₂/H₂</td>
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<tr>
<td>PEG-POSS across PEBAX ® 2533</td>
<td>30 °C, 1 bar</td>
<td>1 bar</td>
<td>CO₂, 300; H₂, 43; CH₄, 34.9; O₂, 25.1: N₂, 10.2</td>
<td>CO₂/CH₄; 6.9 CO₂/H₂</td>
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<tr>
<td>POSS-OH across PEBAX ® MH 1657</td>
<td>35 °C and 1.01 bar</td>
<td>CO₂ permeability: CO₂, 118</td>
<td>8.9 CO₂/H₂</td>
<td>153</td>
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<tr>
<td>Acid POSS across PEBAX ® MH 1657</td>
<td>35 °C and 1.01 bar</td>
<td>CO₂ permeability: CO₂, 126</td>
<td>8.7 CO₂/H₂</td>
<td>153</td>
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<tr>
<td>PA</td>
<td>30 °C and 1 bar</td>
<td>O₂, 5.05; N₂, 2.48; CO₂, 25.73</td>
<td>2.03 O₂/N₂, 10.37 CO₂/N₂</td>
<td>155</td>
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<tr>
<td>PA with POSS 20 wt.%</td>
<td>30 °C and 1 bar</td>
<td>O₂, 3.31; N₂, 1.40; CO₂, 18.6</td>
<td>2.42 O₂/N₂, 13.28 CO₂/N₂</td>
<td>155</td>
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<tr>
<td></td>
<td>Temperature</td>
<td>Gas Composition</td>
<td>Gas Viscosity</td>
<td>Reference</td>
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<td>----------------</td>
<td>-------------</td>
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<td>-----------</td>
</tr>
<tr>
<td><strong>PIM - 1</strong></td>
<td>35°C and 1 bar</td>
<td>N₂, 72.5; O₂, 275; CH₄, 88; CO₂, 13.1 CO₂/CH₄</td>
<td>1,117</td>
<td>[156]</td>
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<tr>
<td><strong>PIM - 1 with PhE-POSS 7.5 wt.%</strong></td>
<td>35°C and 1 bar</td>
<td>N₂, 231; O₂, 897; CH₄, 401; CO₂, 13.1 CO₂/CH₄</td>
<td>4,917</td>
<td>[156]</td>
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</table>
2.3.5 Proton exchange membrane

Proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) have also been developed by incorporating POSS nano-particles for energy storage applications. Proton exchange membrane (PEM) is usually made from perfluorosulfonated acid polymers which allow proton migration from the anode to the cathode to produce electrical energy [157]. The high cost and environmental footprint of fluoropolymers represent a hindrance to PEMs development and low cost, high-performance non-fluorinated materials were discussed to replace the perfluorosulfonic acid membrane [157].

Although low cost sulfonated aromatic polymers can achieve sufficient proton conductivity, the high degree of sulfonation always results in the swelling and physical expansion of the materials in the PEMs thus leading to mechanical failures. The incorporation of nano-particles became one of the solutions to lock the structures and prevent damage. POSS hybrid materials have been considered as one of the potential candidates due to the inorganic core to generate interfaces between the organic and inorganic phases which affects the hydrophilic routes for proton exchange [157]. The potential of POSS nano-composite membranes for improving the electric properties of materials used in the fuel cell and for addressing the methanol crossover phenomenon was evaluated [158, 159]. A nano-composite made from PVA and sulfonated POSS (sPOSS) showed improved conductivity of 121 % and reduced methanol permeability up to 86.3 % as 0.042 S.cm⁻¹ compared to pure Nafion™ at room temperature with a 95 % relative humidity (RH) level, as shown in Table 2-8 [158]. The low permeability resulted from the higher crosslinking which prevent the methanol crossover behaviour. Sulfonated POSS across in sulfonated poly(phenyl sulfone) (SPPSU) membranes with multilayer structure have been developed to yield 34 % higher conductivity to 0.071
S.cm\(^{-1}\) compared to pure SPPSU for at room temperature with 25 % RH [160]. The multilayered structure also reduced the brittleness of the membrane with a 1202 MPa storage modulus at 170°C compared to 3 MPa for the neat polymer, due to the thermal resistance from the POSS nano-particles [160, 161]. For sPOSS across sulfonated poly(arylene ether sulfone) (SPAES) nanofiber membranes, the conductivity reached 0.094 S.cm\(^{-1}\) representing an increase of 56.7 % compared to plain SPAES and 240 % compared to Nafion 212 at 30°C with 80 % RH [162]. The high concentration of protogenic groups across the SPAES-sPOSS and the nanofiber structure increased water uptake which led to a higher material conductivity [162]. Sulfonated poly(ether ether ketone) (SPEEK) polymer with a degree of sulfonation (DS) 60 % has been used in conjunction to trisilanol phenyl POSS (TSP-POSS) for DMFC application. TSP-POSS/SPEEK nano-composite membranes offered an increase in methanol selectivity against water by 582 % compared to pure SPEEK and 268 % compared to Nafion 117 [60]. However, TSP-POSS/SPEEK nano-composite membranes methanol permeabilities’ decreased by 48.1 % compared to pure SPEEK and 63.7 % compared to Nafion 117 due to a higher degree of crosslinking which led a more tortuous pathway for methanol passing [60]. The proton conductivity was estimated to be 200 % higher than that of the pristine membranes which was found to be suitable for DMFC application [60]. With a higher DS 65 %, SPEEK reached a 0.0609 S.cm\(^{-1}\) conductivity compared to 0.313 S.cm\(^{-1}\) from 55 % DS SPEEK at 100°C and 100 % RH [163]. The incorporation of TSP-POSS with extra ethylene glycol (EG) cross-linker led to a further 45.2 % increase of conductivity to 0.0884 S.cm\(^{-1}\) compared to pure SPEEK (DS 65 %) [163]. However, to have a good thermo-chemical stability, a lower DS of 55 % SPEEK was reported upon the incorporation of TSP-POSS while the nano-composite
membranes offered a 106% improved conductivity as 0.0646 S.cm\(^{-1}\) than bare SPEEK (DS 55%) [164].

In order to reduce the cost of the PEM materials, sulfonated poly(aryl ether ketone) (SPAEKs) polymers have been used to produce nano-composite membranes with multi-acid-functionalized POSS (POSS–SO\(_3\)H) [165]. Although the proton conductivity of the POSS nano-composite membrane was 79.1% lower than Nafion 117, the selectivity of methanol from water was 653% higher for the POSS nano-composite compared to pure Nafion 117 [165]. Nafion 112 POSS nano-particle composites were developed to enhance the electric properties of the membranes [166]. An increase of 13.4% in proton conductivity from the bare Nafion 112 was observed while the electric properties were enhanced by native groups across the POSS fillers [166]. A higher proton conductivity was also achieved through the crosslinking of 0.4 mol.% octaaminophenyl POSS (OAPS) with sulfonated PI (SPI). Conductivities achieved were as high as 0.111 S.cm\(^{-1}\) at 80°C compared to 0.095 S.cm\(^{-1}\) for the bare Nafion 117 [167]. Selectivity for methanol uptake compared to the bare Nafion 117 membranes was increased by 619% as 96.4 \(\times\) 10\(^3\) Ss.cm\(^{-3}\) with a 70% reduction in methanol permeability to 0.55 \(\times\) 10\(^{-6}\) cm\(^2\).s\(^{-1}\) [167]. However, the thermal stability of the membrane at a high temperature exhibited a sharper mass loss below 250°C compared to the pristine material due to water molecules release which were locked across the POSS nano-particles [167]. Furthermore, a linear SPI incorporated with octaphenylbisaniline POSS were processed to enhance the dispersion of the nano-particle within the matrix and increase the proton conductivity [168]. The achieved permeabilities and selectivities increased by 92.2% and 6.4% respectively when the POSS nano-particles were uniformly dispersed across the matrix compared to pure SPI [168]. The selectivity for methanol was also increased by 142% compared to previous
SPI-POSS nano-composite while the maximum proton conductivity reached 0.114 S.cm$^{-1}$ [168]. Poly(arylene ether sulfone)s (PAES) with sulfonated POSS nanoparticles led to higher conductivities on the order of 0.142 S.cm$^{-1}$ compared to 0.122 S.cm$^{-1}$ for Nafion 117 under the same condition [169]. The PAES-sPOSS membrane presented a 58 % decrease of methanol permeability compared to Nafion 117 but higher than SPI-POSS membrane with 164 %, as well as the selectivity as shown in Table 2-8 [169]. The higher hydrophilicity of the material was pointed as a challenge since methanol was found to preferentially diffuse.

POSS incorporated PEMs offer great potential for use as fuel cells but the impact of corner functional groups chemistry is critical to ensure very high selectivity.
Table 2-8 Performance of IEM from POSS nano-composite membrane

<table>
<thead>
<tr>
<th>Materials</th>
<th>Target application</th>
<th>Temperature (°C)</th>
<th>RH (%)</th>
<th>Membrane performance</th>
<th>Conductivity (S.cm⁻¹)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion™ (117)</td>
<td>DMFC</td>
<td>25</td>
<td>95</td>
<td>Permeability: $1.83 \times 10^{-6}$ cm².s⁻¹</td>
<td>0.019</td>
<td>[158]</td>
</tr>
<tr>
<td>PVA with sPOSS (50 wt.%)</td>
<td>DMFC</td>
<td>25</td>
<td>95</td>
<td>Permeability: $2.5 \times 10^{-7}$ cm².s⁻¹</td>
<td>0.042</td>
<td>[158]</td>
</tr>
<tr>
<td>SPPSU</td>
<td>PEMFC</td>
<td>25</td>
<td>25</td>
<td>Not recorded</td>
<td>0.053</td>
<td>[160]</td>
</tr>
<tr>
<td>SPPSU with sPOSS (20 wt.%)</td>
<td>PEMFC</td>
<td>25</td>
<td>25</td>
<td>Not recorded</td>
<td>0.071</td>
<td>[160]</td>
</tr>
<tr>
<td>SPAES</td>
<td>PEMFC</td>
<td>30</td>
<td>80</td>
<td>Not recorded</td>
<td>0.06</td>
<td>[162]</td>
</tr>
<tr>
<td>SPAES with sPOSS (40 wt.%)</td>
<td>PEMFC</td>
<td>30</td>
<td>80</td>
<td>Not recorded</td>
<td>0.094</td>
<td>[162]</td>
</tr>
<tr>
<td>SPEEK (DS 60 %)</td>
<td>DMFC</td>
<td>90</td>
<td>100</td>
<td>Permeability: $7.7 \times 10^{-7}$ cm².s⁻¹</td>
<td>0.0015</td>
<td>[60]</td>
</tr>
<tr>
<td>SPEEK with TSP-POSS (2 wt.%)</td>
<td>DMFC</td>
<td>90</td>
<td>100</td>
<td>Permeability: $4 \times 10^{-7}$ cm².s⁻¹</td>
<td>0.0045</td>
<td>[60]</td>
</tr>
<tr>
<td>SPEEK (DS 65 %)</td>
<td>PEMFC</td>
<td>100</td>
<td>100</td>
<td>Not recorded</td>
<td>0.0609</td>
<td>[163]</td>
</tr>
<tr>
<td>Material</td>
<td>Fuel Cell Type</td>
<td>Temperature</td>
<td>Humidity</td>
<td>Performance</td>
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<tr>
<td>SPEEK (DS 65%) with</td>
<td>PEMFC</td>
<td>100</td>
<td>100</td>
<td>Not recorded</td>
<td>0.0884 [163]</td>
<td></td>
</tr>
<tr>
<td>TSP POSS and EG cross-linker</td>
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<td></td>
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<tr>
<td>SPEEK (DS 55%)</td>
<td>PEMFC</td>
<td>100</td>
<td>100</td>
<td>Not recorded</td>
<td>0.0313 [164]</td>
<td></td>
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<tr>
<td>SPEEK (DS 55%) with</td>
<td>PEMFC</td>
<td>100</td>
<td>100</td>
<td>Not recorded</td>
<td>0.0646 [164]</td>
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<tr>
<td>TSP-POSS (2 wt.%)</td>
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<tr>
<td>Nafion 117</td>
<td>DMFC</td>
<td>80</td>
<td>100</td>
<td>Permeability: $2.76 \times 10^{-8}$ cm$^2$.s$^{-1}$, Selectivity: $0.543 \times 10^5$ Ss.cm$^{-3}$</td>
<td>0.148 [165]</td>
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<tr>
<td>SPAEK</td>
<td>DMFC</td>
<td>80</td>
<td>100</td>
<td>Permeability: $2.657 \times 10^{-8}$ cm$^2$.s$^{-1}$, Selectivity: $1.07 \times 10^5$ Ss.cm$^{-3}$</td>
<td>0.029 [165]</td>
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<tr>
<td>SPAEK with PAM and</td>
<td>DMFC</td>
<td>80</td>
<td>100</td>
<td>Permeability: $7.35 \times 10^{-8}$ cm$^2$.s$^{-1}$, Selectivity: $4.09 \times 10^5$ Ss.cm$^{-3}$</td>
<td>0.031 [165]</td>
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<tr>
<td>POSS</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion 112</td>
<td>PEMFC</td>
<td>80</td>
<td>100</td>
<td>Not recorded</td>
<td>0.0276 [166]</td>
<td></td>
</tr>
<tr>
<td>Nafion with sPOSS</td>
<td>PEMFC</td>
<td>80</td>
<td>100</td>
<td>Not recorded</td>
<td>0.0313 [166]</td>
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<tr>
<td>Membrane Type</td>
<td>Membrane Form</td>
<td>Temperature</td>
<td>Permeability</td>
<td>Selectivity</td>
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<tr>
<td>Nafion 117</td>
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<td>80</td>
<td>$1.86 \times 10^{-6}$ cm$^2$.s$^{-1}$</td>
<td>$13.4 \times 10^3$ S.s.cm$^{-3}$ (30°C)</td>
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<tr>
<td>SPI</td>
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<td>$0.65 \times 10^{-6}$ cm$^2$.s$^{-1}$</td>
<td>$76.9 \times 10^3$ S.s.cm$^{-3}$ (30°C)</td>
<td>[167]</td>
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<tr>
<td>OAPS with sulfonated PI</td>
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<td>$0.55 \times 10^{-6}$ cm$^2$.s$^{-1}$</td>
<td>$96.4 \times 10^3$ S.s.cm$^{-3}$ (30°C)</td>
<td>[167]</td>
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<tr>
<td>SPI</td>
<td>PEMFC</td>
<td>80</td>
<td>$1.54 \times 10^{-7}$ cm$^2$.s$^{-1}$</td>
<td>$21.9 \times 10^4$ S.s.cm$^{-3}$</td>
<td>[168]</td>
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<td>SPI-POSS-5</td>
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<td>$2.96 \times 10^{-7}$ cm$^2$.s$^{-1}$</td>
<td>$23.3 \times 10^4$ S.s.cm$^{-3}$</td>
<td>[168]</td>
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<td>$18.6 \times 10^{-7}$ cm$^2$.s$^{-1}$</td>
<td>$4.25 \times 10^4$ S.s.cm$^{-3}$</td>
<td>[169]</td>
<td></td>
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<tr>
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<td>Membrane Type</td>
<td>Permeability</td>
<td>Selectivity</td>
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<tr>
<td>PAES-sPOSS-14</td>
<td>DMFC</td>
<td>$7.81 \times 10^{-7}$ cm$^2$.s$^{-1}$</td>
<td>$14.05 \times 10^4$ Ss.cm$^{-3}$</td>
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</table>
2.3.6 Conclusions on POSS nano-composite membranes development

The efficient synthesis of POSS nano-composite membranes requires extensive work on uniform POSS dispersion and control over the level of crosslinking with the surrounding matrix to achieve homogenous membranes [26]. Hence, POSS nano-particles if used as fillers should possess specific functionalities for chemically or physically binding with the polymeric matrix.

Functionalization of unmodified POSS nano-particles should be processed prior to incorporation within polymers due to the high cost of commercial functionalized POSS. The chemical synthesis of POSS nano-particles with desired functional groups usually involves high toxicity chemicals leading to chemical wastes while being extremely time-consuming. The membrane synthesis steps may require extensive casting and evaporation durations at low POSS concentrations thus leading to potential re-agglomeration [26].

Plasma gas treatments and polymerization are routes to potentially solve these challenges. Plasma systems may allow achieving homogenous dispersions of nano-particle across polymeric structures in one step without using highly reactive chemicals. The interactions between the nano-particles and polymer can be controlled through different plasma polymerization systems to yield high levels of covalent bonding with limited waste from the membrane manufacturing. Thus, plasma gas activation and polymerization provides a promising option for membrane fabrication and will be presented in the next section.
2.4 Plasma technologies and strategies for POSS functionalization and thin film membrane fabrication

2.4.1 Introduction

Plasma was first named by Irving Langmuir and Lewi Tonks in 1929, to refer to an ionized gas [170]. It was defined as the fourth state of matter in the universe other than solid, liquid and gas. In general, plasma was fully or partially ionized gas with free ions, electrons, radicals, neutral atoms, molecules, and photons [20]. Due to the almost equal amount of positive charge and negative charge, the overall charge of plasma represents neutral and it is the most common matter in the universe [171, 172].

There are two plasma states separated by the degree of ionization: hot plasma and non-thermal plasma or cold plasma [69]. The fully ionized gas is hot plasma whereas the partially ionized gas is non-thermal plasma with a lower degree of ionization [69]. The ionization of the gas generally occurs by applying an electric field across a gas. There are two types of cold plasma systems based on their pressure, which are namely atmospheric pressure plasma and low-pressure plasma. Low-pressure plasma usually produces a lower power plasma under a low-pressure condition, which is suitable for materials with low-temperature stability, while atmospheric plasma creates plasma at atmospheric pressure which is more convenient than low-pressure plasma but will produce more heat across the surface of the material [69]. Hence, an application using plasma was chosen depends on the purpose of the process, such as functionalization with controllable and reproducible functional groups could be better in low-pressure plasma, and the large-scale industrial process could be better using atmospheric plasma [173].
In the plasma glow, electrons are important for transferring energies between activated gas radicals or ions and the target samples. Electrons are the lightest species in a plasma with high energy generated from their surrounding electrical field. Thus, electrons can be seen as energy carriers which collide with other atoms or molecules within the plasma, to result in excitation, ionization and dissociation [174, 175]. These reactions will produce active species for forming required materials and structures [174]. The produced ions can affect the bonding between molecules or atoms across the surface of the material to create anchoring sites for functionalization or polymerization. Then, the free-radicals can attach or form polymeric layers on the active surface of the material. The emitted UV photons from the plasma glow may also affect the surface and yield to the introduction of other radicals within the plasma [176-179].

2.4.2 Plasma treatment fundamentals

In the surface engineering [180-183], plasma is often used to modify the surface of material via etching, activation, and functionalization with selected gases [178].

Non-thermal plasma treatments for surface functionalization have been used in bio-applications, energy application, nanotechnology, and environmental control result from environmentally benign and simple processing [180-183]. All different dimensions of the sample can be treated by plasma in the reaction zone while the range of the treatment is under nano-scale and the functionality comes from different gases [178].
Gases in the plasma dominate the reactive species and result in functionality on the sample. Helium (He) and Argon (Ar) are usually used for cleaning and activating the substrate surface before introducing functional groups from reactive gases due to lower electron excitation energy and hardly forming functional species to introduce on samples [178, 184]. Typically, nitrogen-containing functional groups as a common functionality for composite applications include amine, amide, and imine for bonding with polymeric chains. Gases for plasma such as NH₃, NH₃ mixed with H₂ or Ar, a mixture of N₂ and H₂ or ethylene, and N₂ provide pathways for improving wettability, printability, bondability, and biocompatibility with amine groups [178, 185, 186]. Primary amines are however the most studied surface functional groups for biomaterials and polymer composites design [178, 187].

Other common functionalities include oxygen-containing functional groups produced from O₂, air, H₂O, CO₂ or CO gas plasma and the formation of bonds including C-O, C=O, O-C=O, C-O-O and CO₃ [178, 185, 186]. Plasma with oxygen gas can not only introduce oxygen-containing functional groups but also etch the surface of the material simultaneously. The etching from oxygen plasma treatments is caused by both radical species such as ions and UV photons able to generate atomic oxygen to react with carbon atoms. This is leading to volatile products formation across the surface of the polymer which results in rougher surfaces after evaporation [185]. Hence, the balance between etching and functional group formation needs to be controlled by plasma conditions [186]. Similarly to the nitrogen-containing functional groups, oxygen-containing functional groups also improve printability and biocompatibility for the polymer material, which the carboxyl (COOH) and hydroxyl (OH) groups were used in bio-applications [178].
Nonthermal low-pressure plasma polymerization treatments are techniques allowing for the functionalization and potential deposition of a thin layer onto a substrate through ionization of precursors of a polymer [188]. During the process, a gas or vapor of monomer will be carried across to the plasma reaction area and produce reactive species which then re-combine together as functional groups or polymerize as a film across the substrate [189]. Plasma treatments usually only take one step for forming functional groups or polymer films while traditional methods require either long treatment durations or high energy inputs under chemically active environment [188].

The supply power through the generator may be controlled by activating or inactivating the field with either continuous waves (CW) or pulsed (P) plasma modes. A combined CW followed with P (CW + P) system for plasma polymerization is typically used to increase polymerization yield and allow for better control of the microstructure and properties of the polymerized thin films [190, 191].

During CW plasma, the electric field is permanently applied during operation typically with an alternative power (AC) supply. The excitation, ionization levels, and dissociation processes, therefore, happen in a homogeneous and continuous manner throughout the process [190, 192]. Due to high energy plasma species bombardment in CW plasma, active sites may be formed across the material surface for either introducing functional groups or etching the material [190, 192]. P plasma, however, operates on the principle on an alternating on/off plasma activation system. An electric field is applied for a fixed duration prior to being switched off, typically with a direct current power (DC). The repetition of “on” and “off” time as a frequency was called as duty cycle (DC), which is determined by the following equation [193]:
\[ DC = \frac{t_{on}}{t_{on} + t_{off}} \]  
(2.14)

Where the average power \((P_{av})\) is:

\[ P_{av} = DC \times P_{peak} \]  
(2.15)

Where \(P_{peak}\) is the input power.

A lower \(P_{av}\) can be maintained in P plasma compared with CW plasma due to the repetition of plasma “on-time” and “off-time” which is referred to the “on-time” interval. P plasma favours the formation of long half-life species, which can finally become functional groups on the surface of the substrate [194]. During the \(t_{on}\) period, P plasma produce active species in the same way as for CW plasma, but charged species will disappear or react more efficiently during \(t_{off}\) period. Only radicals with a relatively long lifetime will continuously remain in the reaction area and react with the substrate surface, which results in the formation of functional groups or polymerized layers [194].

The combination of CW + P plasma mode offers advantages of both systems [190, 191]. Therefore, for functionalization of a material surface, CW + P mode presents high retention of desired functional groups with good adhesion on substrates. Hence, for plasma polymerization, it can produce a better cross-linked structure by allowing for more relaxation time for the polymerized species and thus improving the stable bonds formed during the process.

2.4.3 Plasma functionalization of nano-particles

Plasma functionalization provides a simple one-step process to complete the functionalization with an environmental benign due to low hazardous chemical use.
Ammonia (NH₃), N₂ and N₂ with H₂ or Ar gases have been studied for the functionalization of the CNTs, which results in the different amount of introduced primary amine groups by controlled plasma conditions [195-198]. A total of 2.3 at.% of primary amine groups have been formed across MWCNTs by using N₂/H₂ gases plasma, and higher concentration as 3.5 % can be achieved by coating a thin layer of plasma polymerized heptylamine [191]. The developed CW + P power mode for the plasma provides an efficient method for functionalization compared with only CW or P plasma [190]. The CW + P plasma generates more active sites on the CNTs surface than CW and P individually [191]. With the duty cycle (DC), the radicals have time for forming primary amine groups and attaching on the material surface [191]. These routes improve the dispersion and interfacial bonding with epoxy which also improves the mechanical properties [190, 191].

The developed stirring plasma system has provided uniformly functionalization environment for plasma treatment of CNTs [199]. The combined CW and P plasma polymerization of heptylamine presents the high level of amine groups that coat on the MWCNTs surface [199]. This work has presented clear advantages of plasma functionalization compared to the chemical functionalization.

POSS nano-particles have been directly modified for the first time by plasma without the combination of polymers to have functionalization of nitrogen-containing groups [105]. Samples were placed in a low-pressure plasma system with an N₂/H₂ (15 vol.%) reactive gas in order to have amine functionality on the octamethyl POSS substituents [105]. Due to the limitation of physical size reduction of the raw POSS powder, the production of functionalized POSS was limited to 0.1 primary amine groups per cage [105]. However, the low yield came from the non-uniform functionalization to the powder form sample, which the estimation of POSS nano-
particles in the top layer of the sample could receive 6 primary amine groups. Therefore, the plasma may represent efficient routes for functionalizing POSS nanoparticles towards their implementation into nano-composite materials.

2.4.4 Plasma functionalization of POSS hybrid composite materials

POSS nano-particles usually disperse uniformly in solutions thanks to their relatively low dimensions (order of 2 nm per side) towards nano-composites fabrication. The modification by plasma treatments leads the surface of the POSS nano-composite changes their wettability, surface morphology, mechanical properties, and introduce desired functionality for further processes [200, 201].

An oxygen plasma was used on a nano-composite film (poly[(propylmethacryl-heptaisobutyl-polyhedral oligomeric silsequioxane)-co-(methylmethacrylate)] (POSS-MA)) for biomedical application such as microfluidic devices [202]. Remote plasma presents as plasma treatment for samples not in the region of plasma reaction which prevents the strong etching from excited ions [202]. The oxygen plasma changed the isobutyl bonding by oxidation on the POSS moiety which presented as a fast converting from hydrophobic (85°) to hydrophilic (41°) with 25 W plasma for 20 s [202]. As a result of oxygen plasma surface treatment on POSS-MA films, oxidation of functional groups on the corner sites led POSS nano-particles across the surface of the film became hydrophilic and performed a more oxidation resisted surface [202]. An approach for oxygen plasma treatment on POSS coated Kapton® HN PI film was investigated for minimizing the adhesion issue of lunar dust to the surface of the object during lunar activities [203]. With the octakis(dimethylsilyloxy) silsesquioxane (POSS) across the PI film, the water contact
angle increased from 77° to 104° due to the hydrophobic POSS nano-particles on the surface of films [203]. However, the contact angle was reduced to 5° after 5 h of exposure to oxygen plasma at 100 W which suggested the increase of surface energy after modification [203]. Therefore, the POSS nano-particles were likely degrading to a SiO₂ structure after a long duration of oxygen plasma which could resisted more oxidation than pristine film [203]. In the cardiovascular surgical implant applications, POSS-PCU (polyhedral oligomeric silsesquioxane/poly (carbonate-urea) urethane) nano-composite film was developed by using plasma surface treatment [200, 201]. The plasma was generated by 300 W and 40 kHz in a low-pressure system (RF 13.56 MHz) with O₂ gas to produced polar species and enhanced the bio-compatibility [200]. Polar species such as hydroxyl (-OH), carbonyl (-C=O), and carboxylic acid (-COOH) groups with polar radicals (-O, -OH, and –OOH) were produced by oxygen plasma to improve network linking in the composite [200]. Plasma treated POSS-PCU improved the response from endothelial cells (ECs) which made them to a bypass graft material in bio-implant applications [200]. Furthermore, poly-p-phenylene benzobisthiazole (PBO) fibers were treated with a low-pressure (0.1 mbar) oxygen plasma at 175 W to bond with POSS and enhance the interfacial adhesion with epoxy resin [204]. With the oxygen species on PBO fibers, octaglycidyldimethylsilyl POSS was successfully grafted on fibers presented as the increased content of silicon (0 to 10 at.%) from XPS results [204]. The interfacial shear strength (IFSS) characterization indicated a 50 % increase to 54.9 MPa compared to untreated fibers while the tensile strength kept only 4 % decrease [204]. Therefore, the grafting of POSS nano-particle on plasma treated PBO fibers effectively improve the interaction between fibers and epoxy resin [204]. Therefore, to have covalent bonding between POSS nano-particle and matrix, the
control of functionality for nano-particle is required which towards a request of strategies for direct functionalization methods by plasma.

2.4.5 Plasma polymerization using the aerosol-assisted method under an atmospheric pressure

Compared to low-pressure plasma technique, atmospheric pressure plasma offer largely reduce the costs of operation. Such polymeric coatings developed by atmospheric plasma depositions have been used as a barrier or selective layers with thicknesses lower than 100 nm much faster than that obtained through wet chemical polymerization routes. However, plasma is usually used for depositing or polymerizing single chemicals to form a homogeneous coating.

Aerosol-assisted methods have been widely used to prepare films from heterogenous solutions or mixed reactive chemicals [205]. In the case of the formation of nano-composite layers, the nano-particles must be dispersed in a suitable solvent or monomer [206]. The mixture of particles and liquid monomers may then be sprayed out into very fine droplets (~ 1 µm) in order to uniformly generate polymerization spots across the surface of the supports. The aerosol-assisted chemical vapour deposition (AACVD) can be seen as a single step nano-composite coating route whereby a carrier gas from the aerosolizer is used to transport the precursors into the reaction chamber and form the coatings thanks to the temperature activation [207, 208].

Aerosol-assisted plasma deposition (AAPD) offers opportunities to incorporate nano-particles simultaneously with the precursor into the plasma reaction region to use plasma instead of temperature as for AACVD, as the driving force to produce the coatings across the substrates. In order to better forming homogenous film
structure, the aerosol generation using pneumatic or ultrasonic atomizers to produce an aerosol as very fine droplets to the plasma polymerization for homogenous structure [208].

The first development of AAPD at atmospheric pressure for functional coatings was performed for acrylic acid monomers [209]. Nano-composite structures were developed from organosilicone coatings, such as hexamethyldisilane (HMDSO) with aluminum-cerium oxide (AlCeO$_3$) nano-particles for corrosion protection in a parallel plate dielectric barrier discharge (DBD) reactor [210]. Titanium oxide (TiO$_2$) nano-particles were introduced in tetramethoxysilane (TMOS) to study the homogeneity and thickness of the deposited film with dispersion within a point to plate reactor using plasma jet [211]. The incorporation of nano-particles during the AAPD was also investigated as nucleation sites to grow plasma polymerized polymer and doped with anions from the organic-inorganic coating to increase the conductivity of the composite [212, 213]. Therefore, based on the development of the AAPD, metal nano-particles such as Silver (Ag) were also incorporated across a HMDSO matrix using a cold plasma jet. A mixed HMDSO and silver nitrate solution was used as the precursor for the aerosol [214]. Zinc oxide (ZnO) nano-particles were incorporated across a hydrocarbon polymer like poly(ethylene) structure to form superhydrophobic thin films with up to 170° of water contact angles, as shown in the Figure 2-9. These materials were developed for photocatalytic, self-cleaning, and anti-staining applications [208].

The AAPD process, therefore, provides great potential to produce thin film composites with controllable homogeneity and thickness so it can be used for membrane production to alter the free volume and surface energy in one single step. The HMDSO with octamethyl POSS nanoparticles has discussed with the AAPD
method and suggests the potential in the membrane fabrication recently from this project [215].

![Image: Contact angle of water for the advancing and receding state from nano-composite film along the deposition time, and SEM images of the nano-composite cross-section at different deposition duration [208]](image)

Figure 2-9 a) The contact angle of water for the advancing and receding state from nano-composite film along the deposition time, and b) SEM images of the nano-composite cross-section at different deposition duration [208]

2.4.6 Plasma polymerization of membranes for solvent separation application

Since plasma polymerization is attractive to membrane manufacturing as a simple and controllable process, the application on solvent separation for thin film preparation has been discussed since 1988 for the ethanol-water separation [216].

Plasma fabricated membrane as NF and PV for solvent separation has been introduced due to fast process and highly crosslinking structure from plasma. HMDSO
monomer was used to form PDMS-like films to develop a cost-effective route for alcohol-water separation in order to obtain hydrophobic and alcohol-philic surfaces across Nucleopore membranes by low-pressure plasma [216]. In Table 2-9, plasma HMDSO film indicated a flux as 0.46 kg.m⁻².h⁻¹ which was 293 % higher than the PDMS with silica particles nano-composite and 50.3 % higher than the commercial PDMS at 1 mbar pressure [141, 216]. However, the selectivity dropped to 4.5 compared to 28 from PDMS with silica of ethanol against water at 4 wt.% ethanol feed concentration due to the degree of crosslinking [141, 216]. Membranes prepared from plasma polymerized octamethyltrisiloxane monomers offered a slightly higher separation factor than HMDSO as 5.1 for the same feed solution due to better crosslinking [217]. The flux of permeate obtained with an increase of 1250 % compared to polymerized HMDSO film as 6.2 kg.m⁻².h⁻¹ which the crosslinking also provided better alcohol philicity for preferential ethanol diffusion [217]. The deposition of hydrolyzed vinyl acetate (VAc) on a Nylon-4 membrane was also investigated for alcohol/water separation as a thin film composite membrane (TFC) [218]. A separation factor of 13.5 (H₂O/EtOH) was obtained from the plasma TFC as 237 % higher than pristine while the flux was increased by 20 % as 0.42 kg.m⁻².h⁻¹ compared to pristine at a 90 wt.% ethanol/water solution at 25°C under 0.133 mbar at downstream side [218]. Another study on plasma polymerization was grafting styrene to a porous PVDF film. Results suggested an ethanol against water selectivity of 21 compared to 4 from bare PVDF membrane [219]. The flux of solution from plasma film decreased by 6.1 % compared to 6.6 kg.m⁻².h⁻¹ from bare PVDF in a 60 wt.% ethanol solution at 50°C [218, 219]. Additionally, plasma treatments have been used for initiation of porous PAN/PET membrane support to have a self-assemble process to produce a layer by layer structure and result in an ultrathin film [220].
Poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate sodium salt) (PSS) were deposited on a supporting membrane which produced a separation factor of water from ethanol as 70 with 0.23 kg.m⁻².h⁻¹ flux [220].

Furthermore, a thin film composite membrane prepared by plasma polymerized tetraethoxysilane (TEOS) on poly(carbonate) (PC) support was reported in PV of an 80 wt.% aqueous tetrafluoropropanol (TFP) solution [221]. The performance of PV was proofed by a selectivity of 567.4 of water from TFP solution which resulted a 99.3 % water remaining in the permeate with a flux 0.346 kg.m⁻².h⁻¹ at 25°C and 0.133 mbar [221]. However, the performance of the plasma polymerized membrane still cannot reach a high-level separation compared with other nano-composite membranes likely due to limitations in free volume control. Stearyl methacrylate (C18) alkane side chains were polymerized across PES membranes from atmospheric plasma polymerization to yield hydrophobic vinyl based polymers [19]. A 51 % higher separation factor of isobutanol from water than commercial PDMS (Sil20) was performed while the flux for plasma film and neat membrane were similar at a 6 vol.% isobutanol/water solution [19]. The nano-composite membrane for NF and PV provide advanced performance on separation, therefore, plasma fabrication also toward the production of nano-composite thin film. With the control of plasma strategy, the process for nano-composite thin film formation can be a more cost-effective method compared to traditional solution casting.

Hence, although promising to generate very thin coatings, limitations of plasma polymerization for membrane fabrication for PV are primarily related to the need to better and more carefully control the crosslinking degree to further enhance permeation while increasing selectivity.
Table 2-9 Membrane fabrication for solvent separation using plasma technique

<table>
<thead>
<tr>
<th>Type</th>
<th>Materials</th>
<th>Purpose</th>
<th>Condition</th>
<th>Selectivity</th>
<th>Flux (kg.m(^{-2}).h(^{-1}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PV</td>
<td>PDMS</td>
<td>Ethanol water</td>
<td>30°C, 4 wt.% ethanol, 1013 mbar permeate side</td>
<td>13 EtOH/H(_2)O</td>
<td>0.306</td>
<td>[141]</td>
</tr>
<tr>
<td>PV</td>
<td>PDMS with TMS-H silica</td>
<td>Ethanol water</td>
<td>30°C, 4 wt.% ethanol, 1013 mbar permeate side</td>
<td>28 EtOH/H(_2)O</td>
<td>0.117</td>
<td>[141]</td>
</tr>
<tr>
<td>PV</td>
<td>HMDSO</td>
<td>Ethanol water</td>
<td>25°C, 4 wt.% ethanol, 1 mbar permeate side</td>
<td>4.5 EtOH/H(_2)O</td>
<td>0.46</td>
<td>[216]</td>
</tr>
<tr>
<td>PV</td>
<td>Octamethyltrisiloxane on</td>
<td>Ethanol water</td>
<td>24.85°C, 4 wt.% (5 vol.%) ethanol feed, 4 mbar permeate side</td>
<td>5.1 EtOH/H(_2)O</td>
<td>6.2</td>
<td>[217]</td>
</tr>
<tr>
<td>PV</td>
<td>PVA pristine</td>
<td>Water alcohol</td>
<td>25°C, 90 wt.% mixture ethanol/water solution, 0.133 mbar permeate</td>
<td>4 H(_2)O/EtOH</td>
<td>0.35</td>
<td>[218]</td>
</tr>
<tr>
<td>PV</td>
<td>Hydrolyzed vinyl acetate (VAc) on</td>
<td>Water alcohol</td>
<td>25°C, 90 wt.% mixture ethanol/water solution, 0.133 mbar permeate</td>
<td>13.5 H(_2)O/EtOH</td>
<td>0.42</td>
<td>[218]</td>
</tr>
<tr>
<td>PV</td>
<td>PVDF support</td>
<td>Ethanol water separation</td>
<td>50 °C, 60 wt.% ethanol solution, 1.3 mbar permeate side</td>
<td>1.3 EtOH/H₂O</td>
<td>7 [218, 219]</td>
<td></td>
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<td>-------------</td>
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<td>--------------------------------------------------------</td>
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<td></td>
</tr>
<tr>
<td>PV</td>
<td>Plasma grafted styrene on porous PVDF film</td>
<td>Ethanol water separation</td>
<td>50 °C, 60 wt.% ethanol solution, 1.3 mbar permeate side</td>
<td>21 EtOH/H₂O</td>
<td>6.6 [219]</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>Poly (allylamine hydrochloride) (PAH) and poly (styrene sulfonate sodium salt) (PSS) on a porous PAN/PET supporting membrane</td>
<td>Ethanol water separation</td>
<td>27.5 – 58.5 °C, 6.2 wt.% water/ethanol solution, 0.2 mbar</td>
<td>70 H₂O/EtOH</td>
<td>0.23 [220]</td>
<td></td>
</tr>
<tr>
<td>PV</td>
<td>TEOS monomer on PC substrate</td>
<td>80 wt.% aqueous tetrafluoropropanol</td>
<td>25 °C, 80 wt.% TFP aqueous solution, 1.3 mbar permeate side</td>
<td>567.4 water/TFP</td>
<td>0.346 [221]</td>
<td></td>
</tr>
<tr>
<td>NF</td>
<td>PDMS (Sil20)</td>
<td>Isobutanol water separation</td>
<td>25 °C, 6 vol.% isobutanol feed, 1 mbar permeate side</td>
<td>Isobutanol/H₂O</td>
<td>6.7 [19]</td>
<td>1 [19]</td>
</tr>
<tr>
<td>NF</td>
<td>C18 alkane side chains on PES from vinyl monomer polymerization</td>
<td>Isobutanol feed</td>
<td>25 °C, 6 vol.% isobutanol</td>
<td>10.1</td>
<td>0.8</td>
<td>[15]</td>
</tr>
<tr>
<td>----</td>
<td>---------------------------------------------------------------</td>
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<tr>
<td></td>
<td></td>
<td>water separation</td>
<td>Isobutanol/H₂O side</td>
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</tbody>
</table>
2.5 Research gaps, questions, and work outline

2.5.1 Research gaps

POSS nano-materials bearing chemical functional groups such as amines are sought after for covalent attachment to polymers for nano-composite applications [22, 23, 28]. The chemical modification of POSS often requires the use of costly catalysts and/or highly hazardous chemicals while the process is complex involving several synthetic procedures [23, 95]. Hence, a physical plasma modification is alternatively considered to cut down the lengthy procedure with the limitation of size reduction. In addition, in order to incorporate POSS in the polymer, POSS is required to be dispersed uniformly in the matrix to avoid the agglomeration by either functionalization or fabrication method [26]. Plasma technology has provided not only functionalization for nanomaterials and, recently reported for octamethyl POSS, but also fabrication through aerosol-assisted atmospheric plasma system. In the membrane research, the difficulty of separate azeotropic mixtures has been discussed for industrial recycling and purification which membranes require enhancements in permeability without loss selectivity. The aerosol-assisted plasma concept provides a potential route for the incorporation of POSS nano-particles with polymers as a single one-step deposition on a substrate. Hence, with controllable conditions of plasma, a desirable homogenous and continuous nano-composite thin film membrane can be achieved. It has a great potential to form nano-composite thin film with controllable homogeneity and thickness.

2.5.2 Research questions

The main research question is:
How does the interface between POSS nano-particle and polymer matrix contribute to the membrane performance in the solvent separation?

⇒ The cross-linked network within the composite matrix will be resulted by the bonding between the functional groups at 8 sites of the POSS nano-particle and polymeric matrix. The free volume of the dense nano-composite membrane will be tuned by the degree of the crosslinking which controlled by the amount of POSS nano-particles in the composite and their functionality. Therefore, the permeability of the membrane will be improved by increasing the free volume and lead more components pass through the membrane. Selectivity of the dense membrane will be controlled by surface charge maintained from the polymeric matrix while POSS nano-particles will tune the surface charge when their functional groups are compatible with the desired separation of solvents.

This rationale is leading to 3 sub-questions which will also be answered in this thesis.

First, what is the impact of plasma on the POSS nano-particles and how to control the functionalization yields?

⇒ Reactive functional groups across the surface of POSS particles will be tuned to control the crosslinking degree with the polymer matrix across the membrane, therefore leading to selective functionalization will be required for proper incorporation. Gas plasma functionalization with CW + P mode will be used for introducing nitrogen and oxygen-containing functional groups on the octamethyl POSS without damaging the nano-cage features.
Second, what are the interactions between POSS nano-particles and monomer during the plasma generation?

- It is the theoretical aspect of the work which will dictate the interactions between the POSS and the polymer matrix, ultimately affecting the performance of the membranes. Due to the compatibility of the POSS nano-particles and the HMDSO polymeric matrix, free volume of the semi-permeable nano-composite membranes will be affected by both covalent bonding and van der Waal bonding. Hence, nano-particles will be more likely to create interfacial spacing for the ease of selected component passing. Interfacial space formation will also be affected by the uniform dispersion of the POSS nano-particles which the agglomeration will lead a larger space compared to bare matrix and lose selectivity.

Third, how to control the degree of crosslinking from plasma polymerization and how they affect the separation factor of the membrane?

- The preparation of plasma polymerized membranes will be performed by an atmospheric pressure plasma deposition system to break and recombine the monomer and nano-particles into a nano-composite thin film deposited across a nano-porous substrate. The degree of crosslinking will be affected by the plasma input energy, rate of precursor input, and amount of POSS nano-particles in the precursor. Hence, the relationship between crosslinking and separation performance will be studied by evaluate the interfacial
interactions between the nano-particles and the polymeric matrix through the membrane performance for ethanol and water separation.

2.5.3 Work outline

Therefore, this Thesis is aiming to develop a feasible fabrication for POSS nano-composite by plasma polymerization to improve the membrane performance under solvent environment.

The functionalization efficiency on POSS nano-particles by plasma will be firstly focused on the introduction of relatively high reactive functional groups include amine and carboxylic groups to form bonding between polymer and POSS nano-particles. A low-pressure plasma polymerization system will be used to determine the quantity of the amine functional groups on octamethyl POSS particles dispersed across the surface of a silicon wafer as in Chapter 4. To further improve the number of functional groups on POSS nano-particles, carboxylic functional groups will be studied by a stirring plasma system with low-pressure and as well as the amount of input POSS nano-particles for functionalization as in Chapter 4. The fabrication of POSS nano-composite thin film membrane will be prepared and discussed by atmospheric plasma polymerization as a candidate material for membrane application as in Chapter 5. To prevent aggregates formation during the plasma polymerization, an aerosol-assisted method has been developed previously at Bari University (Italy) and will be used to prepare thin films across PSf membranes. The interaction between polymerized HMDSO monomer and POSS nano-particles will be focused by evaluating the permeances and selectivitis from ethanol-water separation as in Chapter 5. To further enhance the effective deposition area, an atmospheric pressure
plasma system has developed at Deakin University and will be studied for producing thin films by monomer HMDSO with an X-Y moving stage as in Chapter 5. The control of interfacial bonding of the deposition will be discussed through the comparison between two systems towards the future development of plasma polymerization.
Chapter 3 Materials and Methodology

3.1 Introduction

Hybrid nano-composite thin films are produced by combining nano-fillers and polymers. The interaction between the fillers and polymeric matrix will dictate the macro-properties of the composite and such changes in performance of properties may be directly related to either the fillers properties or the fabrication process.

The POSS derivatives were both functionalized and incorporated into the polymerization pathway using plasma technologies. This chapter will describe the materials selected and designed for this thesis aiming for solvent separation including the POSS deviates and precursor for the base polymer. Hence, this chapter will discuss the nanomaterials functionalization route achieved by plasma prior to developing the membrane fabrication routes. Finally, the characterization techniques and conditions used to examine the properties of the resulting samples will be introduced prior to the membrane performance benchmark tests for separating solvents in the form of alcohol-water mixtures.
3.2 Materials

3.2.1 Purchased POSS nano-particles for plasma treatments

Commercial octamethyl POSS deviates (> 97 %) were purchased from Hybrid Plastics Inc.[27, 105]. The POSS agglomerates received exhibited a large particle size distribution on the order of 25 to 100 µm and the chemical structure of POSS molecules are shown in Figure 3-1a and b.

3.2.2 Samples preparation for plasma functionalization

The as received POSS powders required a pre-processing prior to plasma treatments for functionalization to reduce their size. An air jet milling (AJM) method was used to grind the crystals at high pressure. Raw particles were put into a 2-inch Sturtevant micronizer with a 90 PSI pressure which resulted in a 0.1 – 1 µm crystal size distribution as shown in Figure 3-1c [105]. The fine POSS micro-powders were then uniformly dispersed in an acetone solution with a concentration of 10 g/L [105]. A drop of 0.05 mL from the suspension was deposited on an approximately 1.0 × 1.0 cm² cleaned silicon wafer (15 min ultrasonication in acetone, ethanol, and deionized water individually for cleaning organics, dust, moistures and contaminations from the substrate) [105]. Finally, the liquid sample was dipped onto the silicon wafer and dried in an oven at 50°C for 1 min [105].
3.2.3 Preparation for the precursor of the polymerized polymer

3.2.3.1 Silicon-based monomer for polymerization

Hexamethyldisiloxane (HMDSO) is a monomer previously reported to have PDMS liked chemical structure after polymerization [216]. Thus, HMDSO was used as a precursor for producing thin film membranes, either as a pure polymeric structure or as composites upon adding POSS particles. HMDSO was purchased from Aldrich ® at NMR grade and exhibited a purity > 99.5 %. The basic chemical structure of the monomer is presented in Table 3-1. HMDSO contains chemical functionalities (methyl groups) and also presents on the octamethyl POSS particles which may favour their intermixing and compatibility in solution, prior to plasma polymerization.

The precursor for plasma polymerization was prepared from a suspension of the fine POSS micro-powders in the HMDSO solution and sonicated for 2 h at 396 W in a bath sonication system (Model CP 104 Digit; CEIA S.p.A., Arezzo, Italy) at room temperature to homogenize the distribution of particles. The concentrations used to prepare the aerosols were 0.16, 0.8 and 1.6 mg.mL⁻¹ of POSS in HMDSO solution which corresponded to 0.02, 0.1, and 0.2 wt..% The base PSf membrane supports used for plasma deposition were used as provided without further treatments.
Table 3-1 Monomer sample with its chemical structure

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexamethyldisiloxane (HMDSO)</td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
</tbody>
</table>

3.2.3.2 Supporting membrane for the deposited film

The plasma polymerized layer was directly deposited onto a supporting poly(sulfone) (PSf) ultrafiltration (UF) membrane used for mechanical reinforcement. The performance of the composite membrane was also benchmarked against these PSf supporting membranes. Commercial PSf UF membranes (PUREACH®, 20k Da cut-off value) was selected as the supporting layer. The relatively hydrophilic nature of the PSf was also seen as an advantage to favour wetting of the permeate side, and thus diffusion away from the membrane upon permeation.

3.2.4 Solvents for membrane performance evaluation

Solvents for testing the membrane include deionized water (DI water) and ethanol. The ethanol was from ChemSupply, SA, Australia with an ACS grade and > 95% purity. The properties of the solvents are presented in Table 3-2.
Table 3-2 Properties of the water and ethanol

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Molecular weight (g mol⁻¹)</th>
<th>Density (g cm⁻³)</th>
<th>Boiling point (°C)</th>
<th>Viscosity at 25°C (cP)</th>
<th>Vapour pressure at 25°C (kPa)</th>
<th>Vapour pressure at 20°C (kPa)</th>
<th>Surface tension at 20°C (mN·m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DI water</td>
<td>18.015</td>
<td>1</td>
<td>100</td>
<td>0.89</td>
<td>3.17</td>
<td></td>
<td>72.86</td>
</tr>
<tr>
<td>Ethanol</td>
<td>46.07</td>
<td>0.7893</td>
<td>78.2</td>
<td>1.04</td>
<td>7.83</td>
<td></td>
<td>22.39</td>
</tr>
</tbody>
</table>
3.3 Functionalization of POSS derivatives by plasma gas treatment

To facilitate the incorporation of the POSS particles into the polymeric matrix, functionalization of the POSS was investigated by plasma gas treatments towards a more environmentally friendly and quicker process compared to existing solvent chemistry-related functionalization routes. Particularly, the 8 sites of corners of the octamethyl POSS nano-particles were targeted to yield amine and carboxylic functional groups due to their high reactivity with the polymeric matrix. Hence, different level of the crosslinking can be achieved when controllable functionalized POSS used in polymerization membrane.

3.3.1 Plasma functionalization process

An inductively coupled RF plasma system set up by plasma group at Deakin University was chosen for the plasma functionalization process due to the stability of energy transfer (~100 %) and multi plasma mode operation (both continuous wave (CW) and pulse (P)). The plasma reaction chamber was obtained from a glass cylinder with a size of 150 mm in diameter and 300 mm in length which was covered by a Faraday cage to prevent the escape or electron and UV radiation presented in Scheme 3-1. A copper wire with a 3.74 mm in diameter was used as a circular loop antenna and covered the outside of the glass chamber to generate an electric field inside the glass chamber. The RF generator (Kurt J. Lesker Co., USA) can tune the generating parameters including modes, power, duty cycle in P mode, while the maximum operating input power is 300W. The plasma would generate in the glass cylinder by the RF power through the antenna around the gas inlet which forming gas ionization, while the rest of the region without antenna covered, has been seen as the afterglow field in the chamber. The input RF power has been transferred to plasma using a
matching network (EJAT6, Kurt J. Lesker Co., USA) with automatic transferring up to 100%. The samples on the silicon wafers were placed on the stainless steel platform located at the centre of the antenna in the chamber so that result plasma could affect the sample. To introduce different functional groups across the samples different inlet gases were selected, including Ar, O₂, N₂, and H₂. The vacuum condition was monitored by a pressure gauge which minimum pressure can be drop to 10⁻⁴ mbar controlled by a rotary pump. Therefore, before beginning the functionalization, the chamber was vacuum pumped down to 10⁻⁴ mbar for 15 min to remove traces of air. The purge of Ar in the chamber before and after plasma generating has also been taken in the operation which again preventing the oxidation from the remaining air or reactive sites.

![Scheme 3-1 Schematic of the plasma polymerization system [222].](image)

Before producing plasma from the mixed N₂ and H₂ gases, a CW plasma pre-treatment using Ar gas for 60 s (100 W input power with 3.6 sccm flow rate to maintain a pressure of 8 × 10⁻² mbar) was performed to clean the sample surface and create the activated sites for later functionality attachment. In order to produce as much amount
of functional groups as possible, the potential most efficient plasma mode, which the CW + P mode was used for the process. The impact of the input power corresponds to the result which plasma energy was investigated by characterising three different input plasma power at 80, 100, 130 W for a duty cycle in P plasma fixed at 10 % and a frequency of 2,000 Hz [105]. The lower plasma power could lead a lower concentration of nitrogen species to introduce on POSS nano-particles compared to 80 W plasma [223]. The influence from the duration of plasma occurrence, corresponding to the duty cycle in P plasma mode was studied using three different duty cycles at 5, 10, and 20 % with a 2,000 Hz frequency and same input power of 80 W. The duty cycle is calculated from the ratio of “on” time (t_on) and total time (t_on + t_off) for one interval which the t_on has been estimated as 0.025, 0.05, and 0.1 ms referring as 5, 10, 20 % duty cycle [105]. For introducing amine rich functionality, this project has used a mixture of gases from N_2 and H_2 with a volume rate of 17:3 while the working pressure was maintained as 8 × 10^{-2} mbar by a 5.4 sccm flow rate for all experiments. The plasma process for all samples was set at 60 s of CW plasma followed with a 600 s P plasma. The general procedures of the plasma functionalization are presented in Figure 3-2.
3.3.2 Functionalization using low-pressure stirring plasma system

In order to scale up the production of the yield for the functionalization, a homemade low-pressure system for generating plasma has been considered in the study. The plasma reactor chamber has been made from a Pyrex glass tube with a 400 mm in length and 40 mm in internal diameter which ends with a round flask as shown in Figure 3-3a and b. The round flask can be taken out before and after plasma in order to place and collect the sample. The round flask was connected to the glass tube using a clamp with well-sealing by vacuum grease in order to minimise the effect of the oxidation from the air. Since the particle sample was located at the bottom of the round flask, a magnetic stir bar was used to continuously stir the particle during the plasma to yield uniform treatment. The stir bar was controlled by a magnetic stirrer under the round flask for both stirring speed and temperature. The same copper wire (3.74 mm in diameter) from the low-pressure plasma polymerization system was used as an antenna around the bottom round flask while the supplied power was from the same RF generator (Kurt J. Lesker Co., USA).

The plasma condition for stirring plasma was based on the low-pressure plasma polymerization system with an increased duration with a higher amount of sample. On average 80 mg of the octamethyl POSS was used in the stirring system, resulting in average 60 mg treated sample after plasma which the remaining 20 mg stuck on the chamber inside wall and considered as lost. The testing pressure was still fixed at $8 \times 10^{-2}$ mbar for oxygen gas or N$_2$/H$_2$ gases as well as purging time of Ar gas with plasma.
polymerization system. Several series of the functionalization had been investigated including single CW plasma from 50 to 100 W, single pulsed plasma from 50 to 150 W with 10 % duty cycle, combined CW + P plasma with either increased CW power or pulsed power as shown in Table 3-3. The duration of the process was fixed for 3 min of Ar pre-treatment, 5 min of CW plasma, and 30 min of pulsed plasma while the Ar plasma has shown in Figure 3-3c. The study of plasma mode was also processed through using same energy input (550 W.min) including CW alone, pulsed alone, and combined mode.
Table 3-3 Main series of stirring plasma functionalization experiments and their conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>CW power (W)</th>
<th>P power (W)</th>
<th>CW duration (min)</th>
<th>P duration (min)</th>
<th>Duty cycle (DC %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>O₂ plasma with same power input (550 W.min)</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 CW</td>
<td>50</td>
<td>-</td>
<td>11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>100 P</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>55</td>
<td>10</td>
</tr>
<tr>
<td>50 CW + 100 P</td>
<td>50</td>
<td>100</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td><em>O₂ plasma with CW power only</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 CW</td>
<td>50</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>60 CW</td>
<td>60</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80 CW</td>
<td>80</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 CW</td>
<td>100</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td><em>O₂ plasma with P power only</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 P</td>
<td>-</td>
<td>50</td>
<td>-</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>100 P</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>150 P</td>
<td>-</td>
<td>150</td>
<td>-</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td><em>O₂ plasma for CW + P mode with different P power</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50 CW + 50 P</td>
<td>50</td>
<td>50</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>50 CW + 80 P</td>
<td>50</td>
<td>80</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>50 CW + 100 P</td>
<td>50</td>
<td>100</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>50 CW + 120 P</td>
<td>50</td>
<td>120</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>50 CW + 150 P</td>
<td>50</td>
<td>150</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td><em>O₂ plasma for CW + P mode with different CW power (include different duty cycle)</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 CW + 100 P</td>
<td>60</td>
<td>100</td>
<td>5</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>60 CW + 100 P</td>
<td>60</td>
<td>100</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
<tr>
<td>P-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 CW + 100 P</td>
<td>80</td>
<td>100</td>
<td>5</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 3-3 Low-pressure stirring plasma system, a) Scheme of the stirring plasma system, b) Set up of the stirring plasma system, c) Visual view of an Ar plasma treatment by stirring plasma system
3.4 Membrane fabrication with incorporating of POSS nano-particle

The POSS nano-particles with different functionalities were incorporated into the polymer to study the interactions between the particles and matrix which may yield improved separation performance in terms of permeability and selectivity. Hence, both functionalized POSS and unmodified commercial POSS were required in the project to investigate the different bonding correspond to the influence on the interactions.

3.4.2 Plasma fabrication for POSS nano-composite thin film membrane

The plasma polymerization process is an ionising operation whereby the vaporised monomer travels through the plasma reaction zone and recombines monomer fragments into a highly cross-linked polymeric matrix and deposit as a thin film on the substrate [224]. Hence, thin film composites can be produced from a plasma polymerization of a mixture precursor made of the monomer and fillers. Thus, a method to bring both monomer and fillers together in the plasma reaction zone need to developed for fabricating the thin film composite which called aerosol-assisted method [208]. Fine octamethyl POSS powders were dispersed in the HMDSO liquid to work as the mixture precursor. The concentration of the precursor prepared was 0, 0.02, 0.1, and 0.2 wt.% of octamethyl POSS in the HMDSO which were ultrasonicated for 2 h before used in plasma deposition to study the effect of nano-particle density in the matrix of the film.
3.4.2.1 Aerosol-assisted atmospheric pressure plasma process with parallel plane electrodes

The POSS nano-composite thin films were prepared using an atmospheric pressure dielectric barrier discharge (DBD) as cold plasma to polymerize the precursor and deposited on a substrate which general schematic setup is shown in Figure 3-4 [215]. The plasma chamber in the system was built with two plane electrodes in parallel for a 5 mm gap and 50 × 50 mm² area. The plane electrode was covered with a 0.635 mm thick Al₂O₃ plate (CoorsTek, 96 %) and the power was supplied by a homemade generator [208, 225]. The whole system was covered with a Plexiglas chamber with a volume of 14 L and connected with a dry diaphragm pump (Pfeiffer) to keep the working pressure constant [225]. The precursor for the plasma deposition was placed in a container which connects to a pneumatic atomizer (TSI, model 3076) in order to generate the aerosol into the chamber [225]. The carrier gas was using He (AirLiquide, 99.999 %) for generating the aerosol and also diluting the aerosol before taking in the plasma chamber [225]. The He gas flow was controlled by MKS mass flow controllers (MFC) which He gas has been used for purge the chamber before the plasma generates with a flow rate of 4 SLM (i.e. standard litres per minute) for 5 min [208]. When produced the discharge in the chamber, the He gas for an aerosol generation was 1.5 SLM, and for diluting the aerosol was 8 SLM. The deposition time has been checked with profilometer in order to control the thickness of the film. Since the generator of plasma was a homemade system, the actual electrical conditions have been measured by diagnosis which contains 23 kHz frequency with 2.63 ± 0.19 kV for peak-to-peak voltage shown in Figure 3-5. Therefore, the power generated for the plasma has been determined as 0.37 ± 0.025 W cm⁻².
Figure 3-4 Schematic setup of aerosol-assisted DBD system with electrodes as parallel plates. The gas for carrying aerosol and diluting the aerosol (Gas carrier) was He.

Figure 3-5 The electrical measurement for generating plasma for the polymerization at frequency of 23 kHz including: a) He plasma with a peak to peak voltage of 2.56 kV and 0.40 W.cm\(^{-2}\) power generation; b) He with HMDSO monomer plasma contained a peak to peak voltage of 2.84 kV and 0.37 W.cm\(^{-2}\) power generation; c) He with POSS containing HMDSO monomer plasma contained a peak to peak voltage of 2.48 kV and a 0.35 W.cm\(^{-2}\) power generation.
3.4.2.2 *Aerosol-assisted atmospheric pressure plasma process with parallel cylindrical electrodes*

An alternative system using parallel cylindrical electrodes covered with a quartz tube and where the precursor inlet is located above the electrodes so that deposition of the films on the substrate occurs below the electrodes to have uniform film as shown in Figure 3-6a. Since the thin film deposition occurred in the previous parallel plate system, the thickness of the film was not perfectly uniform due to the residence time of the gas flow across the chamber. The flow of precursor could lead to more deposition on the substrate area which was closer to the precursor inlet port compared to the area closer to the output port. Therefore, the settled cylindrical electrode in bath system contained a gap between the electrodes as 1.5 mm while the distance between the electrode and sample holder was 10 mm to avoid contact of sample and electrode. The bath head was 32.5 mm above the electrode to allow the aerosol to have enough time to disperse uniformly prior to polymerizing. A sample holder was placed on an X-Y moving stage to ensure a large area deposition with uniform thickness on the sample substrate for a $100 \times 100$ mm$^2$ square area as shown in Figure 3-6b. In Figure 3-6c, the pattern for the movement of sample holder during the plasma deposition was settled with a speed of 10 mm.$s^{-1}$ in the X forward direction with a total 100 mm distance from 0 position, then move in Y direction with 10 mm and then 100 mm in X backward direction. The speed of holder in Y direction was 10 mm.$s^{-1}$ and returned to the 0 position when total distance in Y direction was reached 100 mm and started another run until turn off the stage. The flow rate of the monomer was fixed at 0.7 LPM (litre per minute) while the Ar carrier gas was set at 25 LPM due to the long distance between bath head and electrode as well as the nozzle size on the bath head. A high voltage/medium frequency generator, G2000 for plasma is from
Redline Technologies with an external transformer as the accessory of the generator to amplifier the power, was used to generate a stable plasma. The power of the atmospheric plasma input was set as 180 V with 85 kHz with 50 % duty cycle (around 110 W based on the working current, 10 ms $t_{on}$ and 10 ms $t_{off}$) for different duration of the deposition on substrates including silicon wafers, glass slides, and PSf UF membranes. The monomer precursor and the system were purged by Ar gas for 30 min and 10 min respectively while atomizer was purged for 5 min before starting plasma polymerization. The duration of the deposition was investigated with 2, 5, 8, and 13 min to calibrate the deposition rate and homogeneity of the film.
Figure 3-6 Aerosol-assisted atmospheric pressure DBD system with parallel cylindrical electrode system and showering inlet, a) Schematic setup of the aerosol-assisted DBD system, b) The sample holder was set on a moving X-Y stage for uniform deposition thickness on a support membrane, c) The moving pattern of sample holder on the X-Y stage during the plasma deposition
3.5 Characterization techniques

3.5.1 Measurement of particle size of POSS with Dynamic Light Scattering

The particle size distribution of the sample powder was measured by Dynamic Light Scanning (DLS) to study the effect of particle size with plasma treatment. Since the octamethyl-POSS powder as purchased contains large size particles which around 50 µm, their size distributions were measured with a Malvern Mastersizer for microscale materials. After Air jet milling (AJM), the size of the POSS powder was submicrometer.

The particle size distribution of the POSS in the HMDSO monomer precursor was measured by Zetasizer Nano ZS from Malvern Panalytical. 1 mL of the 0.1 wt.% POSS concentration precursor was chosen in a quartz cell for checking the particle size with 3 repetitions scan and 5 measurements per scan. The suspension was taken for measurement after different sonication time, 0, 5, 15, 30, 60, 90, and 120 min.

3.5.2 Measurement of thickness - Profilometer

The thickness of the coating was first estimated using a KLA Tencor D-120 surface profilometer [226]. Measurements were repeated 3 times across different areas of a film on 10 mm × 40 mm silicon wafers. The samples were scratched twice each time with a diamond blade to yield an average thickness. The thickness of the film was measured from the 2 min plasma deposition and the rate of deposition per minute was calculated from the profiles. The deposition durations for the target 50, 150, and 300 nm thicknesses were also determined after evaluation of the deposition rate for the different concentrations of POSS precursor solutions. The amount of film on the
silicon wafer was found to be similar to that on films deposited on PSf membranes with the same plasma conditions and thus used as a reference [227, 228].

3D measuring laser microscope OLS4100 LEXT from Olympus ® also used for thickness measurement of the plasma deposited thin film from homemade parallel cylindrical electrodes with X-Y moving stage system. The scanning step for acquiring images was 10 nm with a 50X lens and resulted in a 43 × 43 µm² image for analysis. Measurements were repeated for 3 times to estimate the height difference between substrate and film surface from laser scanned images. The deposition rate could be estimated from the different duration of the plasma deposition with 2, 5, 8 and 13 min.

3.5.2 Scanning electron microscopy for POSS and membranes morphologies

The morphology of the POSS particles on silicon wafer, PSF supporting membrane, and the plasma deposited film were evaluated by Scanning Electron Microscopy at an accelerating voltage of 5 kV and a current of 87 pA for a working distance 12 mm. Synthesised membranes were also using the Jeol JSM 7800F to evaluate the morphologies of both the membranes surface and cross-section at 10 kV and for a 10 mm working distance. Zeiss Supra 55VP FEG SEM was also used to investigate the morphology of the plasma deposited film from parallel cylindrical electrodes with X-Y stage system with same accelerating voltages as Jeol JSM 7800F. All samples were coated with a 5 nm thick gold (model SC 050 sputter coater, Bal-Tec) before examining the SEM images.
3.5.3 Atomic force microscopy measurement for roughness

The surface roughness of the deposited film was evaluated by atomic force microscopy (AFM) in order to confirm the features appeared from SEM images. The samples for AFM were deposited on either a silicon wafer or directly onto a PSf membrane sample to study the difference of the roughness due to the impact of the different substrates. To scan the surface of the sample, a Bruker Multimode TM 8 SPM instrument with silicon probes with aluminium coating includes TAP300AL-G-10 and TAP150AL-G-10 with a spring constant from 2.5 – 2.7 Nm⁻¹ in tapping mode.

3.5.4 Fourier transform infrared spectroscopy for the nature of the material

3.5.4.1 Solid bonding structure measurement

Fourier transform infrared spectroscopy (FTIR) is a widely used characterization for identifying the near surface chemical composition and structure. In this project, FTIR was used to study the surface chemistry in the treated octamethyl POSS and deposited films. For FTIR characterization of the POSS, samples were prepared by mixing the amount of POSS present on one Si wafer sample (~5-10 mg) and approximate 100 mg KBr, and compressed into tablets for the transmission mode due to the small signal from the nitrogen contained groups from absorbance mode.

The FTIR instrument is Bruker VERTEX 70 spectrophotometer, and the spectra carried out by using transmission mode for POSS and Attenuated total reflectance Fourier transform infrared (ATR-FTIR) mode for a deposited membrane with a resolution of 4 cm⁻¹ and accumulating 128 scans under spectra region between 4000 and 600 cm⁻¹. The band of the FTIR can be analysed with their relative intensity.
ratio with the normalised band Si-O-Si, and the chemistry of the band can be determined through Table 3-4.

Table 3-4 The bands appeared in the FTIR spectra for both untreated POSS and plasma treated POSS

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N – H</td>
<td>3400 – 3500</td>
</tr>
<tr>
<td>N – H/C = O</td>
<td>1580 – 1650</td>
</tr>
<tr>
<td>O – H</td>
<td>3200 – 3500</td>
</tr>
<tr>
<td>C – H (–CH(_3))</td>
<td>2850 – 2990</td>
</tr>
<tr>
<td>-SO(_2)</td>
<td>1320 – 1360</td>
</tr>
<tr>
<td>– CH(_3)</td>
<td>1370 – 1380</td>
</tr>
<tr>
<td>Si – CH(_3)</td>
<td>1250 – 1280</td>
</tr>
<tr>
<td>Si – O – Si</td>
<td>1075 – 1135</td>
</tr>
<tr>
<td>Si – C</td>
<td>720 – 860</td>
</tr>
<tr>
<td>C – NH(_2)</td>
<td>1000 – 1050</td>
</tr>
</tbody>
</table>

3.5.4.2 Ethanol concentration measurement

The ATR-FTIR with detecting absorbance in the liquid can use in ethanol concentration determination. Different ethanol concentrations contribute to a different absorbance base on the same background. To define an unknown ethanol concentration solution, using standard ethanol concentration to calibrate a measurement curve is a method. Standard ethanol concentrations in Figure 3-7, 0 %, 0.05 %, 0.1 %, 0.1577 %, 0.2 % were used in low ethanol concentration measurement, and 10 %, 75 %, and 100 % were used in high ethanol concentration measurement while Figure 3-7a is the calibration of the ethanol concentration under low ethanol content condition, and
Figure 3-7b is the calibration for the high concentration ethanol solution. The resulting curve from the height of the peak in 1040 cm$^{-1}$ indicates the stretch of C-O bond from the CH$_2$-O-H or CH-O-H which suggests the ethanol in the solution [229]. Therefore, based on the relationship between the intensity of the band and ethanol concentration, a calibration plot of ethanol concentration was prepared.

Figure 3-7 Calibration curve plot for ethanol concentration from FTIR, a) For a range of ethanol concentration 0 to 0.2 wt.% ethanol, b) For a range of ethanol concentration 0 to 100 wt.% ethanol
3.5.5 X-ray photoelectron spectroscopy for the efficiency of the functionalization

X-ray photoelectron spectroscopy (XPS) is widely used in quantitative analysis of elements and identification of functional groups in the material surface. X-rays can be absorbed by atoms of a material, which generate the ejection of photoelectrons. The binding energy that refers to each element can be defined by the photoelectrons. Due to the uniqueness and sensitivity of those energies, which correspond with elemental and chemical states, elements on the surface of a material can be identified through the determination of energies. Therefore, for plasma surface modification, XPS is a powerful technique for surface chemical analysis.

The instrument for XPS analysis was a K-Alpha X-ray photoelectron spectrometer from Thermo Fisher Scientific in RMIT University. The working pressure in the chamber was usually at around $5 \times 10^{-9}$ mbar, and the spot size for scanning the binding energies was 400 µm for both peak scans and survey scans. A flood gun was used for minimizing the excessed charging of sample. For C1s binding energies, the lowest binding energy peak has been defined as 284.8 eV for comparison of other samples. Survey spectra contain a pass energy of 100 eV, but the peak scans only perform 20 eV for high-resolution spectra. Peak scans were processed by 10 scans for each element at each point in order to determine the elemental composition of C, Si, O, and N in the octamethyl POSS. The data from XPS analysis can be fitted by Gaussian-Lorentzian (G/L) product. XPS measurements were also processed by Kratos AXIS Nova XPS spectrometer in Latrobe University with the same set of the K-Alpha XPS spectrometer from Thermo Fisher Scientific.
3.5.6 Chemical derivatization for quantifying the amount of primary amine group

The nitrogen amount can be defined using XPS and the N/C ratio. However, it is difficult to isolate nitrogen-containing functional groups and identify their type. Hence, the use of TFBA for chemical derivatization can help in determining and quantifying primary amine groups (-NH₂) from the surface of plasma treated samples. TFBA will react with primary amine groups to produce an imine group and the terminal fluorine label can be used to quantify the NH₂ groups (Figure 3-8a). Due to the reaction, the primary amine can be determined from the transfer equation of fluorine in the XPS.

The functionalised POSS samples were treated with TBFA directly after plasma treatment for XPS analysis with 20 µL of TFBA. The TBFA vapours were left to react with the sample in a sealed vessel for 2 h at room temperature (Figure 3-8b).
Figure 3-8 TFBA derivatization for quantifying the yield of primary amine groups after plasma treatment, a) Scheme of chemical derivatization by TFBA on treated octamethyl POSS, b) Experimental set up of the TFBA derivatization

The estimation for the degree of functionalization NH₂/C and the efficiency of primary amine NH₂/N have been defined in the following equations from the fluorine content from the XPS data [193]:

\[
\frac{[NH_2]}{[C]} (\%) = \left( \frac{[F]}{3} \times \frac{1}{[C] - \frac{8[F]}{3}} \right) \times 100 \quad [NH_2/N] (\%) = \frac{[NH_2]}{[N]} \times 100 \quad (3.1)
\]

Where NH₂/C (%) presents primary amine percentage relative to carbon concentration and NH₂/N (%) refers as the selectivity of the amine from total nitrogen content. [F] and [C] are the fluorine and carbon concentrations from the XPS data. [F]/3 refers to the number of primary amines, 8[F]/3 indicates the amount of carbon introduced with TFBA molecules, and [C] – 8[F]/3 represents the real carbon concentration within the sample surface.
3.5.7 Nuclear magnetic resonance spectroscopy for confirming the material structure

After the XPS measurement for the composition of the material after plasma treatment, a nuclear magnetic resonance spectroscopy (NMR) has been used to confirm the change of the substituents on the octamethyl POSS. The treated POSS (80 W, 10 % DC) has been dissolved in dimethyl sulfoxide (DMSO) at a field strength of 11.7 T to obtain a solution-state $^{13}$C NMR spectrum. A quantitative spectrum has obtained from direct excitation of a 9.1 µs 90° RF pulse and a recycle delay for 20 s. The total scan of the measurement was 4000 scans with $^1$H decoupling (Waltz16, 80 µs pulse length) only during the signal acquisition period in order to prevent nuclear overhauser effect (NOE) enhancements. Additionally, the chemical shift scale has been referenced to the $^{13}$C signal from tetramethylsilane (TMS) at 0 ppm.

3.5.8 Small angle X-ray scattering and wide-angle X-ray scattering measurements

Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) are used for presenting the structure of the material which using the coherent scattering of scattered X-ray across over the matter. With the X-ray scattering principle of the characterization, Rayleigh scattering with the Bragg equation has been used for SAXS. Hence, the scattering angle leads a relationship between scattering vector and diffraction angle $\theta$ shown below:

$$q = 4\pi \cdot \sin\theta / \lambda$$  \hspace{1cm} (3.2)

where $\lambda$ is the wavelength of the X-ray beam.

The SAXS and WAXS experiments were processed at Australian Synchrotron during the beam time of SAXS/WAXS (AS, Melbourne, Australia). The measured
patterns were analysed with software Scatterbrain 2.10 provided by SAXS technical groups. The beam energy was obtained as 16 keV with the detector of Pilatus 1M (Melbourne, Australia) with a camera length of 0.9 and 7 m for smaller (0.9 – 55 nm) and larger (7.5 – 450 nm) features.

### 3.5.9 Wettability from contact angle measurement

The wettability of the deposited film has been measured using contact angle instrument. Testing was performed with a 4 µL liquid drops on the film surface and collected the images from a goniometer (KSV instruments model CAM 101). Drops were placed on the film across three random locations for determining an average value of contact angle. Pictures were acquired when the drops were in a steady state. The contact angle was calculated from the fitting of the taken images and the Young-Laplace equation was used to obtain both side value and average from the optical tensiometer software, One Attension Theta Lite.
3.6 Membrane performance test

The deposited membrane on PSf support was tested its performance on permeating the different liquid including deionized water and ethanol. The ideal selectivity of the solvent from the water has been measured through the pure liquid permeation driven by pressure. The flux of the permeation has been converted to permeability and estimates the ideal selectivity. Due to the error on manual control of the pressure, porometer has been used to determine the minimum permeate pressure of the solvent.

3.6.1 Porometer measurement of liquid entry pressure of permeation

The produced thin film was also tested with a Porometer 3G from Quantachrome intruments for the liquid entry pressure (LEP) determination. Since the porometer could control the pressure much precisely than manual control, the instrument provides actual permeate pressure of the membrane for input liquid. With the instrument sample holder, the sample area was reduced to 26 mm diameter. When sample area is not enough, a poly(ethylene terephthalate) support with a $8 \times 8 \text{ mm}^2$ spot was used to glue a $10 \times 10 \text{ mm}^2$ membrane. It has used 3GWin2 V2.1 software to control the instrument from 1 to 10 bar for water with 256 reading points, and from 0.1 to 5 bar for ethanol with 256 reading points.

3.6.2 Dead-end filtration tests

To measure the flux of the liquid, a dead-end filtration has been processed using Sterlitech HP4750 cell which can stand for a high pressure with 250 mL liquid permeating. Conditioning of the membrane is important to ensure the completely
wetting of membrane in the tested solvent which leads stable solvent permeation during the filtration experiment [230]. Therefore, all membrane sample has been conditioned for at least 24 h in the tested solvent at room temperature before the testing. To avoid the issue of the compaction from the membrane, membrane sample has been compacted in a 4 bar pressure for 0.5 h and then 10 bar pressure for 0.5 h before collecting the data of flux.

3.6.1.1. Pure solvent filtration tests

Measurements were performed with deionized water and ethanol with a volume of 250 mL per each testing. The flux of permeation has been collected on a mass balance and monitored with 5 s per reading within 20 min. The data of the flux has been performed under pressure 8, 9, and 10 bar in order to have a pressure trend and could be transferred to permeability through the division of time and pressure which finally come out the ideal selectivity from the pure solvent flux.
Chapter 4 Plasma functionalization of POSS powder

4.1 Plasma functionalization through low-pressure gas plasma system

The control of the interactions between nanomaterials and matrix towards advanced nano-composite materials must be achieved through specific modifications of the surface of nanomaterials [22]. Such control may allow for improved dispersion or loading of nanomaterials within the main matrix and good adhesion between nanomaterials and the matrix, providing invaluable opportunities towards the design of materials with custom-designed thermo-electrical, mechanical or catalytic properties [22].

Polyhedral oligomeric silsesquioxanes (POSS), a class of such nanomaterials, is inorganic, highly crystalline, 3D building blocks based on a silicon cubic cage nano-structure [24]. POSS nano-particles were used as fillers in composite materials for a wide range of applications for optical and electrical devices, aerospace, biomaterials and nano-composites due to their nanoscale size (1-3 nm), flexible functionality, and bio-compatibility [22-24]. The mechanical properties of mixed matrix-POSS polymer nano-composites can be significantly improved through long range order organization by covalently bonding functional POSS cages with the polymer backbone macromolecules [22]. The incorporation of octaaminophenyl POSS (OAPS) and diepoxides or dianhydrides produces highly cross-linked structures with enhanced thermal stability, tensile and compressive strength used for diverse applications [24, 99, 121]. In addition, the interactions between such functionalized POSS nano-cages and polymer materials were also shown to generate interfaces allowing for improved permeability of selected components, such as solvent vapours during PV operation or
seawater desalination [20, 71, 136]. However, in order to develop proper anchor points in POSS, the surface of POSS must contain specific reactive points [231].

Although already developed via chemical synthetic routes to have functional groups, efficient and tailor-made functionalization routes of native POSS materials, allowing for control of the density of functional groups is still required [24]. Current production methods to functionalize POSS, include hydrolysis and condensation from silica derivatives and functionalization from pre-formed POSS cages by chemical reactions. These methods are generally lengthy, require costly chemicals, lead to a range of sub-products and produce environmentally unfriendly waste effluents [22, 23].
4.1.1 General introduction

Here, an innovative and cost-effective alternative technique for the plasma functionalization of POSS micro-powders without damaging the cage structure is proposed for the first time. Plasma functionalization techniques are typically single-step, environmentally friendly and offer homogeneous treatment and fine control towards the grafting density of functional groups across surfaces [173, 178, 184, 232, 233]. The functionalization of nanomaterials such as carbon nanotubes, and recently boron nitride nanotubes, was previously achieved using a plasma methodologies, called continuous wave (CW) plus pulse (P) plasma (CW + P plasma), and previously developed by the Dai group. This system was utilized in this project to yield high efficient functionalization of nitrogen containing groups [190, 191, 193, 199]. Here, the plasma process was composed of a sequence of three steps including i) a CW plasma with Ar gas for cleaning surface of POSS powder and activating the surface, ii) a CW plasma with N₂/H₂ gases to further generate activation sites and start forming functional groups across the surface of POSS and iii) a pulsed (P) plasma of N₂/H₂ performed to gently introduce higher amount of desired functional groups onto the POSS reactive sites surface.

Pulsed plasmas are a combination of low power conditions and novel fragmentation routes which provide long living active species [234] and higher amounts of N-containing groups [235, 236]. Surface plasma treatments were performed on the octa-methyl POSS micro-powders with a mixture of nitrogen and hydrogen (N₂/H₂ (15 vol. %)) gas to introduce N-groups with high amine character. A variety of N and H containing functionalities can be formed onto the surface of crystalline POSS material, e.g. amines (NH₃), imines (-CH=NH), cyanides (-C≡N), and amides (-CONH₂), but a high content of primary amines (-NH₂) is desirable
towards further grafting reactions for composite materials design (Figure 4-1). The development of a high content of amine, amide and imine functional groups is desirable for using the functionalized POSS micro-powders as crosslinking materials for acylation or amidation reactions [22]. Additionally, H₂ can prevent the reaction of oxygen from air contamination during plasma treatment [178, 185-187]. Octamethyl POSS was chosen as a demonstration compound since it is naturally unreactive, symmetrical and highly crystalline as well as being one of the cheapest forms of POSS available [27]. The chemical characterization results were correlated to the plasma conditions and critically discussed to demonstrate the breadth of the technique and its applicability to the one-step specific functionalization of octamethyl POSS micro-powders.

Figure 4-1 Chemical structure of octamethyl POSS and theoretical schematic plasma process for amine functionalization. The arrow with the indication CW + P Plasma denotes three steps of the process: step 1) continuous wave Ar plasma, step 2) N₂/H₂ (15 vol.%) continuous wave plasma, and step 3) pulsed plasma with the same feed composition.
4.1.2 Influence of the supplied power

4.1.2.1 POSS particle morphology on the substrate

SEM images have provided the presence of the POSS crystal after air jet milling and deposited on silicon wafer. The particle size of the POSS crystal for plasma functionalization has been characterized through Figure 4-2a, which can be estimated as 0.1 – 1 µm diameter cubic dimension. The inert image in Figure 4-2a presents the particle size of the POSS just from purchased without any processes and suggests an agglomeration of POSS crystal to around 50 µm in size. After plasma functionalization through a low pressure, Figure 4-2b, c, and d provide the similar crystal size of the POSS, which plasma with power until 130 W would not damage the crystalline property as no conversion from crystal to glassy phase.
4.1.2.2 Characterization by infrared spectroscopy

In the first series of tests, the impact of the plasma power at fixed duty cycle of 10% was investigated at 80, 100 and 130 W to study the activation of the crystalline POSS material. The threshold energy for triggering the functionalization of the terminal methyl groups on POSS should be affected by power, duty cycle and ion bombardment density [190]. The activation of the octa-methyl POSS and subsequent potential reactive group formation is directly related to the dissociation energies of the C-H bond from the methyl group (3.5 eV), as well as the Si-C (4.5 eV) and Si-O bond (8.3 eV) from the silica cage [237, 238]. Hence, since the experimental results show
that the cage structure (Si-O bonds 8.3eV) of POSS is preserved, the discharge energy
should be lower than 8.3 eV and higher than 4.5 eV, needed for breaking C-H and Si-
C [238]. The hydrogen elimination reaction should therefore allow for the grafting of
desired functional groups without compromising the POSS cage structure [177]. The
effect of plasma treatment in the following section was monitored by FTIR and XPS
analysis.

FTIR analysis was performed to evaluate the formation and alteration of the
functional groups. Figure 4-3a shows the FTIR profiles and band characteristics of
both untreated and plasma treated POSS micro-powders with different plasma powers.
The Si-O-Si stretching band at 1075 – 1135 cm⁻¹ and Si-C band at 780 cm⁻¹
corresponding to the structural groups from the POSS cage appear clearly and
consistently across all experiments which is supported by the intensity of bands (i.e.
Si-O and Si-C) from FTIR spectra comparison [239, 240]. Hence, the stabilities of the
Si-O and Si-C are presented in Figure 4-4. The bands corresponding to the N-H
vibration at 1580 – 1650 cm⁻¹ and 3400 – 3500 cm⁻¹ are however presented after
plasma treatment. The intensity of these bands as a function of power is displayed in
Figure 4-3b. The 80 W treatment was presented the highest intensity, which may
indicate a higher content of nitrogen rich groups across the POSS. In addition, at 1000
– 1050 cm⁻¹ a small shoulder beside the Si-O-Si main band has appeared for the 80 W
plasma treatment, which is attributed to C-NH₂ groups from primary amine functional
groups [240, 241]. This result suggests that nitrogen-containing functional groups are
successfully introduced [242]. However, the band at 1580 – 1650 cm⁻¹ may correspond
to amine, amide and imine groups and ratios between these species could not be readily
discriminated. The N-H band at 3400 – 3500 cm⁻¹ was also found to overlay with the
O-H band (3200 – 3500 cm⁻¹) and it was therefore difficult to quantitatively evaluate
the amount of amine, amide and imine functional groups based on FTIR. Furthermore, the spectra of Ar plasma pre-treated POSS in Figure 4-5 shows similar bands position at 1630 cm\(^{-1}\) and 3400 cm\(^{-1}\) corresponding to C=O and O-H bonds [241]. The complete series of vibration bands including their main positions are summarized in Table 4-1 [24, 241].

Table 4-1 The bands appeared in the FTIR spectra for both untreated POSS and plasma treated POSS

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Wavenumber [cm(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N – H</td>
<td>3400 – 3500</td>
</tr>
<tr>
<td>N – H</td>
<td>1580 – 1650</td>
</tr>
<tr>
<td>O – H</td>
<td>3200 – 3500</td>
</tr>
<tr>
<td>C – H (– CH(_3))</td>
<td>2850 – 2990</td>
</tr>
<tr>
<td>– CH(_3)</td>
<td>1370 – 1380</td>
</tr>
<tr>
<td>Si – CH(_3)</td>
<td>1250 – 1280</td>
</tr>
<tr>
<td>Si – O – Si</td>
<td>1075 – 1135</td>
</tr>
<tr>
<td>Si – C</td>
<td>720 – 860</td>
</tr>
<tr>
<td>C – NH(_2)</td>
<td>1000 – 1050</td>
</tr>
</tbody>
</table>
Figure 4-3 FTIR spectra for all treated samples and the intensity difference at 1580 – 1650 cm\(^{-1}\) and 3400 – 3500 cm\(^{-1}\), a) FTIR spectrum of the first series of experiment with different power of plasma, b) difference of intensity for the FTIR bands from the first series of experiment, c) FTIR spectrum of the second series of experiment with different duty cycle in the pulsed plasma treatments, d) difference of intensity for the FTIR bands from the second series of experiment
Figure 4-4 The intensity difference for the band Si-O and Si-C in both plasma power and duty cycle series of experiments

4.1.2.3 Influence of Ar plasma pre-treated on POSS

The FTIR spectrum for an Ar plasma pre-treated sample is shown in Figure 4-5 with a plasma power of 100 W under CW mode for 1 min. The working pressure was same as other experiments as $8.0 \times 10^{-2}$ mbar. This experiment is targeted to present the impact of Ar plasma pre-treatment compare with native POSS. The resulting spectrum has contained bands at 1630 cm$^{-1}$ and 3400 cm$^{-1}$. These bands can be
interpreted as effects from reaction with oxygen after plasma treatment, since the Ar plasma has first activated the surface of the POSS without generating stable functional groups on their surface. Therefore, in order to reach stable states, those activated sites react with oxygen when sample exposes to the air.

Figure 4-5 FTIR spectra of Ar plasma pre-treated POSS sample compared to an untreated sample. The appeared band at 1630 cm\(^{-1}\) would be C=O bands which comes from oxidation after plasma, and the 3400 cm\(^{-1}\) should be the water moisture from the air.

**4.1.2.4 POSS degradation using plasma**

Since the binding energy of the peak in XPS will shift if POSS cages are damaged, FTIR data may also provide evidence of the main band (i.e. Si-O-Si) shift. An experiment previously completed with combined heating and plasma treatment at 200 °C and 100 W N\(_2\)/H\(_2\) CW plasma presents a significant shift from 1120 cm\(^{-1}\) to 1030 cm\(^{-1}\) shown in Figure 4-6. The duration of the process is 5 min under 5 × 10\(^{-2}\) mbar [243].
Figure 4-6 ATR-FTIR spectrum of damaged octa-methyl POSS cages by plasma with heat system with a comparison of untreated POSS. The shift of peak Si-O-Si presented the structure change from cage to chain

4.1.2.5 Characterization by X-ray photoelectric spectroscopy

The XPS results provide more evidence of the impact of the plasma treatment on the cage structure and about the type of nitrogen containing functional groups. From the Si2p spectra, the native POSS material exhibits peaks at 102.4 and 102.8 eV which correspond to the Si-C and Si-O bonds from the (CH3SiO1.5)8 cage structure (Figure 4-7a) [244-247]. New peaks appear for all plasma powers at 103.1 eV and 103.6 eV, which also correspond to the Si-C and Si-O bonds of the core cage respectively (Figure 4-7b, c, and d) [239, 245, 248]. The slight shift of these peak positions, compared to the untreated POSS spectrum, was attributed to the environmental change surrounding Si-C and Si-O bonds after plasma treatment (the positions of peaks are displayed in Table 4-2) [244, 246, 249]. The appearances of Si-C and Si-O bonds from XPS indicate that after plasma treatment, the (Si-O-Si) cage structural bonds in POSS are maintained. Theoretically, the silicon-based bonds should be the most difficult bonds
to break due to a higher bond energy. The ratio of the area corresponding to the fitted Si-C and Si-O peaks was calculated to evaluate the proportion of structural bonds over the 80, 100, and 130 W plasma treatment. The ratios presented in Figure 4-8a are found to be constant at around 1 for all the samples. Additionally, the fitted area changes of component peak are obtained in Table 4-2 and the minimum chi-square values for goodness of fitting are presented in Table 4-3 which demonstrates the stability of the core cage bonds [250-252]. This analysis suggests that the silicon cage structure was not physically altered. The effect of the change in electronic environment is also obvious on the O1s spectra for the plasma treated samples (Figure 4-9a, b, c, and d) compared to the untreated sample. The untreated sample exhibits a single peak at 532.2 eV, corresponding to O-Si bonds from O3-Si-CH3 (Figure 4-9a) which is attributed to the cage corner structure [253]. After plasma treatment, the O1s spectra of all treated samples can be divided into three peaks (Figure 4-9b, c, and d) at 531.3 eV, 532.8 eV, and 534.1 eV, which corresponded to amide (O=C), cage structure with methyl group terminal (O-Si-CH3), and cage structure with modified methyl group terminal (O-Si-C-NH), respectively (the positions of peaks are shown in Table 4-2) [253]. Therefore, the peak shifts were attributed to a change of the surrounding environment of core cage, and related to alteration of the methyl groups [254, 255].
Figure 4-7 Insert spectra of XPS high resolution scale for Si2p to determine the shift of peaks after plasma: a) untreated POSS, b) 80 W with 10 % DC plasma treated POSS, c) 100 W with 10 % DC plasma treated POSS, d) 130 W with 10 % DC plasma treated POSS, e) 80 W with 5 % DC plasma treated POSS, and f) 80 W with 20 % DC plasma treated POSS
Figure 4-8 The comparison of the relative area from XPS fitted peaks for bonds: a) XPS Si2p spectra fitted peak area ratio of Si-C/Si-O for all experiments, and b) POSS functionalization percentage ratio for amine (C-N) and amide (CO-NH) groups from carbon concentration (C1s area)
Figure 4-9 Insert spectra of XPS high resolution scale for O1s to determine the O contained bonds: a) untreated POSS, b) 80 W with 10 % DC plasma treated POSS, c) 100 W with 10 % DC plasma treated POSS, d) 130 W with 10 % DC plasma treated POSS, e) 80 W with 5 % DC plasma treated POSS, and f) 80 W with 20 % DC plasma treated POSS.

In Figure 4-10a and b, the survey spectra provide the general overview of the atomic concentration change and the appearance of nitrogen content after plasma
treatment. As opposed to what may be expected, the N uptake decreased with increased power input. As seen in the Cls spectra, the bonding between nitrogen and carbon was altered upon plasma treatment and two new peaks appeared compared to the native POSS (Figure 4-11a, b, c, and d). The pristine POSS nano-particles (Figure 4-11a) did not contain any nitrogen elements and the main peak in Cls spectrum located at 284.8 eV, representing the C-H bonds of the cornered methyl groups on POSS cage [244]. The nitrogen-contained bonding (i.e. amine and amide) was clearly visible on the N1s spectra for all the treated samples (Figure 4-12) [256]. The nitrogen content was found to however decrease from 1.9 at.%, 1.5 at.% to 1.1 at.% along with the increase of the input power. Two new peaks at 285.6 eV and 288.8 eV are appeared across the Cls spectra of 80, 100 and 130 W plasma treated samples, which was attributed to C-N from amine and CO-NH from amide functional groups [191, 193, 199]. The existence of amide groups was likely related to the ageing effect, which came from the reaction between activated amine groups and oxygen during post-treatment air exposure with still reactive corner sites [173, 257, 258].

In Figure 4-13a, the N/C and N/Si ratios are plotted to represent the efficiency of the functionalization. The 100 W plasma treated samples exhibits the highest N/C ratio, at about 8.2 %. However, this higher ratio could come from the decrease of the carbon content from the surface of the POSS, due to increased etching effects leading to the methyl groups elimination at higher power treatment. Therefore, the efficiency based on the silicon content was presented since silicon-containing bonds (i.e. Si-O-Si) was not found to be affected by the plasma treatment. Hence, the highest total nitrogen amount, at 7.1 % efficiency (N/Si) was found to be achieved for the 80 W samples. Furthermore, the functionalization ratio in Figure 4-8b is presented by amount of carbon (Cls area) functionalized with nitrogen containing functional groups
(C-N area) and amides (CO-NH area) which presents a highest ratio of 45 % in the 80 W treated sample.

Figure 4-10 XPS survey spectra for a) power series, b) duty cycle series, c) TFBA power series, and d) TFBA duty cycle series
Figure 4-11 XPS high resolution spectra of C1s to determine the change on C contained bonds and the appearance of N contained groups: a) Untreated POSS, b) 80 W with 10 % DC plasma treated POSS, c) 100 W with 10 % DC plasma treated POSS, d) 130 W with 10 % DC plasma treated POSS, e) 80 W with 5 % DC plasma treated POSS, and f) 80 W with 20 % DC plasma treated POSS
Figure 4-12 High-resolution spectra of N1s from XPS data for detecting the amine and amide intensities of related areas included untreated and treated POSS: a) Controlled sample; b) 80 W with 10 % duty cycle plasma treated sample; c) 100 W with 10 % duty cycle plasma treated sample; d) 130 W with 10 % duty cycle plasma treated sample; e) 80 W with 5 % duty cycle plasma treated sample; f) 80 W with 20 % duty cycle plasma treated sample
Figure 4-13 The efficiency of functionalization with the selectivity of primary amine: a) Efficiency of functionalization from ratios of N/C and N/Si, and b) the degree of functionalization (NH$_2$/C) and selectivity (NH$_2$/N) at the surface of both series of plasma treatments with different plasma power (i.e. include both CW and P power) and different duty cycle.

Although the efficiency of the N/Si functionalization presents a measure of nitrogen content, it is not sufficient to quantify the different nitrogen containing functional groups in detail. This is because the chemical shifts of nitrogen signals in the C1s and N1s spectra were too difficult to deconvolute due to their proximity [193]. Hence, in order to quantify quantitatively the functionalization degree (NH$_2$/C) and
selectivity (NH$_2$/N) of primary amine groups across the POSS cubic structures formed during the plasma treatment when there was no imine groups observed, a derivatization reaction between the primary amine and TFBA was carried out [191, 193, 259, 260]. During the derivatization reaction with TFBA, the C-NH$_2$ groups were converted to imine -HC=\=N-C- groups for bonding TFBA molecules. In Figure 4-10c and d, the XPS survey spectra suggest the appearance of F1s which correspond to the NH$_2$ groups. The XPS spectra of C1s, O1s, Si2p, N1s, and F1s are shown in Figure 4-14, Figure 4-15, Figure 4-16, Figure 4-17 to estimate the amount of terminal CF$_3$ and calculate the amount of primary amine. The amount of primary amine groups were therefore assessed quantitatively after grafting of the TFBA [105, 191]. The NH$_2$/C, and NH$_2$/N ratios for both series of experiments are presented in Figure 4-12b.

In the series of plasma power experiments, the 80 W plasma treatment led to the highest functionalization degree (NH$_2$/C) and selectivity (NH$_2$/N), as shown in Figure 4-13b as 1.5 % and 18.7 % respectively. Therefore, it results one N atoms per 16 sites (i.e. 2 cages) and one primary amine groups per 80 sites (i.e. 10 cages) from the XPS atomic percentage of components. However, since POSS material was presented as a powder in the experiment which cages were aggregated into big micro-particles, therefore plasma was hard to affect all cages in the agglomeration. Then, calculation with assumption of only first layer without bottom surface of the agglomeration can be functionalised by plasma. The estimation became 4.2 N atoms per sites while 6 primary amine groups per 8 sites (i.e. one cage). Hence, statistically, the cages on the surface of agglomeration should catch more N-moieties then the centre and bottom of the cluster. The solution of aggregation will be studied using stirring plasma system which has been used in carbon nanotubes [199]. The wet chemical route for POSS functionalization usually provides a higher yield but with
exceed 100 % reactant for introducing primary amines and requires a longer duration for the reaction [78, 94, 261]. Therefore, although plasma functionalization of POSS cannot offer same yield as wet chemical method, it requires gentle gases reactants and less waste production as a single environmental friendly functionalization process. Generally, the formation of primary amine is arising from the NH radicals generated within the plasma [262, 263]. At higher power input, more energetic plasma reacted species might destroy the NH2 groups which were already grafted on the surface of POSS [262, 264]. Therefore, the threshold of higher energy reached at powers higher than 80 W reduces the formation of amine groups across the POSS materials. Hence, compared to the 100 and 130 W plasma, 80 W plasma likely led to less ion bombardments, thus maintaining a higher level of functionality. It therefore appears that relatively lower plasma powers, which are more effective to functionalise POSS corners.
Figure 4-14 XPS high resolution spectra of C1s for TFBA treated POSS: a) untreated POSS, b) 80 W with 10 % DC plasma treated POSS, c) 100 W with 10 % DC plasma treated POSS, d) 130 W with 10 % DC plasma treated POSS, e) 80 W with 5 % DC plasma treated POSS, and f) 80 W with 20 % DC plasma treated POSS
Figure 4-15 XPS high resolution spectra of Si2p for TFBA treated POSS: a) untreated POSS, b) 80 W with 10 % DC plasma treated POSS, c) 100 W with 10 % DC plasma treated POSS, d) 130 W with 10 % DC plasma treated POSS, e) 80 W with 5 % DC plasma treated POSS, and f) 80 W with 20 % DC plasma treated POSS
Figure 4-16 XPS high resolution spectra of O1s for TFBA treated POSS: a) untreated POSS, b) 80 W with 10 % DC plasma treated POSS, c) 100 W with 10 % DC plasma treated POSS, d) 130 W with 10 % DC plasma treated POSS, e) 80 W with 5 % DC plasma treated POSS, and f) 80 W with 20 % DC plasma treated POSS
Figure 4-17 High resolution spectra of XPS for a) N1s after TFBA derivatization for both untreated POSS and plasma treated POSS, b) F1s after TFBA derivatization for both untreated POSS and plasma treated POSS
Table 4-2 The XPS fitted peaks for both untreated POSS and plasma treated POSS

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-H</th>
<th>C-N</th>
<th>CO-NH</th>
<th>O=C</th>
<th>O-Si-CH</th>
<th>O-Si-CN</th>
<th>Si-C</th>
<th>Si-O</th>
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<tbody>
<tr>
<td>Control</td>
<td>284.8</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>532.2</td>
<td>/</td>
<td>102.4</td>
<td>102.7</td>
</tr>
<tr>
<td>80 W – 10 % DC</td>
<td>284.8</td>
<td>285.5</td>
<td>288.8</td>
<td>531.1</td>
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<td>285.7</td>
<td>288.7</td>
<td>531.3</td>
<td>532.7</td>
<td>534.2</td>
<td>103.1</td>
<td>103.5</td>
</tr>
<tr>
<td>130 W – 10 % DC</td>
<td>284.8</td>
<td>285.6</td>
<td>288.7</td>
<td>531.1</td>
<td>532.7</td>
<td>534.2</td>
<td>103.1</td>
<td>103.6</td>
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<td>80 W – 5 % DC</td>
<td>284.8</td>
<td>285.6</td>
<td>288.7</td>
<td>530.9</td>
<td>532.7</td>
<td>534.1</td>
<td>103.1</td>
<td>103.6</td>
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<tr>
<td>80 W – 20 % DC</td>
<td>284.8</td>
<td>286.0</td>
<td>288.9</td>
<td>531.2</td>
<td>532.7</td>
<td>534.0</td>
<td>103.0</td>
<td>103.5</td>
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Table 4-3 Summary of sum of square error of peak fitting

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<thead>
<tr>
<th>$\chi^2$ value</th>
<th>C1s</th>
<th>O1s</th>
<th>Si2p</th>
<th>N1s</th>
<th>Sum</th>
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<tr>
<td>Control</td>
<td>11.8</td>
<td>22.7</td>
<td>7.99</td>
<td>0</td>
<td>42.5</td>
</tr>
<tr>
<td>80 W – 10 % DC</td>
<td>1.61</td>
<td>3.84</td>
<td>6.05</td>
<td>2.82</td>
<td>14.3</td>
</tr>
<tr>
<td>100 W – 10 % DC</td>
<td>1.39</td>
<td>2.92</td>
<td>4.13</td>
<td>1.12</td>
<td>9.56</td>
</tr>
<tr>
<td>130 W – 10 % DC</td>
<td>1.37</td>
<td>2.10</td>
<td>3.07</td>
<td>1.13</td>
<td>7.67</td>
</tr>
<tr>
<td>80 W – 5 % DC</td>
<td>1.97</td>
<td>3.77</td>
<td>5.02</td>
<td>3.61</td>
<td>14.4</td>
</tr>
<tr>
<td>80 W – 20 % DC</td>
<td>5.0</td>
<td>10.5</td>
<td>9.17</td>
<td>4.73</td>
<td>29.4</td>
</tr>
</tbody>
</table>
4.1.2.6 Quantitative $^{13}$C NMR Analysis

The $^{13}$C signal visible at approximately −4 ppm represents the methyl carbon on the unaltered POSS molecule, and, assuming that any chemical modification of the molecular structure will cause this chemical shift to change, this peak thus can be used to quantify the fraction of unaltered POSS shown in Figure 4-18. This peak represents $(3.6 \pm 0.9)$ % of the total $^{13}$C NMR signal intensity observed. It should be noted that this value represents an upper limit to the fraction of unaltered molecules, as smaller $^{13}$C peaks no visible above the noise level cannot be ruled out.

Assuming that the chemical modification of the methyl groups is randomly distributed, this fraction of unaltered molecules is consistent with a (minimum) methyl group modification level of 34 % (i.e., the probability of a molecule being left completely unaltered being $(1 - 0.34)^8 = 0.036$). Therefore, these results suggest that statistically around 34 % of the 8 corners of each cage have been successfully substituted with either nitrogen rich functional groups or oxygen atoms. These results are in an agreement with the general intensities trend obtained during the FTIR analysis, XPS analysis, and for which the 80 W plasma treatment yields the highest substitution ratio.
4.1.3 Influence of the duty cycle in pulse plasma mode

In N$_2$/H$_2$ CW + P plasma treatment, after activation of the POSS surface (i.e. CW plasma), nitrogen containing radicals were produced and led to the formation of amine groups across the surface of the POSS during the pulse (P) plasma [190, 264]. The duty cycle of the P plasma mode corresponds to a sequence during which the power is alternatively switched on and off for fixed durations [264]. Therefore, in the second series of experiments the duty cycle was altered at fixed plasma power to evaluate the impact of duty cycle on the efficiency of the amine functionalization. Since in the first series of experiments, 80 W plasma power was provided the highest amount of nitrogen, therefore this power was used in the second series of experiments and the duty cycle was altered from 5 %, to 10 %, and 20 %.
4.1.3.1 Composition analysis by FTIR

As seen on the FTIR spectra in Figure 4-3c, the band at 1075 – 1135 cm\(^{-1}\) is found to be constant for all samples, which is again corresponded to the Si-O-Si bond. This result indicates, just as for the plasma power series, that the cage structure of the POSS was maintained during and after plasma treatment. In Figure 4-3d, a small variation of the N-H band intensity at 1580 – 1650 cm\(^{-1}\) and the 3400 – 3500 cm\(^{-1}\) has appeared across the all plasma treated samples compared to the control sample. This new band suggests the existence of nitrogen-rich functional groups. The integrity of the cage structure was further confirmed by XPS results, where all the plasma treated samples obtain similar Si2p spectra (Figure 4-7b, e, and f). The proportion of structural bond Si-O (103.7 eV) and corner bond Si-C (103.3 eV) (Figure 4-8a) related to cage structure also exhibit similar values compared to the control sample, which support the hypothesis of the unchanged POSS structure upon plasma treatment.

4.1.3.2 Composition analysis by XPS

Peaks in the O1s spectra for the duty cycle series (Figure 4-9b, e, and f) at 531.2 eV and 534.1 eV correspond to O=C from amide bonding and O-Si-CN [253] while the C1s spectra (Figure 4-11b, e, and f) confirm that C-N and CO-NH bonds has appeared. Additionally, the N1s spectra (Figure 4-12b, e, and f) further support the FTIR results since only amine and amide groups are found to be introduced upon plasma treatment on the POSS materials. The 10 % duty cycle samples yield the highest atomic percentage of nitrogen element as 1.9 % and for a functionalization efficiency (N/Si) of 7.1 % (Figure 4-13a). On the other hand, lower amounts of nitrogen-containing functional groups are achieved at 5 and 20 % in Figure 4-13a. A higher value of N/C was obtained at 20 % duty cycle treatment, but it was likely due
to the carbon atom loss compared to the other samples. This result suggests that the most efficient set of plasma parameters for stabilizing the nitrogen rich corner functional groups was reached at 80 W and 10 % duty cycle plasma. After TFBA derivatization, the 10 % duty cycle plasma treatment was also gained the highest functionalization degree (i.e. 1.5 %) and selectivity (i.e. 18.7 %) which was matched the first series of experiments (Figure 4-13b).

Since the input power for the second series of experiments was fixed at 80 W, the effect of plasma on POSS surface should be same for all samples in the CW plasma phase. The higher selectivity for the formation of primary amine groups resulted from a suitable time length of both plasma on and off-time periods, which were controlled by the duty cycle in the pulse plasma phase. It appears that at 10 % duty cycle the highest selectivity and efficiency of functionalization was reached. Although a longer \( t_{\text{off}} \) time in duty cycle with shorter \( t_{\text{on}} \) time (5 % DC) led to a comparable ratio of N/Si to 10 % duty cycle sample, the selectivity (\( \text{NH}_2/\text{N} \)) was however found to be lower. This effect may be due to shorter \( t_{\text{on}} \) time for generating nitrogen containing species required for grafting primary amine groups [235]. The shorter \( t_{\text{off}} \) time with longer \( t_{\text{on}} \) time (20 % DC) also led a decrease of both efficiency and selectivity. This condition may not only correspond to a destruction of introduced N-moieties on POSS surface due to a longer plasma time, but also a shorter time for grafting primary amine groups [235, 265].

These results suggest that 80 W treated samples with 10 % duty cycle lead to a higher degree of primary amine functional groups introduction and thus a greater degree of efficiency for the sought purpose.
4.1.4 Summary

This work has investigated for the first time the plasma functionalization of octa-methyl polyhedral oligomeric silsesquioxane (POSS) by low-pressure sequential continuous wave (CW) followed by pulsed (P) plasma mode in a nitrogen/hydrogen gas environment. The collective outcomes of the data gathered from XPS, and FTIR evidence that this methodology was effective in functionalising the crystalline octa-methyl POSS materials with terminal nitrogen rich species including primary amine and amide functional groups without damaging the core cage structure of the POSS materials. While the results reported here are confined to one type of POSS derivative the results provide a new platform to template POSS materials with a controllable degree of functionality using an environmentally friendly yet more effective methodology.
4.2 Functionalization with stirring plasma system

4.2.1 General introduction

The functionalization of the POSS nano-particles by the low-pressure plasma described in Section 4.1 was still limited in terms of scalability for producing enough quantities (< 10 mg) of functionalized nano-particles for further processing. The implementation of a different equipment design, called stirring plasma system at low-pressure, was used to functionalize POSS samples with over 60 mg per run, as shown in Figure 4-19.

A magnetic stir bar is used at the bottom of the chamber to homogenise the powder sample in order to continuously expose fresh surface of the nano-particle to face the plasma glow and introduce target functional groups to the sample. This
configuration allows for “bulk” plasma modifications by supporting a more homogeneous surface treatment particularly relevant for powder sample. Therefore, as opposed to the low-pressure reactor system where only field-of-view functionalization was achieved, a higher amount of powder sample can be treated continuously with the stir plasma system. The size of the powder sample must also be considered since small (nanoscale) particles may stick onto the wall of the chamber due to electrostatic interactions thus limiting the treatment uniformity. Due to the poor vacuum levels from the stirring plasma system compared to the low-pressure plasma polymerization system, nitrogen functional groups grafting is not considered at this stage due to the oxygen species replaced nitrogen species introduction. Therefore, oxygen plasma is considered for scaling up the production with the current system. The result obtained for this system for the oxygen gas plasma functionalization of octamethyl POSS in stirring plasma system is here presented and discussed to produce carboxylic and hydroxyl functionalized POSS. Ar plasma pre-treatment has also been used in all experiments of the stirring plasma system for cleaning the surface of the POSS as well as initialing the activation of the surface.

**4.2.2 Effects from different plasma mode**

Three different plasma modes were investigated to study the difference between each mode towards a high efficiency of functionalization of octa-methyl POSS nano-particles with the stirring plasma system. Therefore, first of all, at fixed energy input, CW only, pulsed only, and CW followed pulsed plasma modes were demonstrated for comparison.
The mechanism for plasma functionalization in the low-pressure environment is the same for the stirring system as that previously discussed [199]. The stirring system only offers continuous exposure of fresh powder samples to the plasma glow. Plasma provides high energy to reach the excitation or ionization state of the C-H bonding, thus forming or replacing the H atoms with other elements or functional groups to alter the chemical properties [105, 191].

The oxygen gas plasma was used to generate oxygen-rich functional groups such as carboxylic and hydroxyl [266] on octamethyl POSS nano-particles which studied by FTIR spectra. In Figure 4-20a, three treatments with the same power input at 550 W.min are against the control POSS to investigate the impact of plasma (i.e. 11 min for CW only, 55 min for pulsed only, and 35 min for CW + P plasma). In Figure 4-20b, a slight difference is observed in the range of 1030 to 1100 cm\(^{-1}\) which corresponds to the changing of the structure from Si-O bonding.

The density of the resulting bonds was studied by evaluating the intensity of the bands corresponding to the chemical structure of octamethyl POSS as shown in Figure 4-20c and d [244]. The ratio of C=O (1610 cm\(^{-1}\))/Si-O and –OH (3300 cm\(^{-1}\))/Si-O were investigated to demonstrate the relative amount of possible carboxylic and hydroxyl groups compared to core Si-O-Si structure. All three plasma treated samples contain higher ratios of the C=O and -OH bands against Si-O with at least 42.8 % increase compared to the control POSS. Therefore, since the control octamethyl POSS only contains methyl –CH\(_3\) groups, the appearance of C=O and –OH can be interpreted as a demonstration of oxygen-containing groups [267]. In Figure 4-20c, pulsed only plasma mode indicates a 22 % increase of C=O/Si-O compared to the CW only and CW + P plasma modes suggests a higher amount of potential carboxylic groups introduction compared to other two modes. On the other hand, CW + P plasm mode
yields a higher ratio of –OH/Si-O which indicates potential hydroxyl groups formation, corresponding to an increase of 147 % compared to CW only and P only plasma modes. Therefore, as from the comparison in Figure 4-20c, CW only plasma suggests a successful activation and introduction of the oxygen-containing groups on octamethyl POSS, however limits with the amount of functional groups. Pulsed only plasma presents a highest amount of functionalization to potential carboxylic groups (C=O band) which was due to the sufficient time for the survived free radicals to form functional groups during the interval of $t_{on}$ and $t_{off}$. The CW alone and the CW in the CW+P plasma mode suggested a longer duration of plasma activation and functionalization across the POSS and continuously excited the bonds within the structure compared to pulsed alone plasma. Therefore, with the continuous excitation of bonding, the formed C=O bonds from the recombination of oxygen species on the CH$_3$ corner will be etched again and then form the more stable –OH groups compared to C=O. Hence, CW+P plasma mode with a long duration of activation from CW and stabilization of functional groups from pulse plasma mode suggest the highest –OH amount from FTIR. The combined plasma mode gains both advantages on activation and functionalization as a presence of highest –OH groups with same density of C=O with CW only plasma which enhanced the existence of oxygen containing functional groups on octamethyl POSS. Thus, the combined plasma mode demonstrated an effective functionalization by stirring plasma system for octamethyl POSS nanoparticles.

Furthermore, a slight difference of the bands at 1030 to 1100 cm$^{-1}$ corresponding to Si-O bonds was found, which may be due to different plasma modes and can be divided to R-SiO$_3$ (R refer to CH$_3$) structure from cage-like POSS and SiO$_2$ structure from possibly opened cage-like structure [268]. The spectrum of the bare
octamethyl POSS shows that the R-SiO$_3$ structure is visible at 1080 cm$^{-1}$ therefore a shoulder-liked band at 1030 cm$^{-1}$ can be interrupted as SiO$_2$ structure (Figure 4-20b) [268, 269]. Hence, ratios of intensities for R-SiO$_3$ and SiO$_2$ are estimated from the spectra as shown in Figure 4-19d, which higher the SiO$_2$ band intensity leads a higher possibility losing cage-like structure of octamethyl POSS nano-particle. When the shifting of band to 1030 cm$^{-1}$ shows a higher intensity than 1080 cm$^{-1}$, the integrity of the POSS particles may be compromised, leading to an open cage structure [269]. Due to the higher ratio of R-SiO$_3$ compared to SiO$_2$ bands, all three plasma treated POSSs confirmed in that methyl groups have been replaced by carboxylic groups and hydroxyl groups without influence on the cage-like structure. Therefore, analysis for CW only and pulsed only plasma were investigated for understanding the effective conditions for combined CW + P mode to improve the functionalization yield for the octamethyl POSS nano-particle.
Figure 4-20 FTIR spectra for different plasma mode (CW only, P only, and CW+P) with same energy input 550 W.min, a) whole spectra for all the sample, b) shifting behaviour for the Si-O-Si band compared to control POSS, c) intensity ratio change for bands -OH and C=O, d) intensity ratio change for R-SiO₃ (Si-O-Si for cage-like structure) and SiO₂ (Si-O-Si for cage opening as chain structure) against total Si-O

4.2.3 Composition analysis through different plasma power

As the highest density of the functionalization resulted from the CW + P plasma mode, further control of the conditions were discussed to improve the yield of functionalization. Hence, as for the low-pressure gas plasma system, the power for both CW and pulsed modes and duty cycle for pulsed plasma was changed to alter the production of functional groups [190, 259].
CW only plasma mode has been used to investigate the degree of functionalization which mainly corresponded to the equivalent activation step during the CW + P plasma mode [191]. Pulsed only plasma could provide an enhancement of C=O density towards the formation of target carboxylic acid groups which mainly enhanced amount of functional groups formation during the combined plasma mode. Therefore, single CW from 50 to 100 W, single pulsed plasma modes from 50 to 150 W were investigated for the trend of functionalization in different powers for single plasma mode. The combined CW + P plasma treatments with CW power from 50 to 80 W or pulsed power from 50 to 150 W were investigated to discuss the energy input related to the yield of functionalization. Furthermore, the duty cycle was the other parameter discussed under same power input during the CW + P modes which focused on 5 % and 10 %. The general comparison between previous low-pressure gas plasma and stirring plasma for nitrogen-containing functional groups introduction was demonstrated at the end.

4.2.3.1 Effect of power in the CW plasma mode

In the CW only plasma, exciting and ionizing bonds of the input materials were studied with 50, 60, 80, and 100 W and same duration for all treatments. The effect of Ar pre-treatment was also demonstrated compared to the reference with no Ar pre-treatment and analysed by FTIR as shown in Figure 4-21.

First of all, the appearances of C=O (1610 cm\(^{-1}\)) and –OH (3300 cm\(^{-1}\)) represent the oxygen-containing functionalities in FTIR from all treated samples compared to controlled octamethyl POSS (Figure 4-21). Hence, began with 50 W plasma treatment, oxygen-rich functional groups could introduce on POSS nano-particles and reach a
highest ratio of band intensity of C=O/Si-O and –OH/Si-O at 100 W as shown in Figure 4-22a. Thus, the C=O/Si-O ratio is increased by 90 % at 100 W compared to 50 W and –OH/Si-O ratio is increased by 350 % at 100 W compared to 50 W treated sample. Therefore, the absence of new moieties visible on IR likely suggests replacement by H atoms in the methyl sites.

However, as discussed previously, with higher energy input it is easier to break down the cage-like structure of the nano-particle which lose its unique 3-dimension building block property. In a close view of the Si-O band (Figure 4-21b), R-SiO₃ at 1080 cm⁻¹ starts shifting to SiO₂ at 1030 – 1050 cm⁻¹ after 60 W plasma and reached a highest intensity at 100 W suggesting the cage opening. The appearance of CH₂ out of plane bands at 950 cm⁻¹ is shown in 100 W treated POSS leads a significant decrease of the methyl groups on POSS. The band at 2700 cm⁻¹ is referred to Si-CH₃ also has decreased due to the loss of methyl groups. In addition, a small shift from 1100 to 1090 cm⁻¹ at 50 W without Ar plasma would be due to the effect of replacement on CH₃ groups which stretched the Si-O bonding. In Figure 4-22b, ratios of R-SiO₃ and SiO₂ against total Si-O indicate an increase of density for bonding SiO₂ due to the loss of R (CH₃) groups compared to R-SiO₃ from the raw cage-like POSS at 100 W. Hence, POSS nano-particles could become partially condensed cage-like structures with extra –OH groups on the corner Si-O-Si bonding. Therefore, with higher input powers, it is more likely to lose the cage-like structure of POSS nano-particles which the power below 60 W for CW mode is preferred for further investigation.

Furthermore, the comparison between the Ar pre-treatment process and without pre-treatment process is also reported for the ratio of C=O/Si-O and –OH/Si-O, which pre-treatment enhances a 10 % increase of C=O and 180 % increase of –OH compared to no pre-treatment (Figure 4-22c). In Figure 4-21d, the 50 W CW plasma
without pre-treatment of Ar plasma suggests a 14.3% increase of density for R-SiO₃ structures compared to normal 50 W plasma. Normal 50 W plasma results in a 50% increase of the SiO₂ against total Si-O ratio compared to treatment without Ar pre-treatment. Therefore, plasma with pre-treatment provided a better efficiency of functionalization compared to without pre-treatment for octamethyl POSS nanoparticles.

Figure 4-21 FTIR spectra of CW plasma treated POSS with different power under the same duration including 50, 60, 80, 100 W and an extra 50 W without Ar pre-treatment
refer as 50 W*, a) whole spectra of different CW plasma treatments; b) shifting behaviour in the area of 700 cm⁻¹ to 1400 cm⁻¹ for defining the change in Si-O-Si bands

Figure 4-22 The intensity ratio of different bands from FTIR spectra for different CW power and same power but without Ar pre-treatment, a) ratios of –OH/Si-O and C=O/Si-O at different powers, b) ratios of R-SiO₃ (Si-O-Si for cage-like structure) and SiO₂ (Si-O-Si for cage opening as chain structure) against total Si-O for different power, c) ratios of –OH/Si-O and C=O/Si-O through 50 W and 50 W without Ar pre-treatment, and d) ratios of R-SiO₃ (Si-O-Si for cage-like structure) and SiO₂ (Si-O-Si for cage opening as chain structure) against total Si-O for 50 W and 50 W without Ar pre-treatment
To compare the impact of bonding structure shifting on cage-like structure of octamethyl POSS nano-particles at 50 W and possible cage opening at 100 W in CW only plasma, XPS characterization provided complementary information to the IR data shown in Figure 4-23. In the C1s spectra, both 50 and 100 W oxygen plasma treatment provide peaks of 284.8 (C-H), 286.5 (C-O), and 288.8 eV (C=O) which therefore confirmed the appearance of oxygen-containing functional groups on octamethyl POSS nanoparticles [269]. The appearance of the O=C bonding from the fitting in the O1s spectra suggests again the evidence for hydroxyl and carboxylic functional groups, but higher O-Si intensity was found at 100 W which might refer to the damaged cage [105, 248]. Hence, the significant difference in Si2p spectra was obtained due to structure changed as a confirmation of FTIR spectra for 50 and 100 W plasma. The 50 W plasma maintained the structure of Si-C (102.1 eV) and Si-O (102.9 eV) as the plasma modification was successful introduce the oxygen-rich functional groups without etching the cage-like structure. As the large shift of Si-O band from the FTIR at 100 W compared to 50 W plasma, the Si2p spectrum of 100 W only shows a single fitting for Si-O at 103.1 eV represents the SiO₂ structure as a partial condensed cage-like structure [202, 269]. Therefore, XPS confirms the selection from the FTIR characterization that CW plasma power cannot reach too high due to the loss of cage-like structure. Hence, 50 and 60 W CW plasma have been selected for further CW + P mode study.
Figure 4-23 XPS spectra for 50 and 100 W CW plasma treated POSS sample a) and b) C1s for 50 and 100 W, and (c) and (d) O1s for 50 and 100 W, and e) and f) Si2p for 50 and 100 W
4.2.3.2 Effect of power in the P plasma mode

After the determination of CW plasma power for activation of functionalization, the increase of functional groups during the plasma can be achieved by tuning the pulsed plasma in the CW + P plasma mode. In Figure 4-24, 50, 100, and 150 W pulsed only plasma with same duty cycle of 10 % with same pre-treatments of Ar plasma were evaluated by FTIR. Compared to the pulsed plasma, the CW plasma with same power suggested a higher possibility to shift from caged POSS structure to open caged structure which was caused by the longer duration of the plasma excitation phase during the 100 % duty cycle. Appearances of –OH and C=O are found from the spectra which suggest the introduction of hydroxyl and carboxylic functional groups and the close view for Si-O band shows no change in the POSS core Si-O-Si structure. Pulsed plasma usually requires longer durations than CW plasma for the same energy input due to the duty cycle as a repetition duration of fixed time of plasma generated and plasma off. Hence, free radicals with functionality have more time to introduce on the material without affect the cage-like structure of octamethyl POSS nano-particles. In Figure 4-24c and d, the intensity ratios of –OH/Si-O and C=O/Si-O indicate an increase trend through the increase of pulsed power with same duration of plasma while the cage-like structure is maintained due to unchanged ratios of R-SiO₃ and SiO₂. The intensity ratio of –OH/Si-O reached a highest value at 100 W power as an increase of 200 % compared to 50 W but ignorable due to their small intensities. Thus, the pulsed plasma with input power highest at 150 W slightly increase the efficiency of functionalization without affect the cage-like structure from Si-O bonding.
Figure 4-24 FTIR spectra for different power in the pulsed plasma mode with same duration and duty cycle including power 50, 100, and 150 W, a) The whole spectra of three plasma treatments, b) The behaviour of Si-O-Si band in the area of 700 to 1400 cm\(^{-1}\), c) intensity ratio of bands -OH and C=O, d) intensity ratio change of Si-O-Si band come from cage structure (R-SiO\(_3\)) or open cage (chain) structure (SiO\(_2\))

In the XPS characterization, C1s spectra provide fittings of the C-O (286.5 eV) and C=O (288.8 eV) which in an agreement of FTIR bands for carboxylic and hydroxyl groups which are shown in Figure 4-25. The O1s spectra suggest the appearance of O=C (531.9 eV) confirmed the existence of COOH structure with possible O-C=O bonding. The Si-C (102.1 eV) and Si-O (102.9 eV) bonding from the Si2p spectrum suggest that the cage-like structure was maintained since the fitting did not shift to
103.1 eV for single Si-O bonding from SiO₂ structure compared to the damaged cage [248, 269]. Therefore, XPS results provided a same expectation of successful functionalization without cage-like structure opening from pulsed plasma compared to FTIR results. Hence, the pulsed plasma requires an activation except the Ar pre-treatment for octamethyl POSS nano-particles before increasing the amount of functional groups, which makes the CW plasma suitable for the function. Thus, the combined plasma mode CW + P for gaining the activation from CW oxygen plasma followed with continuously formation of functional groups from pulsed plasma should be considered to enhance the degree of functionalization.
Figure 4-25 XPS spectra of pulsed plasma with 100W power treated POSS sample, a) C1s, b) O1s, and c) Si2p spectra
4.2.3.3 Impact of power in the P plasma mode during the combined plasma mode

As the CW only and pulsed only plasma were contains some limitation on improving the yield of functionalization, the combined plasma mode (CW + P) suggested a combination of advantages from both single modes [191]. From Section 4.2.3.1, CW plasma maintained a relatively stable cage-like structure with introduction of oxygen-rich functionality below 60 W, a 50 W CW power was fixed for all treatments in the combined plasma mode to activate the surface of octamethyl POSS nano-particles.

The pulsed plasma power in CW + P was then selected to investigate the relationship between efficiency of functionalization and energy input as the pulsed power were 50, 80, 100, 120, and 150 W. In Figure 4-26a and b, appearances of -OH (3300 cm⁻¹) and C=O (1610 cm⁻¹) in the FTIR spectra for oxygen-containing groups are found from all plasma treatments while the shifts of Si-O bands with the increase of pulsed power after 120 W are presented. The ratio of intensities –OH/Si-O and C=O/Si-O have been studied in Figure 4-26c while the existence of the C=O is maintained with a less than 10 % variation through all pulsed powers. The density of –OH groups presents a less stable ratio compared to C=O and reaches an increase of 125 % compared with other pulsed power. The fluctuated trend of –OH/Si-O ratio suggests the treated POSS with active sites includes C-O, C=O, -OH, and C-H in the plasma could trap CO₂ or water from the environment and varies the intensity of –OH during FTIR. However, again when plasma energy input becomes sufficient, the Si-O band for cage-like structure could start shifting from 1080 (R-SiO₃) to 1030 cm⁻¹ (SiO₂) such as 150 W pulsed power. Thus, the ratio of intensities for R-SiO₃ against total Si-O band presents a decrease of 29 % compared to other powers and SiO₂ against total Si-O band leads an increase of 64.5 %, which are shown in Figure 4-26d. Therefore,
when pulsed power at 150 W, the cage-like structure began to break down for introducing more –OH groups at the corner Si atoms [269]. Hence, relatively highest intensities of C=O and -OH bands can be found at 50 W CW with 100 W pulsed plasma without losing cage property.

Figure 4-26 FTIR spectra for different pulsed plasma power in the combined plasma mode with the same duration, duty cycle, and CW power of 50 W, a) Whole spectra of all combined plasma treatments, b) shift of Si-O-Si band in the area of 700 to 1400 cm⁻¹, c) intensity ratio of -OH and C=O bands, d) intensity ratio of the Si-O-Si band comes from cage structure or open cage (chain) structure.
Due to the possible cage-like structure opening behaviour at 150 W pulsed plasma power, a further analysis for bonding after plasma was processed by XPS for 80, 100, and 120 W pulsed powers. The 50 W pulsed plasma input was not analysed due to the relatively lower input compared to other three powers. In Figure 4-27, all treatments in C1s spectra present the appearance of the C-O (286.5 eV) and C=O (288.8 eV) for hydroxyl and carboxylic groups which as an agreement with FTIR results. In the comparison of O1s spectra, the intensity of the O=C band increases at 100 W and 120 W compared to 80 W which presents as the improvement of the density of carboxylic groups on POSS after plasma. The O-Si band from O1s spectra also presents a continuously increase in intensity, which could suggest more bonding of Si-OH formatted due to the possible cage-like structure opening. In Si2p spectra, the Si-O structure for the core cage-like structure is possibly maintained due to the existence of Si-C (102.1 eV) and Si-O (102.9 eV) [202, 248, 269]. However, the decrease of the total Si content at 120 W pulsed plasma indicates a loss for the Si-O cage-like structure due to the influence of plasma etching when the input energy over the limit. Therefore, the behaviour of Si-O structure suggested the stable bonding of cage could sustain the power of plasma below 120 W pulsed plasma in combined mode.
Figure 4-27 XPS spectra for plasma condition 50 W CW with different pulsed power (same duty cycle, 10 %) a), b), and c) belong to the 80 W pulsed plasma for C1s, O1s, and Si2p spectra respectively; d), e), and f) belong to the 100 W pulsed plasma for C1s, O1s, and Si2p spectra respectively; g), h), and i) belong to the 120 W pulsed plasma for C1s, O1s, and Si2p spectra respectively.
Therefore, quantifications based on general XPS measurement to determine the amount of carboxylic and hydroxyl groups on the plasma treated POSS nano-particles have been accessed and are shown in Figure 4-28. Compared to the single peak from the control POSS discussed in the previous low-pressure gas plasma functionalization which referred as methyl groups (C-H), oxygen plasma functionalized POSS reported C-H, C=O, and C-O. According from the appeared fitted area in the C1s spectra, the amount of methyl groups (C-H), carboxylic groups (C=O), and hydroxyl groups (C-O) have been calculated to present the rate of functionality increase with increased power. Since a single octamethyl POSS nano-particle contains 8 sites of methyl at cage corners in this project, C=O and –OH gain a continuously increase of modified sites on POSS when pulsed plasma power increases as shown in Figure 4-28. The 120 W pulsed plasma suggests a 28.9 % increase of COOH (carboxyl) as 1 groups per POSS nano-particle compared to 80 W treated sample, while the –OH (hydroxyl) increased by 33.3 % as 1.2 groups per nano-particle. Therefore, without losing cage-like structure from the POSS nano-particle, the pulsed plasma power in the combined mode functionalization results in a nearly “1” carboxylic group per POSS cage.
4.2.3.4 Impact of power in the CW plasma mode during the combined plasma mode

Compared to pulsed plasma power, the power of CW plasma would also affect the yield of functionalization in the CW + P mode. Therefore, the target to maintain the structure of the cages after plasma at 50, 60, and 80 W power with the CW plasma mode were investigated to establish the relationship between the CW plasma power and the efficiency of functionalization. The limit of the CW plasma power was studied previously in the CW only section, which the threshold plasma power has been found at 80 W. Furthermore, a comparison of 5 % and 10 % duty cycle in the pulsed plasma was presented in the 60 W CW with 100 W pulsed plasma to investigate the effect from the duration for functional radicals introducing during the plasma switch off interval.

In Figure 4-29a and b, all plasma powers perform similar features as the appearance of the C=O (1610 cm$^{-1}$) and –OH (3300 cm$^{-1}$) which firstly represent the
introduction of oxygen-containing functional groups [248, 250]. The density of the functional groups can be interrupted by the ratio C=O/Si-O and –OH/Si-O which the 80 W power suggests a 10 % increase of C=O and an 163 % increase of –OH compared to 50 W (Figure 4-30a). In the band of Si-O at 1030 – 1100 cm\(^{-1}\), it is significant that when the CW power reached 80 W, a similar feature of Si-O shifting occurred as the 100 W CW only plasma in Figure 4-21 suggesting the cage-like structure opening [269]. Compared to 80 W, the 50 and 60 W CW powers maintained the features of R-SiO\(_3\) at 1080 cm\(^{-1}\) with small shoulder signal from SiO\(_2\) (1030 cm\(^{-1}\)) which represent the cage-like structure maintained with successful introduction of functional groups. In Figure 4-30b, the ratio of R-SiO\(_3\)/Si-O and SiO\(_2\)/Si-O presents the effect from the plasma power on the cage-like structure. The power of 80 W indicates a larger ratio from SiO\(_2\) than R-SiO\(_3\) while 50 and 60 W remain a larger R-SiO\(_3\) ratio than SiO\(_2\). Therefore, CW power for oxygen plasma was defined as below the 60 W to maintain the cage-like structure of POSS nano-particles.

Furthermore, in the CW power of 60 W, 10 % duty cycle performs an increase of C=O by 33.3 % compared to 5 % duty cycle while an increase of –OH by 83.3 % under same Si-O density compared with 5 % duty cycle in the pulsed plasma which are shown in Figure 4-30c. The behaviour of the Si-O has also analysed through the ratio of R-SiO\(_3\) and SiO\(_2\) for 5 and 10 % duty cycle, but no shifting of Si-O bonding was observed, which indicates the 5 % duty cycle can effectively increase the yielding of the functionalization without, lose cage-like structures (Figure 4-30d).

Hence, the slightly increase of duty cycle provides higher energy input for plasma to tune the yield of the functionalization with ignorable effects on cage-like structure except 100 % duty cycle which towards an open cage-like structure.
Figure 4-29 Spectra of FTIR for the different CW plasma power in the combined plasma mode and an additional experiment on different duty cycle in the same combined plasma mode, a) whole spectra of all treatments, b) behaviour of Si-O-Si band in the range of 700 and 1400 cm\(^{-1}\)
Figure 4-30 Intensity ratio of bands from FTIR spectra in the different CW plasma power during the combined plasma mode and different duty cycle of P plasma and the comparison of two duty cycles in the 60 W combined plasma treatment, a) ratios of –OH/Si-O and C=O/Si-O through different power, b) ratios of R-SiO₃ (Si-O-Si for cage-like structure) and SiO₂ (Si-O-Si for cage opening as chain structure) against total Si-O for different power, c) ratios of –OH/Si-O and C=O/Si-O through different duty cycle, and d) ratios of R-SiO₃ (Si-O-Si for cage-like structure) and SiO₂ (Si-O-Si for cage opening as chain structure) against total Si-O for different duty cycle.

4.2.3.5 Amine functionalization using stirring plasma system

The N₂/H₂ gases plasma were also performed in the stirring plasma system for scale-up to laboratory use of amine groups introduction on POSS nano-particles.
compared to the previous low-pressure plasma system. However, due to the less strong of vacuum capability in the connection as making removal of trace oxygen difficult. Oxidation from oxygen during plasma was considered a hindrance of the stirring plasma system, which could largely affect the amine functionalization yield by introducing oxygen-rich functional groups. Therefore, the oxidation is easier to replace the bonding C-H in methyl group than amine groups introduction. With the expectation, FTIR spectra presents no difference between O$_2$ plasma and N$_2$/H$_2$ plasma which hardly to define the existence of the N-H bonding on the POSS nano-particle under CW + P plasma without lose the feature of cage-like structure (Figure 4-31). The appearances at 3300 cm$^{-1}$ and 1630 cm$^{-1}$ might present as N-H bonding from amine groups but also overlayed with –OH and C=O groups from carboxylic bonding due to the oxidation during the plasma. Furthermore, a precise analysis of atomic composition was evaluated by XPS measurement showed that the N1s spectrum was absent, confirming the inappropriate treatment condition, as shown in Figure 4-32. Therefore, it confirms that the appearance at 1630 cm$^{-1}$ is more likely come from the oxidation of methyl groups and form C=O groups on the POSS nano-particle towards the limitation of the stirring plasma system. Hence, stirring plasma system requires improvements on sealing for functionalization of amine groups.
Figure 4-31 FTIR spectra for a comparison of oxygen, and nitrogen with hydrogen mixture plasma treatments presenting a) whole spectra of all treatments with controlled POSS, b) Si-O-Si behaviour compared to pristine POSS in the range of 700 to 1400 cm\(^{-1}\).
Figure 4-32 XPS spectra for combined plasma mode, 50 W CW with 100 W pulsed plasma for an N\textsubscript{2}/H\textsubscript{2} gases treatment for amine functionalization a) C1s, b) O1s, c) Si2p, and d) N1s spectra
4.2.4 Summary on stirring plasma functionalization

Low-pressure stirring plasma system provided successful oxygen-bearing functional groups introduction across the corners of the octamethyl POSS nanoparticles. The highest yield of the functionalization under current demonstration was nearly one hydroxyl and one carboxyl group per POSS nano-particle. The quantification was performed by analysing the XPS spectra in the C1s region based on the combined mode of CW 50 W and pulsed 120 W plasma with oxygen gas. However, since cross-linking usually requires two reactive sites to bridge a connection between polymeric chains and nano-particles, one carboxyl group alone cannot form a network. Hence, improved density of functionalized sites is still required in the plasma process for modifying POSS nano-particles.

In the functionalization of nitrogen-containing functionality, but XPS spectra proof the hardness of the amine introduction which due to the limitation of sealing. Furthermore, to improve the yield of functionalization other than improving the sealing, a better reactive precursor includes NH3 or amine containing monomers to instead of N2/H2 for plasma could enhance the introduction of amine functionality on octamethyl POSS nano-particles [270].

Therefore, current stirring plasma system for functionalizing POSS nanoparticles still requires further improvement for introducing nitrogen-containing functionality. Both enhancement of vacuum environment during the plasma and high reactive precursor could potentially lead the production raising. The increase of sites for oxygen-containing functional groups on POSS would also be achieved by careful control of vacuum and preparation of non-aggregated POSS nano-particles by a sublimation process.
4.3 General Conclusions

Direct functionalization of octamethyl POSS nano-particles was successfully performed with low-pressure plasma systems leading to the introduction of nitrogen-rich or oxygen-rich functional groups in lieu of the native methyl groups present across the cage corners. The degradation of the POSS cage-like structure has prevented by controlling the input energy for generating plasma to modify the nano-particle. The number of functional groups introduced on the 8 sites of POSS cage-like structure has tuned by input plasma energy allowing a semi-controllable degree of functionalization. The amount of solid octamethyl POSS nano-particles for functionalization was also increased with the stirring system to continuously expose nano-particles to the plasma.

However, the average degree of functionalization was limited to 1 carboxylic groups per POSS nano-particle, which is insufficient for bridging the POSS to polymeric chains during the synthesis of the nano-composite membranes. The amine groups were not successfully generated with the stirring plasma process which was attributed to the poor vacuum environment. Lab-scale production of oxygen-containing functional groups on POSS nano-particles was achieved with less than 1 h duration compared to more than 1 day duration from wet chemical functionalization [94, 96, 271].

Further improvements on vacuum condition as less than $10^{-4}$ mbar environment for stirring plasma to reduce the oxidation effects from air contamination. The selected precursor for introducing functional groups can be altered by a more reactive gas or monomer to improve the density of functional groups in the plasma. The preparation of nano-particle into nano-scale distribution in the plasma can effectively enhance the degree of functionalization.
Chapter 5 POSS nano-composite thin film composite fabrication

5.1 General introduction

Nano-composite membranes offer a number of advantages in separation applications since selectivity and permeation may be finely tuned by controlling the interface between the nanofillers and the main matrix [272]. This approach allows for control of free volume, porosity, and surface charge towards pathways for selective nano-sieving [273]. POSS has been discussed as a unique and flexible nano-particle suggested the high crystallinity in the nano-composite to design suitable free volumes and surface charges for nano-composite membranes [18, 274-277]. Recent works highlighted that barriers with thicknesses below the 100 nm benchmark have potential to lead to highly enhanced fluxes, without impeding selectivity [63]. To develop a simple fabrication compared to the lengthy wet chemical processes with challenges on agglomeration of nano-fillers [136, 142, 278], plasma polymerization is focused on depositing thin film coatings with aerosol-assisted method [279, 280]. Therefore, in this chapter, uniform distribution of POSS nano-particles in the process of plasma polymerization will be discussed through size distribution characterization in HMDSO solution. The aerosol generation will be also studied for reducing the size of aggregates towards the homogeneity of produced nano-composite. POSS nano-composite thin films will be demonstrated by an atmospheric pressure plasma with lateral configuration and aerosol-assisted strategy on PSf supporting UF membranes for ethanol-water separation. Interactions between POSS nano-particles and matrix will be studied by characterizations of chemistry and membrane performance. The other
configuration of atmospheric plasma as through the electrodes (i.e. showerhead) will then introduced for larger effective deposition area compared to lateral electrodes [281]. Benefits and limitations will be discussed by the comparison of two systems to summarize the possibility of plasma technique on the fabrication of thin film nano-composite membranes.
5.2 POSS dispersion during the process

HMDSO monomer is a silicon-based monomer with Si-O-Si backbone and methyl groups at the terminal which is similar to the octamethyl POSS nano-particle and provides PDMS-liked materials after polymerization. The HMDSO was first mixed with POSS nano-particles to form a suspension. This suspension is then used to generate in the later stage of the work an aerosol with an atomizer, prior to being injected into the plasma reaction zone. Therefore, in order to have the homogenous structure of the film, the dispersion of the POSS nano-particle in the HMDSO monomer is critical and must be controlled. This section details the protocols evaluated to optimize the particle size distributions in the suspensions.

5.2.1 Dispersion of POSS in the solution

Octamethyl POSS nano-particles may aggregate in solution rapidly as their small size even after probe sonication and were tested in ethanol solution prior HMDSO solution by DLS to evaluate the particle size which as shown in Figure 5-1a and b. In ethanol solution with 0.1 wt.% concentration of POSS, 5 min sonication suggests an average particle size of 700 nm as a 58.8 % decrease from the non-sonicated solution at 1.7 µm. In Figure 5-1b, the POSS particle size does not further decrease after 5 min sonication represents the ethanol cannot disperse POSS into nanoscale particles due to aggregation. When POSS dispersed in HMDSO solution to prepare the precursor of nano-composite fabrication, DLS data performed the particle size of POSS with different probe sonication duration to investigate the behaviour of POSS in the precursor. In Figure 5-1c and d, the particle size of POSS is slightly decreased by 5 % after 5 min sonication to 1190 nm and is further decreased by 11 % after 15 min as a trend of decreased size with increased duration until 30 min to
maintain a size of around 1000 nm. The fast aggregation of POSS nano-particles in HMDSO is observed by a large variation of particle size in the repetition measurements for a 5 min sonication as shown in Figure 5-1d. Compared to ethanol solution, HMDSO solution presents an higher particle size of POSS in the solution after sonication, which represents not only aggregation occurred, but also network formation between HMDSO and particles. Therefore, according to the particle size distribution of DLS, the dispersion of POSS in HMDSO cannot reach a particle size less than 100 nm to produce ultra-thin film less than 50 nm. However, atomizer as the second dispersion process in the nano-composite fabrication of POSS/HMDSO usually produces a droplet with size less than 200 nm which can effectively break down the agglomeration of POSS clusters.
Figure 5-1 Particle size distribution from dynamic light scattering measurement for 0.1 wt.% POSS in the ethanol and HMDSO monomer with different sonication duration, a) particle size distribution in ethanol, b) Z-average value for the POSS nano-particle in ethanol, c) particle size distribution in HMDSO monomer, and d) Z-average value for the POSS particle in HMDSO monomer.

5.2.2 Aerosol generation before injecting precursor to the plasma reaction

The aerosol generated by atomizer should yield very high mechanical shearing forces on the solution, dispatching given the nozzle used droplets in a size range of 20 to 200 nm before plasma polymerization [282]. Hence, the POSS nano-particles, likely loosely aggregated in solution into clusters were likely to further mechanically suspended into clusters way below the 200 nm range, prior to being transported as mist.
in the carrier gas towards the dielectric barrier discharge (DBD) for plasma activation, and thereafter polymerization and deposition [225, 283]. The energetic plasma activation was also shown previously to support the “break down” of clusters by vaporizing the monomers, present in a liquid form here to that point, and also increasing surface charge repulsions [282]. The aerosol droplets will migrate across the discharge area under the generator electrical field and the gas, here a mixture of monomer and POSS nano-particles, which may individually react or cross-link together. The energy input from the plasma activation may therefore further support the suspension and breakage of nanoscale clusters.

As previously demonstrated in Chapter 4, the POSS nano-particles shall be stable in such mild plasma conditions and the cage-like structure should be statistically maintained. Therefore, during the reaction, only the polymerization of the monomer and crosslinking between the activated corner groups of the cubic POSS nano-particles should occur. Depending on the discharge conditions, the polymerized HMDSO may exhibit similar chemical properties but more randomly crosslinking to that of PDMS [283-285], however, in this case, a higher level of crosslinking due to the POSS-polymer linkages is expected as shown in Figure 5-2.

The droplets shall be largely vaporized in the glow to generate a mist of reactive species [286] which will progressively cover the surface and cross-link to generate a continuous thin film. If the substrate contains pores or an intrinsic surface roughness, the uniformity of the deposition may be affected but long enough deposition durations should remove surface features from the substrate include pores and roughness.
Figure 5-2 Concept of forming POSS nano-composite by plasma from the aerosol precursor
5.3 POSS-HMDSO thin film nano-composite fabrication as membrane material using parallel plane electrodes

5.3.1 Introduction

Aerosol-assisted chemical vapour deposition (AACVD) was shown to be a potential single-step strategy to produce nano-composite coatings. Among them, it has not been applied to membranes due to the need to work at a low operating gas pressure which is limiting [207, 287]. Therefore, a modified method is called aerosol-assisted atmospheric plasma deposition (AAAP) and it was used to investigate nano-composite thin film formation [225, 288, 289]. During AAAP, the precursor is fed with a carrier gas and the aerosol of the monomer/nano-particle solution is sprayed into the plasma reaction zone, called dielectric barrier discharge (DBD), to activate the monomer and yield to its deposition and crosslinking at room temperature and onto a pre-determined substrate [288].

In this section, octamethyl POSS nano-particles were incorporated for the first time by AAAP deposition to generate ultra-thin selective films with thicknesses ranging between 50 and 300 nm. The 0 nm deposition is assigned as PSf substrate which no deposition from plasma on the substrate. The relationship between the film microstructure and the performance of the membrane were accessed by preparing a range of POSS concentrations in the plasma deposition. Specifically, POSS nano-particles were suspended in hexamethyl disiloxane (HMDSO) monomer precursor to produce POSS polymerized HMDSO nano-composite membranes in a single step by a lateral designed AAAP deposition at Bari University (Italy) [216, 284]. Such ultra-thin nano-composite membranes were developed and used for solvent separation and the POSS-polymer interface was tuned to alter selective pathways for selective liquid diffusion [189]. This strategy opens the route for ultra-high solvent permeability.
materials in conditions which may be easily up-scaled for membrane mass production. In addition, functionalized POSS nano-particles are not applied by the nano-composite fabrication due to the limited yield of functionalization from plasma modification in Chapter 4. The purchased functionalized POSS nano-particle is also not applied to nano-composite fabrication due to the limitation of study with only 2-month duration in Italy.

5.3.2 Results and discussion

The atmospheric plasma deposition from POSS nano-particles – HMDSO monomer mixture successfully formed Janus nano-composite thin films with both hydrophobic and alcohol-philic properties. The solvent diffusion across the films was correlated to morphological and chemical structural properties of the plasma polymerized membranes as well as filtration performance.

5.3.2.1 Thickness determination

A thickness calibration curve was established prior to producing the target 50, 150, and 300 nm thick POSS nano-composite film on PSf substrates. All the concentrations of POSS precursors were used for a 2-min plasma process to estimate the thickness of the film from $10 \times 40$ mm$^2$ silicon wafers by profilometry. The thickness of each concentration of POSS/HMDSO mixture was measured and were summarised in Table 5-1.
Table 5-1 The deposition rate for different concentration of POSS in the film from the plasma process

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average Deposition rate (nm.min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mon (pure monomer deposition, 0 wt.%)</td>
<td>178.1 ± 19.8</td>
</tr>
<tr>
<td>LC (low concentration of POSS, 0.02 wt.%)</td>
<td>182.8 ± 17.6</td>
</tr>
<tr>
<td>MC (medium concentration of POSS, 0.1 wt.%)</td>
<td>182.7 ± 21.8</td>
</tr>
<tr>
<td>HC (high concentration of POSS, 0.2 wt.%)</td>
<td>81 ± 65.1</td>
</tr>
</tbody>
</table>

In Table 5-1, the deposition rate was initially relatively constant upon addition of small amounts of POSS nano-particles to the HMDSO monomer solution (i.e. at 0.02 and 0.1 wt.% of POSS). However, when the POSS nano-particles content reached the highest concentration at 0.2 wt.%, the deposition rate decreased from 180 nm.min⁻¹ to approximately 80 nm.min⁻¹ through a length of 40 mm. The reduction of deposition may be related to the attraction between the nano-particle and the monomer during the plasma glow stage due to a relative variation of the vapour pressure of the solution compared to a pure monomer solution [281]. Therefore, based on the deposition rates measured, the 150 nm thick films for all concentrations of POSS were prepared while 50 and 300 nm thick film were also processed only by the 0.1 wt.% of POSS in HMDSO.
5.3.2.2 Surface morphology

5.3.2.2.1 Surface feature evaluation by scanning electron microscopy

The surface features of the POSS nano-composite membranes were first compared to untreated PSf membrane supports. In Figure 5-3, the untreated PSf membrane exhibits the typical nanoscale distribution of pores expected for an ultrafiltration membrane, ranging in pore size from 20 to 200 nm [290, 291]. Such pores are too large to provide selectivity for solvent molecules and Knudsen diffusion typically governs permeation across such membranes [292].

Upon plasma polymerization, pores were progressively filled on their outer surface by the deposition of both monomer and nano-composite thin films (Figure 5-4 and Figure 5-5). The films generated at fixed thicknesses were found to be very even upon addition of POSS nano-particles in the monomer source. A minimum deposition thickness of 50 nm was determined as a threshold to achieve continuous films. As discussed in Table 5-1, the thickness of the thin films was controlled by calibrating the plasma condition and duration of the deposition allowing, as well as the concentration of POSS, as previously reported, for an accuracy down to approximately 10 nm in thickness [225]. The impact of the thickness on the surface morphology was first evaluated for 50, 150, and 300 nm thick films and for a concentration of 0.1 wt.% of POSS (Figure 5-4). For every thickness deposited, continuous surfaces with uniform aspects were achieved for all the samples highlighting the homogeneity of the deposition [293]. At 50 nm thickness, the thin films were found to be very even and the pores across the PSf membrane support were not visible anymore suggesting that the complete coverage of the support was achieved from SEMs. At 150 nm of thickness, pore-like features could be the contrast between the relatively thin location and the thick location of the film which results from the aggregation surround POSS.
nano-particles and gaps between aggregates have not fully filled with the deposition. Therefore, the overlapping of the deposition would form a film based on aggregates on the PSf substrate at 150 nm, but the continuously dense deposition cannot be identified from SEMs but in membrane testing results. Surface features however appeared for the thickest depositions of 300 nm, as clusters with size ~ 100 nm on the surface of the film (Figure 5-4e and f). These features were found to be generated homogeneously across the surface of the samples which may be attributed to etching and recombination/deposition of moieties onto the surface of the film during the plasma deposition, as previously reported [294].

The impact of the POSS concentration on the thin films morphology was then investigated for a fixed thickness of 150 nm (Figure 5-5). At 0.02 wt.% of POSS nano-particles concentrations, the morphology of the samples was found to be uniform. At 0.1 wt.% of POSS nano-particles in the film, the polymerization of HMDSO may be started due to aggregations surround POSS nano-particles with incompletely bridging between aggregates which forms a highly contrasted morphology. The presence of surface features, visible as white clusters, were visible at 0.2 wt.% POSS concentrations. The attraction between nano-particles and monomer during the plasma process may form clusters when the concentration of nanoparticles is increased as previously reported. The roughness of the POSS nano-composite membranes was also found to visually increase with respect to larger concentrations of POSS mixed in the monomer source (Figure 5-5g and h).
Figure 5-3 SEM image for PSf UF support membrane
Figure 5-4 Surface morphology for different thickness of the POSS-HMDSO film with 0.1 wt.% addition from SEM images, a) and b) 50 nm thickness; c) and d) 150 nm thickness; e) and f) 300 nm thickness; contrasts was increased to facilitate visualization of the roughness of the materials; the high electrical charging of the samples led to shadowy patterns, which were confirmed from profilometer and separation performance to be roughness related only.
Figure 5-5 Surface morphology for different concentration of the POSS addition in the deposited film from SEM images with same thickness 150 nm, a) and b) pure monomer deposited film; c) and d) 0.02 wt.% concentration of POSS-containing film; e) and f) 0.1 wt.% concentration of POSS-HMDSO film; g) and h) 0.2 wt.% concentration of POSS-containing film
5.3.2.2.2 Surface roughness by AFM

The roughness of the deposited POSS nano-composite film was investigated by AFM as shown in Figure 5-6, Figure 5-7 and Figure 5-8. The film thickness series obtained at 0.1 wt.% of POSS were first evaluated. The roughness of the deposited film at 50 nm was found to be very close to that of the control PSf membrane support at 3.1 nm as shown in Figure 5-6a. Upon increasing the thickness of the plasma deposited layer, the roughness due to continuous overlaying of polymerized POSS-HMDSO mixture was used to progressively increase from 3.1 prior to plateau around to 4.5 nm beyond 150 nm.

The roughness of both the pure monomer and POSS nano-composite membranes generated at a fixed 150 nm thickness but for different POSS nano-particle concentrations was observed to be up to 200 % higher than that of the PSf membrane support, at 3.4 nm, as shown in Figure 5-6b. The surface of the 0.02 and 0.1 wt.% POSS-containing films provided higher roughness than pure monomer deposited a film of 6.8 and 4.5 nm respectively compared to 4.1 nm. The film deposition, as presented across the AFM maps in Figure 5-7 and Figure 5-8, was found to clearly cover the surface of the PSf membrane but to generate 10.6 ± 4.8 nm sized features and to form a rougher surface due to the likely overlapped polymerized nano-droplets generated during the atmospheric aerosolization of the monomer mixture source. The roughness of the 0.2 wt.% concentration POSS nano-composite membranes suggests the lowest value which could due to the stickiness of the surface which may not completely be cured as a solid film and is presented in Figure 5-9.
Therefore, in the present case, the deposition shall be bridging across the voids of the pores across the PSf substrate membrane [295]. As matter brought from the plasma deposition keep increasing the amount of the droplets polymerized across the substrate during the duration increase, nanoscale physical features may overlay on top of the base surface [295]. The bond and cluster formation between particle and monomer may thus generate mild nanoscale agglomeration [296]. The slightly rougher surface obtained at the same deposition thicknesses is likely arising from the nucleation of the polymerization of the material from POSS nano-particle seeds [297].

For these reasons, the morphological changes suggest that nanoscale clusters formation is related to the atomization of the monomer droplets and likely to POSS nano-particle which may lead to aggregates of the nano-particles formation. The overall roughness is however below 10 nm for all tested samples, highlighting the homogeneity and uniformity of the samples, as highlighted across the SEMs series. The chemical composition and structure of the thin films was therefore further investigated in depth to understand the interactions and correlate to both the degree of cross-linking and free volume generation across the materials, critical properties for single molecule diffusion control.
Figure 5-6 Surface roughness of deposited film on membrane substrate and possible mechanism of deposition, a) average roughness of POSS-HMDSO film with a different thickness from the medium concentration of POSS; b) average roughness of POSS-HMDSO film with a different concentration of POSS
Figure 5-7 AFM images for films on the PSf membrane with different thicknesses at 0.1 wt.% of POSS concentration deposited film, a) 50 nm thick film; b) 150 nm thick film; c) 300 nm thick film
Figure 5-8 AFM images for films deposited across PSf membranes, a) uncoated PSf membrane; b) pure monomer deposited film; c) 0.02 wt.% of POSS in the film; d) 0.1 wt.% concentration of POSS in the film
5.3.2.4 Chemical composition analysis

5.3.2.4.1 Chemical bonding characterization by FTIR

After evaluating the mechanisms for the film formation and their morphologies, the composition and chemical structure of the materials were studied to correlate the materials chemistry to the plasma deposition process.

The FTIR spectra of the samples were compared to the uncoated PSf membrane after normalization with the band at 1320 – 1360 cm$^{-1}$ corresponding to the SO$_2$ groups present across the PSf backbone as shown in Figure 5-10. The deposited thin films on the PSf membrane exhibited a clear silicon band as shown in Figure 5-10 across the
range of 1000 to 1100 cm\(^{-1}\) compared with the control PSf membrane. Since the chemical structures of octamethyl POSS and HMDSO are derived from Si-O-Si and Si-CH\(_3\) bonds, it is challenging to characterize differences between the bare POSS nano-particles and the polymerized HMDSO [275, 296]. The pure monomer polymerized samples presented a Si-O-Si bond at 1030 – 1040 cm\(^{-1}\) which suggested a SiO\(_2\) structure across the polymeric matrix and called as the chain-like structure here. However, upon addition of the POSS nanoparticles, the band of SiO\(_2\) was found to be changed, which is attributed to the POSS nano-particles cage-liked structure alteration (R-SiO\(_3\)), and to shift progressively to 1050 – 1060 cm\(^{-1}\) from 0.02, 0.1, and 0.2 wt.% POSS-HMDSO samples [298]. Due to the bonding energy between Si-O (8.3 eV) and Si-C (4.5 eV) as well as C-H (3.5 eV) are different, the energy input from plasma were easier to affect the bonding between Si and C, C and H compared to Si and O. Therefore, the monomer should still keep the backbone of Si-O-Si with random network by Si-C-O or Si-H [105].

The intensities from the absorbance of Si-O-Si bonds from either 1030 – 1040 cm\(^{-1}\) or 1050 – 1060 cm\(^{-1}\) with the normalized SO\(_2\) bond are presented in Figure 5-11. In Figure 5-11a, the pure monomer deposited sample presented a ratio of Si-O-Si from 1030 – 1040 cm\(^{-1}\) to SO\(_2\) bonds of 1.15, the highest in the series which indicated the Si-O-Si bonding came from the polymerized HMDSO while no changes were visible for the PSf substrate alone. Upon addition of POSS nano-particles within the films, the ratio of the Si-O-Si from polymerized HMDSO to SO\(_2\) decreased from 0.99 to 0.6 from 0.02 to 0.2 wt.% of POSS concentration which suggests that the content of Si-O-Si originating from the polymerized HMDSO decreased. Hence, on the other hand, the Si-O-Si bonding induced by POSS nano-particles presence increased. Furthermore, the cage-like structure and integrity of POSS were also evaluated. The ratio of
absorbance from Si-O-Si (1050 – 1060 cm\(^{-1}\)) also decreased but relatively higher than Si-O-Si (1030 – 1040 cm\(^{-1}\)) only from 0.95 to 0.75 between the 0.02 and 0.2 wt.% of POSS in the film. The change of absorbance could be attributed to the increased content of POSS in the same thick polymeric HMDSO matrix. The change of ratio provided evidence that the POSS nanoparticles were successfully incorporated across the films without being damaged. As seen in Figure 5-11b, the intensities of the band of Si-O-Si at both 1030 – 1040 cm\(^{-1}\) and 1050 – 1060 cm\(^{-1}\) were directly related to the film thickness deposition, the most pre-eminent intensity band being obtained at a thickness of 300 nm [298].

In Figure 5-11b, the ratio of the intensity for the caged Si-O-Si (1050 – 1060 cm\(^{-1}\)) continuously increased from 0.31 to 1.48 between the 50 to 300 nm thick samples at 0.1 wt.% of POSS concentration. The absorbance of the Si-O-Si bonding (1030 – 1040 cm\(^{-1}\)) also increased from 0.31 to 1.75. Furthermore, a broad band between 3200 and 3500 cm\(^{-1}\) appeared for the 0.1, 0.2, and thickest 0.1 wt.% of POSS-HMDSO films which could be attributed to hydroxyl groups (-OH) as shown in Figure 5-12. The C-H bonds will break to leave free hydrogen and may react with the Si-O bonds to form Si-OH groups [299]. The OH groups are formed from hydrogen radicals liberated from the monomer HMDSO and POSS nano-particles during activation.
Figure 5-10 Chemical structure of POSS-HMDSO film on PSf substrate membrane from FTIR spectra, a) and b) different concentration of POSS in the film compared to PSf substrate while the legend is used for both spectra, c) and d) different thickness of the film in the 0.1 wt.% POSS concentration compared to pure monomer deposition and PSf substrate while the legend is used for both spectra.
Figure 5-11 Ratio of band intensity from the normalised FTIR spectra of films deposited on PSf membrane substrate for both chain (from polymerized HMDSO) and cage (from POSS) structures, a) comparison of ratio through different concentration of POSS in the film; b) comparison of ratio through different thickness of same concentration of POSS with substrate and pure monomer deposition.
Figure 5-12 FTIR spectra with the background signal of the PSf supporting membrane, a) Samples with different concentration of POSS nano-particle in the film; b) Samples with different thickness of the film at constant 0.1 wt.% of POSS concentration

5.3.2.4.2 Elemental composition characterization by XPS

Based on the results of the FTIR revealing the chemical structure, XPS analysis was also performed to understand more close to the atomic composition which corresponded to the density of the chemical structure in the material. As seen in Table 5-2, all chemical compositions are evaluated by XPS compared to the untreated PSf membrane. A 37.9 % decrease of carbon content is found for pure HMDSO deposition
as 52 at.% compared to bare PSf which results from a 29.2 % increase of silicon due to HMDSO deposition. The 0 at.% of sulfur indicates the full coverage of deposition across the substrate while the 56.6 % increase of oxygen content to 18.8 at.% suggests the stable Si-O structure from the polymerization [296, 300]. In the 0.02 wt.% of POSS-HMDSO deposition with the same target thickness of pure HMDSO, the carbon, oxygen, and silicon content of POSS sample is maintained with less than 1 at.% difference compared to pure HMDSO sample. Therefore, the chemical composition of the deposition is remained as same compared to pure HMDSO deposition when the amount of POSS is small which is hard to tune the polymerized structure. With a continued increase of POSS concentration to 0.2 wt.%, a continuous decrease of carbon with 25.7 % to 38.2 at.% while continuous increases of oxygen with 55.8 % to 28.2 and of silicon with 15 % to 33.6 at.% are found to compare to 0.02 wt.% POSS sample. Hence, the increase of oxygen and silicon content leads the increase of Si-O density for tuning the cross-linked structure by POSS nano-particles towards the change in free volume.

The increase of film thickness also affects the detected chemical structure of the deposition from 0.1 wt.% POSS-HMDSO sample. At a thickness of 150 nm, the carbon and silicon content is increased by less than 2 at.% while oxygen content is decreased by also less than 2 at.% compared to 50 nm which suggests a homogenous polymerization by plasma. However, a large decrease of carbon content with 24.3 % to 33.1 at.% while a 32.9 % increase of oxygen as 33.1 at.% and an 8 % increase of silicon as 33.8 at.% are obtained at 300 nm thickness compared to 150 nm. The even distribution of carbon, oxygen, and silicon indicates the change in crosslinking comes from a longer duration of plasma leads to an enhancement of random recombination from precursors for a thicker thickness.
Table 5-2 Comparison of atomic percentages of the plasma deposition on PSf membrane for 4 different concentrations (include 0 wt.%) and 4 different thicknesses (including PSf plain substrate)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s (at.%)</th>
<th>O1s (at.%)</th>
<th>S2p (at.%)</th>
<th>Si2p (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf substrate</td>
<td>83.69 ± 0.1</td>
<td>11.98 ± 0.02</td>
<td>4.34 ± 0.09</td>
<td>0</td>
</tr>
<tr>
<td>0 wt.%-150 nm</td>
<td>52.02 ± 0.37</td>
<td>18.81 ± 0.04</td>
<td>0</td>
<td>29.18 ± 0.42</td>
</tr>
<tr>
<td>0.02 wt.%-150 nm</td>
<td>51.42 ± 0.07</td>
<td>18.13 ± 0.17</td>
<td>0</td>
<td>30.46 ± 0.09</td>
</tr>
<tr>
<td>0.1 wt.%-50 nm</td>
<td>42.87 ± 0.46</td>
<td>26.92 ± 0.3</td>
<td>0.3 ± 0.03</td>
<td>29.92 ± 0.18</td>
</tr>
<tr>
<td>0.1 wt.%-150 nm</td>
<td>43.59 ± 0.33</td>
<td>24.89 ± 0.21</td>
<td>0</td>
<td>31.53 ± 0.13</td>
</tr>
<tr>
<td>0.1 wt.%-300 nm</td>
<td>33.08 ± 0.07</td>
<td>33.11 ± 0.3</td>
<td>0</td>
<td>33.81 ± 0.23</td>
</tr>
<tr>
<td>0.2 wt.%-150 nm</td>
<td>38.17 ± 0.21</td>
<td>28.21 ± 0.33</td>
<td>0</td>
<td>33.62 ± 0.11</td>
</tr>
</tbody>
</table>

As seen in Figure 5-13 and Figure 5-14, the XPS spectra for different concentration of POSS in the deposition and different thickness of 0.1 wt.% POSS-HMDSO deposition were performed to check the potential existed bonding. Bonding of C-H (284.8 eV), C-O (285 – 285.3 eV) and C=O (286.6 – 287 eV) are mainly located in the C1s for all depositions which C-O and C=O result from recombination of C-H from methyl groups and Si-O from the backbone of HMDSO and POSS [293]. The disappearance of $\pi$-$\pi$ bonding from PSf membrane suggests again the full coverage of the deposition across the substrate which is also supported by the disappearance of the sulfur signal as shown in Figure 5-13 and Figure 5-14 [301, 302]. However, in the 50 nm thick film, a 0.3 at.% sulfur is detected for SO$_2$ from PSf membrane which can be interrupted as ultra-thin depositions with a non-uniform thickness as the XPS depth was around 5 nm. The detected signal could refer to the surface features as discussed
in SEMs. As for the both POSS concentration series and thickness series depositions, O1s spectra suggests the O-Si (532.5 – 532.8 eV) from the backbone of HMDSO and POSS, O=C (530.5 – 530.8 eV) and O-C (533 – 533.3 eV) from the ionization of monomer and POSS by plasma [293]. In the Si2p spectra, two peaks are mainly estimated by different oxygen atoms bond with silicon which located at 102.1 – 102.7 eV for Si-Ox where x is less than 2 represent as the R-SiO3 structure and at 102.7 – 103.3 eV for Si-O2 represent as SiO2 structure from polymerization [269]. When POSS concentration increased, the O1s and Si2p peaks are shifting based on the increased intensity from caged Si-O structure of POSS compared to the polymerized linear Si-O structure. Therefore, due to the similarity of the bonding is reported from the XPS spectra because of similar chemical bonding from HMDSO and POSS, a detail discussion on the ratio of fitted bonding is presented in Figure 5-15 to investigate the change in the density of chemical bonding.

In the series of POSS concentration, 0.02 wt.% POSS-HMDSO deposition obtains a 34.3 % decrease of C-H ratio to 48 % and a 104 % increase of C-O ratio to 51.5 % against total carbon content compared to pure HMDSO deposition as shown in Figure 5-15. The decrease of C-H and increase of C-O with no C=O bonding is not found by the devolution indicate the more network formation based on C-O bonding which is tuned by octamethyl POSS nano-particles [113, 303]. Due to the more network bonding of C-O, the ratio of O-Si is decreased by 15 % as 71 % and O-C is increased by 76.4 % to 28.4 % against total oxygen content at 0.02 wt.% POSS concentration compared to pure HMDSO deposition. As well as in the ratio of Si-O bonding, bonding with oxygen atoms is increased as the formation of SiO2 which can be represented as a 16 % increase of SiO2 while 17.7 % decrease of R-SiO3 against total silicon content. At 0.1 and 0.2 wt.% of POSS concentration samples, the amount
of C-O and C=O from C1s are maintained by a variation of 5 % as a ratio of 50 % against total carbon compared to 51 % ratio from 0.02 wt.% POSS sample. At 0.2 wt.%, the ratio of O-Si is continuously dropped by 16.2 % and a 40.4 % increase of O-C is obtained against total oxygen content compared to 0.1 wt.% POSS sample at 150 nm thickness. The bonding with silicon includes R-SiO₃ and SiO₂ are maintained relatively constant by 4 % variation through the depositions in the series of POSS concentration. Therefore, when POSS concentration in the deposition continuously increased, bonding with oxygen atoms is also increased to form a denser network compared to non-POSS deposition.

In the series of film thickness from 50 to 300 nm with 0.1 wt.% POSS, C-H ratios were maintained by averagely 55 % with a variation of 3 % suggested the same amount of methyl groups were modified to form polymerized network towards the stable discharge for activating species. The C-O ratio is slightly increased by 9 % and 11 % when thickness reached 150 and 300 nm respectively compared to the 50 nm represented as the enhanced polymerization with increased plasma duration. The C=O ratio is slightly decreased by 4.3 % at 150 nm and 6.5 % at 300 nm compared to 50 nm thickness which represents a more randomly network bond by C-O with a longer duration of plasma as shown in Figure 5-15 [209]. The ratios in the oxygen spectra again make an agreement of increased O-C from 22.3 % to 30.8 % from 50 to 300 nm while the decrease of O-Si is estimated by 8.4 % for 300 nm compared to 50 nm. Hence, the same trend in silicon spectra is found with an increase of thickness corresponding the plasma duration which the density of SiO₂ is increased by 11 % and the R-SiO₃ is relatively decreased by 11 % for 300 nm compared to 50 nm. Therefore, with a thicker film of POSS nano-composite, the more oxygen-containing network is produced to
potentially enhance the degree of crosslinking in the matrix towards the control of free volume.

Figure 5-13 XPS spectra for deposition with different POSS concentrations, a) C1s spectra, b) O1s spectra, c) S2p spectra, d) Si2p spectra
Figure 5-14 XPS spectra for deposition with different thickness with 0.1 wt.% POSS addition, a) C1s spectra, b) O1s spectra, c) S2p spectra, d) Si2p spectra
Figure 5-15 Ratios of relative fitted peaks in XPS high-resolution spectra for different POSS concentrations and film thicknesses from 0.1 wt.% POSS concentration, a) and b) C1s for POSS concentration series and film thickness series, c) and d) O1s for POSS concentration series and film thickness series, e) and f) Si2p for POSS concentration series and film thickness series.
5.3.2.4.3 Particle agglomeration characterization by SAXS and WAXS

Furthermore, small angle X-ray scattering (SAXS) experiments were performed to evaluate a degree of particle agglomeration. As seen in Figure 5-16a, no obvious Guinier knee across the series was found while the samples followed a basic Porod low, suggesting relatively uniform and homogeneous distribution of the POSS nano-cages. A power law with an exponent of -4, typical for randomly and homogeneousy distributed system, was found to fit well the curves for short scattering vectors (Figure 5-16).[304] Yet the intensity of the SAXS patterns obtained for the nano-composite samples, were also found to be up to 2 logs higher than that of the pure monomer at the same thickness, supporting the presence of the POSS nano-particles. This result confirmed the uniform distribution of POSS nano-particles in the matrix and the absence of agglomerates.[305, 306] The shift in the WAXS peak position at higher POSS loading or for thicker materials, as seen in Figure 5-15b, was attributed to potential structural changes across the POSS nano-cages microstructure. The wider WAXS peaks visible on Figure 5-16b and higher amount of hydroxyl groups as seen from the FTIR results above 0.2 wt.% POSS and for thicker membranes suggests that some cages may have been partly functionalized and methyl groups substituted with hydroxyl groups, thus deforming the cage structure.[307, 308] The exact deformation or damage was however not further studied in this work since the overall crystallinity was not found to be measurably altered.
Figure 5-16 The a) SAXS and b) WAXS spectra from 4 different concentration of POSS-containing film in same 150 nm thick (0 (Mon), 0.02 (LC), 0.1 (MC), and 0.2 (HC) wt.%) and 3 different thickness of 0.1 (MC) wt.% of POSS (50, 150, and 300 nm) deposited film on Si wafer respectively

5.3.2.5 Wettability

The wettability of the deposited film was studied to evaluate their interactions with water and ethanol. The wettability is related to the surface energy, arising from the chemical functionalities across the materials surface, as well as to the overall material roughness [309, 310]. The bare PSf membranes exhibited water contact
angles of only 55° while ethanol was found to fully wet the membrane as seen in Figure 5-17. The pure HMDSO polymerized films formed across the PSf membranes led to an increase of the water contact angle to 100° as expected from such hydrophobic polymer, while the alcohol contact angle was close to 20° for pure ethanol (Figure 5-17). The hydrophobicity of the film suggests a non-polar surface with low surface energy as compared with PSf substrate [311]. The POSS nano-composite thin films showed slightly lower contact angles but yet a rather hydrophobic behaviours with water contact angles between 83° and 100° in Figure 5-17. The water and ethanol-water contact angles were decreased with the increased concentration of POSS across the film from 0.02 to 0.1 wt.%. A different trend of wettability at 0.2 wt.% POSS concentration in the deposition might be due to the sticky surface detected from AFM. When the thickness of deposition increased from 50 to 150 nm, the contact angle of water and ethanol increased due to the continuous polymerization of HMDSO-POSS with increased plasma duration. However, when the film reached 300 nm thickness, the contact angle decreased which suggests the nano-composite would be hardened by the further polymerization and then loses hydrophobicity. In agreement with the FTIR results regarding the formation of hydroxyl groups, the 0.2 wt.% of POSS containing sample showed provided a more polar surface than the other samples. The water contact angle was found to be lower in this case which corresponded to a higher surface energy [311, 312]. As seen in Figure 5-17a and b, for the ethanol/water mixture, the contact angle decreased with an increase of ethanol concentration while the film coated membrane performed a higher wettability than control substrate. This hydrophobic and the alcohol-philic behaviour of the HMDSO polymerized structures were consistent with previously reported data for PDMS structures [312].
As the amount of POSS nano-particles increased in the dope solution, aggregation of the nano-particles may have affected the microstructure of the polymeric nano-composite matrix as shown in the SEMs and AFM results. Thus, the resulted smaller contact angles for water and ethanol compared to that of the bare monomer samples could be affected by the surface roughness of the material which suggests the change of surface charge [313]. This Janus behavior, allowing for selective wetting by the diverse solvents, indicated great potential for alcohols separation from water mixtures [296, 314, 315].
5.3.2.6 Membrane separation performance

5.3.2.6.1 Liquid entry pressure

The liquid entry pressure (LEP) of the membranes was first investigated for water and ethanol. The uncoated PSf membrane presented a slightly higher LEP for water than ethanol from 3 to 1.9 bar respectively (Figure 5-18). This trend is in good
agreement with the previous diffusion tests across such PSf membranes [316]. The LEP for water from the polymerized HMDSO thin films raised up to 7.5 bar which 2.5 times higher than that of the PSf membranes. However, the LEP of ethanol from the pure monomer deposition remained close to 1.2 bar only 33 % lower than the reference PSf membrane. Therefore, the large LEP gap of ethanol to water for the HMDSO plasma coated samples, suggests a selective layer which helped repulse water compared to the alcohol upon diffusion. The LEP of the POSS nano-composite membranes for water slightly dropped from 7.5 to 7 bar which may due to the facilitated diffusion pathways formation at the POSS/matrix interface across the polymerized HMDSO. The LEP was consistently found to lie between 1 and 2 bar for ethanol which indicated great alcohol selectivity potential compared to the uncoated PSf membranes. The LEP for water of the concentration series was continuously increased up to 8 bar due to the combined addition of the hydrophobic POSS nanoparticles containing methyl groups and to the slightly increase roughness thus generating more water repulsive surface structures [317]. The LEP of the concentration series for alcohols again slightly decrease from 2 to 1.4 bar for ethanol which demonstrated that the selectivity for alcohols was increased compared to the pure HMDSO thin films.

Upon increasing the thickness of the films at constant POSS concentration with 0.1 wt.% (Figure 5-18b), the LEP for water was found to be stable at around 7.6 bar between 50 and 300 nm, suggesting a stable performance of diffusion even in the thicker material. The gap between ethanol and water LEP remained around 6 bar which again agreed with the alcohol-philic properties of the surface.
Figure 5-18 The liquid entry pressure of the deposited film for a) different concentration of POSS nano-particles in the film and b) for different thicknesses of the film at 0.1 wt.% concentration of POSS

5.3.2.6.2 Membrane performance testing

To further evaluate the performance of the plasma deposited films as membranes, single solvent dead-end permeation measurements were carried out. The control PSf membranes used as a benchmark performance material presented water permeance at 40.3 kg.m⁻².h⁻¹.bar⁻¹, while the ethanol permeance only reached 3.3 kg.m⁻².
Upon deposition of polymerized HMDSO, the pure monomer samples at 150 nm of thickness yielded a permeance to water 76.7 % lower than control PSf membranes at 9.4 kg.m⁻².h⁻¹.bar⁻¹ (Figure 5-19a) which is attributed to the closure of the pores by the polymer as the decrease of water selected free volume in the film [318]. In Figure 5-19b, the ethanol permeance of the monomer alone deposited sample presented 990 % higher than the PSf substrate which in a good agreement of LEP results. The free volume across the macromolecular matrix sustained alcohol transfer resulted in the formation of a selective layer for separating ethanol from water. In addition, the surface charge from the plasma polymerized HMDSO also contribute to the selectivity of ethanol from water [318, 319].

Figure 5-19a presents the water permeation values for the POSS concentration series. The permeation continuously dropped from pure monomer to 0.2 wt.% POSS-containing sample and reached a lowest point of 1.79 kg.m⁻².h⁻¹.bar⁻¹ from 9.4 kg.m⁻².h⁻¹.bar⁻¹. The ethanol permeance across the POSS nano-composite membranes (Figure 5-19b) was only reduced by 64.7 % for the 0.02 wt.%, 75 % for the 0.1 wt.%, and 84.3 % for the 0.2 wt.% POSS nano-composite films as compared to the pure monomer polymerized sample. The decrease of the permeance for higher POSS contents suggests a higher densification level of the structure which increased the resistance to liquid diffusion [318, 319]. The continuous decrease of the permeance from both water and ethanol with the increase of the POSS concentration could indicate a smaller distribution of free volume which is likely induced by cross-linking between the particles and the monomer as previously shown for other nano-composite membrane materials [319].

The permeance of the thickness series at fixed POSS concentration led to a continuous decrease of water permeance from 25.3 to 2.8 kg.m⁻².h⁻¹.bar⁻¹ (Figure
5-19c). With the increase of the thickness of the film, the mean free path of the liquid pathway across the film shall strongly increase, thus increasing the resistance of the material to diffusion. The ethanol permeance (Figure 5-19d) show that the thinnest 50 nm films yielded the highest ethanol permeation at 164 kg.m⁻².h⁻¹.bar⁻¹ which supports the impact of nanoscale thicknesses to offer superior performance [63].

With the incorporation of the POSS nano-particles and generation of an ultra-thin film, supported the selective permeation of ethanol against water [320, 321]. The ideal selectivity of ethanol to water was calculated using Equation 5.1 and the results are presented in Figure 5-20 [322]:

\[ S = \frac{k(\text{ethanol})}{k(\text{water})} \]  

(5.1)

Where S refers to the ideal selectivity of ethanol from water, and k corresponds to the permeance of either ethanol or water.

As seen in Figure 5-20, the PSf control membranes, and as expected from their large 10-200 nm pore size distributions, exhibited no ethanol separation selectivity, with an \( S_{PSf} \) value of 0.08. The pure HMDSO deposited membranes, however, showed selectivity up to 3.5 which around 4,370 % higher than the PSf membranes. The ideal selectivity of the POSS nano-composite membranes at 150 nm ranged between 2.3 and 2.7 for increasing POSS concentrations from 0.02 to 0.2 wt.% (Figure 5-20a). The selectivity across the ultra-thin 50 nm thick membranes at 0.1 wt.% reached 6.5 which was 186 % higher than pure monomer deposited sample and 8,130 % higher than PSf uncoated membrane. The permeation and ideal selectivity data suggest that although the presence of the POSS may have increased interfacial diffusion sites, the integration of the POSS nano-cages was good and yielded denser materials, likely with less free volume for diffusion [153, 323]. The flux and selectivity enhancements for the ultra-
thin membranes are highly promising and confirm that the control of the microstructure of nano-composite at the nano-level has the potential to yield high-performance membranes with controlled free volume distributions [63]. Although the free volume of the materials was not assessed in this work due to the challenge to test such thin layers, by positron annihilation spectroscopy, the assessment of diffusion selectivities directly highlighted the role of the POSS into the controlled spacing of macromolecular gaps within the polymer matrix.

Figure 5-19 Permeance of different films from plasma deposition with a pure solvent for water and ethanol permeation tests, a) and b) permeance of water and ethanol from
the different concentration of POSS-containing film respectively; c) and d) permeance of water and ethanol from different thickness of same concentration of POSS deposited film respectively.

Figure 5-20 Selectivity from pure solvents estimation, a) and b) selectivity of ethanol from water when the film was ethanol wetted for different concentration of POSS in the film and different thickness of same concentration.
5.3.3 Concluding remarks

Aerosol-assisted plasma deposition was shown to provide an alternative route for the fabrication of nano-composite thin film membranes with customizable nanoscale surface and bulk structures [215]. The combination of HMDSO monomer and POSS nano-particles has led to the design of a new kind of nano-composite thin film membranes with hydrophobic but alcohol-philic properties, offering separation factors of ethanol over water up to 6.5. Compared to selectivity of ethanol from water as 13 for PDMS membrane and 4.6 for POSS-Pebax membranes [21, 141], POSS-HMDSO deposition suggests the potential of plasma thin film composite for membrane application. It demonstrates the potential impact of this strategy to generate in a single processing step a highly crosslinked particle-matrix separation membrane. The results lead to promising and cost-effective applications for solvent separation, purification or recycling. In addition, mixed ethanol and water solution was not applied to the dead-end filtration due to the limited number of samples prepared in Italy which cannot support a proper study. Furthermore, PV as a relatively complicated process was not applied to the POSS nano-composite membranes also due to a limited number of prepared samples as well as the difficulty of use small deposition area in PV. Hence, dead-end filtration provided a relatively simple and fast process to determine the performance of POSS nano-composite membrane.

Further study should focus on the control of the impact of the chemistry from POSS corner groups on the level of crosslinking with the monomer molecules to adjust the free volume across the thin films and thus the selectivity of the membrane.
5.4 POSS-HMDSO thin film composite fabrication using parallel cylindrical electrodes with the X-Y moving stage

5.4.1 Introduction

Plasma polymerization system using a horizontal lateral gas flow at Bari University (Italy), the mist of the precursor was distributed across the substrate, which was located at equidistance from both plane electrodes. Location of substrates was at the surface of the plane electrode, therefore the deposition led a difference due to the degree of polymerization across the substrate from the input and output position of the gas flow corresponding to a slight difference in the duration of plasma [281]. Therefore, a difference in thickness from 20 to 60 nm between the input and output position was found with a range of 40 mm which has presented in Section 5.3.2.1.

The two deposition systems were designed in a similar manner, but yet had several major differences, highlighted in this section. To overcome the non-uniform thickness of the film, an atmospheric plasma system with an X-Y moving stage was developed with a vertically top-bottom direction for the mist flow. To improve the effective deposition area and further avoid the gradient in deposition thickness from the lateral gas injection, the electrodes were designed as parallel cylindrical electrodes to have an anti-parallel direction with the mist flow [281]. The parallel cylindrical electrodes allowed for a maximum of $100 \times 100$ mm$^2$ area for the field of view deposition. The sample holder was located on the X-Y moving stage and below the electrodes to collect the polymerized mist to achieve homogenous deposition [324]. The atomizer was used for generating the aerosol feed into the parallel cylindrical electrodes system to fabricate nano-composite thin film. A major difference between the two atmospheric deposition systems, however, lies in the width of discharge zone for polymerizing feeds, which plane electrodes suggest longer distance as 50 mm for
feed to polymerize compared to 4 mm distance from cylindrical electrodes. Therefore, cylindrical electrodes with showerhead feed flow indicate a shorter duration for polymerization compared to plane electrodes with lateral gas which might limit the degree of polymerization to have stable film. The difference of geometry for the electrodes leads to the different location of the substrate to collect deposition. Deposition can be initiated by highly active species in the plasma zone when the substrate was placed at plasma zone in the plane electrodes system. Hence, when substrate placed at the after plasma glow zone, the deposition mainly forced by gas injection with assisted by partially polymerized monomers which may drawback the stability of deposition. Due to the larger effective area for deposition, a large volume of the chamber is required by cylindrical electrodes system with moving stage as approximately 0.8 m³, which is 2,500 % larger than that for the plane electrodes system. Compared to the plane electrodes system, the cylindrical electrodes system cannot reach the same level of the seal which may, therefore, lead to possible air contamination.

In the first stage of the deposition, pure HMDSO monomer was deposited with the parallel cylindrical electrodes system prior to testing for ethanol-water separation. Surface morphologies and chemical properties were discussed for investigating the chemical stability of the deposition, and the membrane performance was presented by dead-end filtration to introduce the physical stability of solid coatings.
5.4.2 Pure monomer HMDSO deposition as a thin film on PSf membrane

5.4.2.1 Thickness and roughness – Profilometry

The thickness of the deposition was measured by a laser scanning microscopy on the scratches of the deposited film on silicon wafers with increasing duration of plasma from 0 to 13 min over an area of 50 × 80 mm² by profilometry analysis [325]. In Figure 5-21a, the thickness of the deposition was found to increase with longer deposition duration at an estimated rate of 24.34 ± 0.48 nm.min⁻¹.

In Figure 5-21b, the profilometry data were used to evaluate the surface roughness of the deposition across the PSf supporting membranes. Firstly, a 2.3 % increase in surface roughness Sq has observed by deposition duration until 5 min compared to PSf membrane base roughness of 306.3 ± 6.8 nm. Then, at 8 min, the roughness of Sq decreased by 5.4 % and further decreased by 9.9 % at 13 min compared to 5 min (282.3 ± 10.1 nm). According to the profilometry roughness results, the deposition may not fully cover the pores across the PSf membrane when duration was short which may form patchy areas. When the deposition duration increased, the amount of polymerized HMDSO increased and then fully covered the pores-like features. Hence, the longer duration of deposition may form smoother surface compared to the short duration.
Figure 5-21 Thickness and roughness with an increased duration of plasma, a) estimated thicknesses of the different deposition duration from profilometry, red line presents the linear fitted curve for the measurements, and b) the surface roughness of the deposition on a smooth glass substrate with different duration of deposition from plasma treatments

5.4.2.2 Surface morphology characterization by SEM

Surface features of the deposition on PSf membrane from the parallel cylindrical electrodes system were investigated by SEM to study the surface
morphology compared to untreated PSf membrane (Figure 5-3). As seen in Figure 5-22, pores from PSf membrane are progressively filled up with an increase of duration for deposition from 2 to 13 min. Compared to untreated PSf membrane, depositions start closing the pores larger than 100 nm and perform homogenous features across the surface of the deposition. Surface features at 2 min provide more pit-like features compared to the longer duration of deposition which leads an agreement of high surface roughness with short deposition time. However, the density of solid particle-like features increases after 2 min plasma and forms more than 300 nm size in diameter at 13 min duration which due to the aggregation of polymerized monomers. Furthermore, a feature of pores is reduced by increasing the plasma duration, but small crack-like features between deposited domains are found especially at 13 min. The formation of crack-like features can be interrupted by the brittleness of the film or incomplete bonding between each domain of polymerized monomers. Hence, the settled plasma system for thin film deposition with parallel cylindrical electrodes is successfully achieved to produce homogenous deposition with tuneable surface features by plasma duration.
Figure 5-22 SEMs of the plasma deposition on PSf membrane with different durations, a) and b) 2 min, c) and d) 5 min, e) and f) 8 min, g) and i) 13 min
5.4.2.3 Wettability

As seen in Figure 5-23, liquid contact angles of HMDSO plasma polymerized films were measured by 0, 33, 66, and 100 vol.% ethanol-water solution to investigate the interaction between the surface of deposition and different solvent towards ethanol-water separation. After plasma deposition, the deionized water contact angle is reaching maximum 103° compared to 55° from the PSf substrates which towards the hydrophobic coating [284, 293, 314]. Typically, HMDSO polymerized films obtains a decrease of the contact angle with an increase of ethanol concentration in the solution as a gradient of -1.04° ± 0.06° per one volume percentage of ethanol leads 0° in pure ethanol towards an alcohol-philic surface as a Janus behaviour. The trend of alcohol-philicity is consistent throughout all different durations of deposition suggested stable surface charge control by plasma as suitable for ethanol-water separation due to selected ethanol wetting.

Figure 5-23 Water contact angle for the deposition on PSf substrate compared to the substrate along
5.4.2.4 Chemical composition analysis

5.4.2.4.1 Chemical bonding characterization by FTIR

To identify the chemical bonding in the deposition from plasma, FT-IR analysis was used to examine the chemical structure of the deposition for the different durations. In Figure 5-24, depositions of HMDSO monomer by plasma with durations of 2, 5, 8 and 13 min were compared to bare PSf membranes showing a new Si-O-Si band (i.e. 1040 cm\(^{-1}\)) demonstrating the presence of HMDSO [284]. The appearance of the Si-O-Si band at 1040 cm\(^{-1}\) indicated the chemical structure of polymerization is built from SiO\(_2\) bonding and the intensity of the band increased with larger films thickness upon normalization with the SO\(_2\) band (1320 – 1360 cm\(^{-1}\)), as shown in Figure 5-24. The ratio of intensities from the Si-O-Si band against SO\(_2\) band shows a gradient of 0.087 ± 0.002 for increasing deposition durations represents the function of plasma duration and amount of deposition which can be referred as film thickness. Furthermore, the degree of polymerization was tuned by the appearance of the –OH band comes from the recombination of C-H and Si-O in the plasma polymerization leads a formation of Si-OH to change the network of polymerized HMDSO [284].
Figure 5-24 FTIR spectra for HMDSO deposition from plasma with different durations, a) whole spectra from FTIR measurement, b) Zoom in the area for the appearance of
Si-O-Si bands to present the existence of the deposition. The ratio of absorbance from the FTIR spectra by the Si-O-Si band and SO₂ band which led a relationship between duration and absorbance.

5.4.2.4.2 Elemental composition analysis by XPS

To examine the homogeneity of the film deposited with different durations from HMDSO monomer plasma polymerization, XPS was used to access changes in atomic compositions. As seen in Table 5-3, with an increase of HMDSO deposition duration, 0 at.% of sulfur is found by 13 min deposition compared to 4.34 at.% of sulfur on bare PSf membrane indicates a full coverage across the substrate. The carbon content after 2 min of deposition decreased by 40.7 % at 49.6 at.% while the silicon content increased by 15.6 % compared to bare PSf, demonstrating the polymerization of HMDSO. The formation of Si-O structure in the plasma was correlated to the oxygen composition as a 159 % increase of atomic percentage as 31 at.% compared to PSf substrate at 2 min. However, the sulfur content decreased but still existed 3.2 at.% which suggests that the coverage may be non-continuous across the PSf substrate in agreement with the pit-like features visible on the SEMs after 2 min of deposition. When the duration of the deposition increased to 5 min, the carbon content was further decreased by 61 % to 19.32 at.% compared to 2 min deposition. The silicon content was increased by 105 % to 32 at.% at 5 min deposition compared to the 2 min deposition represented the increased coverage of deposition. The sulfur content can be discussed as the coverage of deposition which the 0 at.% was found at 13 min deposition suggested a full coverage across the PSf substrate while the further increase of oxygen to 53.27 at.% suggested a relatively higher degree of polymerization compared to 2 min. Furthermore, the nitrogen content is found to indicate the
limitation of sealing when deposition duration was less than 8 min which a less than 1 at.% is obtained by either surface contamination or reaction with air during the plasma reaction [300, 326].

Table 5-3 Comparison of atomic percentages of the plasma deposition on PSf membrane for 3 different thicknesses from different duration (including the PSf substrate)

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s (at.%)</th>
<th>N1s (at.%)</th>
<th>O1s (at.%)</th>
<th>S2p (at.%)</th>
<th>Si2p (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf substrate</td>
<td>83.69 ± 0.1</td>
<td>0</td>
<td>11.98 ± 0.02</td>
<td>4.34 ± 0.09</td>
<td>0</td>
</tr>
<tr>
<td>2 min</td>
<td>49.58 ± 9.99</td>
<td>0.65 ± 0.13</td>
<td>30.98 ± 6.17</td>
<td>3.2 ± 0.83</td>
<td>15.61 ± 3.13</td>
</tr>
<tr>
<td>5 min</td>
<td>19.32 ± 0.26</td>
<td>0.41 ± 0.05</td>
<td>47.2 ± 0.25</td>
<td>1.09 ± 0.04</td>
<td>32.0 ± 0.01</td>
</tr>
<tr>
<td>8 min</td>
<td>17.78 ± 6.56</td>
<td>0.2 ± 0.06</td>
<td>46.96 ± 3.83</td>
<td>0.3 ± 0.16</td>
<td>34.78 ± 2.95</td>
</tr>
<tr>
<td>13 min</td>
<td>16.54 ± 0.95</td>
<td>0</td>
<td>53.27 ± 0.13</td>
<td>0</td>
<td>30.69 ± 1.78</td>
</tr>
</tbody>
</table>

In Figure 5-25, the high resolution of the XPS spectra shows the change in bonds upon increasing the duration of deposition. Bonding in the C1s spectra is estimated by fitting of C-O (286.1 – 286.7 eV), C=O (288.6 – 289.4 eV) corresponding with calibrated C-H (284.8 eV) for all samples [296, 326]. PSf membranes also suggest a π-π bonding at 291.5 eV represents the structure of poly (sulfone) [301, 302]. Hence, with a short duration at 2 and 5 min, the appearance of π-π bonding indicates non-continuously coverages across the PSf while 8 and 13 min deposition presents no signal of π-π bonding which suggests a better coverage compared to shorter durations. Therefore, in the S2p spectra, the signal of SO2 decreased to 0 at 13 min deposition which is made an agreement of continuous coverage across the PSf membrane as shown in Figure 5-26a. The formation of C=O comes from the by-product of C-O
bridging due to the recombination of C-H and Si-O fragment during plasma to tune the polymerized structure. Therefore, in Figure 5-27a, ratios of C-H bonding against total carbon are maintained at 80 – 85 % through all durations by the reaction from the same CH₃ groups in the monomer during the polymerization. A 20 % decrease of the ratio of C-O at 13 min is obtained as 12 % compared to 2 min while a 131 % increase of the ratio of C=O to 3 % at 13 min as compared to 2 min deposition. Hence, longer durations of plasma leads a higher degree of polymerization compared to short durations as the monomer molecules can keep reacting with each other and cross-link towards a possible reduction of interfacial spacing in the matrix [326].

In Figure 5-25f, O1s spectra suggest the appearance of O-Si (532.2 – 532.9 eV) by the polymerization of HMDSO, while O-C (533 – 533.9 eV) and O=C (530.2 – 530.7 eV) is generated from the recombination of C-H and Si-O as discussed in C1s spectra [326]. At 2 and 5 min, the ratios of O-Si and O-C are constant at around 58 % and 41 % respectively while O-Si starts increasing at 8 min with 11.2 % and further increased by 53.5 % at 13 min as 89 % (Figure 5-27b). On the other side, ratios of O-C is decreased by 14.6 % at 8 min and further decreased by 81 % at 13 min at 8.5 %. Furthermore, ratios of O=C are maintained at 0.4 – 0.6 % until 13 min as 1.6 % which leads a more cross-linked structure with longer plasma.

The Si2p spectra again confirmed the change of chemical structure based on Si-O from the backbone of HMDSO monomer with the increased oxygen content by increased plasma duration. The R-SiO₃ comes from the Si-Oₓ where x less than 2 at a binding energy of 102.3 – 103.3 eV, while SiO₂ is located at a binding energy of 103 – 103.7 eV as shown in Figure 5-25b [285, 326]. The loss of Si2p intensity for the 13 min deposition would be due to the different patch of XPS measurements which has not normalized. The atomic concentration of each sample is shown in Table 5-3, which
the Si2p is maintained at 30 at.% from 13 min compared to 32 at.% from 5 min and 35 at.% from 8 min depositions. Hence, the ratio of the Si-O structure against the total silicon content is presented in Figure 5-27c which at 13 min deposition contains a 16.9% decrease of R-SiO$_3$ to 54.4% and a 32.4% increase of SiO$_2$ to 45.6% compared to 2 min as a shifting of Si-CH$_3$ to a more cross-linked O-Si-O structure.
Figure 5-25 XPS spectra for deposition with different duration of plasma, a) C1s spectrum for PSf substrate, b) C1s spectrum for 2 min deposition, c) C1s spectrum for 5 min deposition, d) C1s spectrum for 8 min deposition, e) C1s spectrum for 13 min deposition, and f) O1s spectra for all samples.
Figure 5-26 High-resolution spectra from XPS for different durations of deposition, a) S2p spectra, b) Si2p spectra
Figure 5-27 Relative ratios of fitted peaks in, a) C1s, b) O1s, and c) Si2p spectra
5.4.2.5 Membrane performance

5.4.2.5.1 Liquid entry pressure

LEP of ethanol and water were demonstrated continuously and defects of the deposition prior to the evaluation of membrane performance. In Figure 5-28, no change of LEP performance is found at 2 min deposition compared to the pristine PSf membrane indicates the non-continuous deposition which makes an agreement with SEMs. Therefore, when the duration of deposition is short, the coverage across substrates is incomplete and the membranes cannot separate the different solvents. Better coverage of deposition was observed at 5 min of plasma deposition by a 117% increase of water LEP at 6.5 bar compared to the pristine PSf membrane while only 1 bar LEP for ethanol was found at 5 min. At 8 min deposition, a further increase of water LEP by 9.2% was exhibited at 7.1 bar compared to 5 min deposition and a 20% increase of ethanol LEP was reached at 1.2 bar compared to 5 min suggested an improved coverage. Therefore, when the coverage across the substrate is increased, water will have more difficulty to pass through the deposited layer compared to ethanol. However, when the plasma deposition duration further increased to 13 min, a 22.5% decrease of water LEP at 5.5 bar and a 58.3% increase of ethanol LEP was observed at 1.9 bar were found when compared to 8 min deposition as shown in Figure 5-28. Due to the same value of LEP for ethanol from 13 min compared to pristine PSf, it has been suspected that coverage again became non-continuous across the PSf membrane as an agreement of crack-like features in SEMs.
5.4.2.5.2 Membrane performance testing

To further examine the performance of deposition under liquid environment, dead-end filtrations for pure ethanol and water were demonstrated to access permeances and ideal selectivities as the membrane performance. As seen in Figure 5-29a, 2 min deposition presents a 2,173 % increases of ethanol permeance as 75 kg.m$^{-2}$.h$^{-1}$.bar$^{-1}$ compared to pristine PSf while an 86.1 % increase of water permeance with the same value of ethanol compared to pristine PSf. Therefore, a higher permeance of both water and ethanol compared to substrate indicates not only because of the non-continuous coverage across the substrate as discussed in LEP results, but also etching effects from plasma to break through the substrate to enhance the permeance. At 5 min deposition, with a better coverage of deposition across substrates compared to 2 min, the water permeance is decreased by 13.5 %, while water permeance at 8 min is decreased by 40.4 %, and at 13 min is decreased by 62.8 % compared to pristine PSf.

Figure 5-28 The liquid entry pressure of the deposited film for different thicknesses of the film from different deposition duration for HMDSO polymerization

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membrane. Hence, with an increase in film thickness by increased duration, water is more resisted by the complex crosslinking to pass through the membrane. In the ethanol permeance from the deposited film at 5 min, an increase of 658 % as 25 kg.m⁻².h⁻¹.bar⁻¹ is observed compared to bare PSf but is a 66.7 % decrease compared to 2 min deposition. At 8 min deposition, ethanol permeance suggests a relatively highest value as 30 kg.m⁻².h⁻¹.bar⁻¹ compared to 5 min and 13 min which makes a good agreement of LEP for the largest LEP gap between ethanol and water compared to other samples. Hence, with a better continuous coverage of HMDSO deposition across the substrate, the better performance of ethanol permeation compared to water can be found [216, 327]. However, due to potentially non-continuous feature of deposition at 13 min in the pressurized liquid, the ethanol permeance is decreased by 70 % as 9 kg.m⁻².h⁻¹.bar⁻¹ compared to 8 min deposition.

Based on the permeance of ethanol and water, Equation 5-1 was used to estimate the ideal selectivity of ethanol against water as the separation performance [291, 322]. As seen in Figure 5-29b, the ideal selectivity at 8 min deposition was found around 1.3 for ethanol to water solution compared to no ethanol selected bare PSf and other samples. At 2 min deposition, the ideal selectivity is obtained as 1 compared to 0.08 from non-selective bare PSf substrate. This value is very low and suggests non-selective performance due to incomplete coverage of deposition across the substrate which ethanol selected deposition cannot resist water to pass through the membrane. At 5 and 13 min depositions, the ideal selectivities are calculated as 0.65 for ethanol against water which makes agreements of non-continuous deposition and is prove by relatively higher water permeances compared to ethanol permeances. Therefore, although the separation performance is hard to be achieved with current fabrication,
high selectivity of ethanol against water will be eventually achieved by improvements on plasma polymerization to overcome the non-densed coverage.

Figure 5-29 Permeance and ideal selectivity from the estimation of flux from dead-end filtration for water and ethanol along with the different duration of deposition on PSf membrane

5.4.4 Concluding remarks

A parallel cylindrical electrodes system for atmospheric pressure plasma deposition was settled to overcome the non-uniform thickness generated by parallel
plane electrodes system. HMDSO monomer was used to examine the effective deposition properties compared to previous work in the performance of ethanol separation from water. The X-Y moving stage effectively reduced the variation of thickness and controlled the deposition rate as 24.34 nm.min$^{-1}$.

However, due to the non-continuously features from the SEMs and XPS characterizations, the membrane performance of HMDSO deposition performed a selectivity of 1.3 for ethanol against water. Therefore, the improvement of the substrate pre-treatment is required for the continuous film under liquid environment and as well the adjustment of plasma deposition conditions. Furthermore, the POSS nano-particle was not applied to the system due to the non-continuous deposition from plasma polymerization of a pure monomer which the benchmark sample was not successful prepared. The feature of gaps between depositions may come from the configuration of the system in which the duration for monomers passing the electrodes was too short to continuously polymerize monomers on the substrate. In addition, due to the unsuccessful coverage across the substrate, neither mixed ethanol and water solution and PV should be applied for further study until the well-prepared benchmark sample is achieved by improving plasma conditions.
5.5 Comparison between plasma configurations

Based on the results from the chemical properties, surface features, and membrane performance from the atmospheric pressure plasma systems with different geometries of electrodes with different feed injections as shown in Figure 5-30. A discussion of comparison will be used to address the difference between two systems.

In the deposition of pure HMDSO monomer, both atmospheric pressure plasma systems suggested a controllable thickness of the film to prepare designable 50, 150, and 300 nm film. A 150% larger effective area as $50 \times 80 \text{ mm}^2$ was prepared by the cylindrical electrodes with showerhead feed injection and X-Y moving stages compared to $40 \times 40 \text{ mm}^2$ from plane electrodes with lateral feed injection [328, 329]. The homogenous thickness of the film was more likely produced by cylindrical electrodes system with a standard deviation around 9 nm while a gradient in thickness with more than 20 nm was obtained by plane electrodes system [329, 330]. The wettabilities of depositions in both systems are found to be same hydrophobicity with 100° above water contact angle and alcohol-philicity by plasma polymerization [300, 326]. Hence, the surface charge of the deposition from HMDSO monomer can be maintained by the different dimension of electrodes.

However, because of the width of the plasma from the cylindrical electrode is smaller than plane electrode due to the width of electrodes, cylindrical electrodes take more duration to polymerize the same amount of monomer to the substrate as shown in Figure 5-30 [281]. Therefore, a lower deposition rate as $24.34 \pm 0.48 \text{ nm.min}^{-1}$ was obtained by cylindrical electrodes compared to $178.1 \pm 19.8 \text{ nm.min}^{-1}$ by plane electrodes. Hence, more energy required for the polymerization by cylindrical electrodes compared to plane electrodes led to a 159% increase of oxygen content as 47 at.% by cylindrical electrodes system compared to plane electrodes system. The
more complex network of deposition formed by oxygen bonding was produced by cylindrical electrodes and eventually forming polymerized clusters before contact with substrate towards a high roughness and defects on the surface of deposition. Therefore, surface features included pit-like, crack-like features were produced by cylindrical electrodes system and led gaps between depositions occurred to lose the performance of deposition as shown in SEMs. Consequently, the selective performance in the ethanol-water system was nearly 1 for ethanol against water represented as non-selective for ethanol by the non-continuous deposition from cylindrical electrodes.

Furthermore, the uniformity of deposition was also affected by the position of the substrate in the plasma chamber. The deposition was initiated by highly active monomers in the plasma when the substrate was placed in the plasma zone by plane electrodes system as shown in Figure 5-30a. In the configuration of cylindrical electrodes for plasma (Figure 5-30b), the plasma zone is located between cylindrical electrodes which substrate is placed at after plasma glow zone indicates the initiation of deposition is mainly forced by feed flow [281, 331]. Therefore, the initiation of deposition by feed flow from cylindrical electrodes leads a rougher surface compared to initiation of deposition by active monomers due to the continuous polymerization in the plasma by plane electrodes [281, 329]. Therefore, homogeneity of deposition may be effectively enhanced by pre-treatments on the substrate as initiate the deposition by active surface of the substrate.

In addition, large effective area for deposition with X-Y stage requires a large volume of plasma chamber as 0.1 m³ compared to 0.02 m³ from plane electrodes system which air contamination and water were easier to affect plasma with limited sealing [281]. The effects from air oxidation were led by an increase of oxygen content towards again the polymerized network for deposition which the polymerized clusters
may be enhanced by air before deposited on the substrate. The increased heat generated by the small diameter of 4 mm cylindrical compared to plane electrodes which assisted the formation of highly polymerized monomer before deposited on substrate towards a difficulty on bridging each piece of polymerized monomer to a continuous film [281, 331].

Figure 5-30 Configuration of atmospheric pressure plasma system with different feed flow and geometries of electrodes which red electrode presents as the anode and black electrode presents the cathode, a) plane electrodes and lateral feed injection, and b) cylindrical electrodes with showerhead feed injection.
5.6 Summary

POSS nano-composite thin films on PSf membrane for solvent separation has been successfully prepared by plasma polymerization with the aerosol-assisted method by parallel plane electrodes with lateral feed injection system. Interactions between POSS nano-particles and polymerized matrix related were discussed through the membrane performance for pure ethanol and water filtration. Agglomeration of POSS nano-particles in the HMDSO solution was effectively broken down by the atomizer to produce nanoscale droplets towards the homogenous nano-composite deposition. Chemical bonding for the structure of deposition was tuned by increasing the concentration of POSS suggested the increase of oxygen bonding for the nano-composite network as a potential decrease of free volume. A successful separation of ethanol from water was obtained by an ideal selectivity for ethanol against water as 6.5 from a 50 nm thick and 0.1 wt.% octamethyl POSS-HMDSO deposition.

The homogeneous thickness of the film was controlled by the duration of the plasma and the X-Y moving stage in the parallel cylindrical electrodes system. The hydrophobic but alcohol-philic surface was maintained by plasma deposition with the constant trend with different duration of deposition from HMDSO monomer towards an ethanol selected wetting. However, non-continuous coverage of deposition across the substrate was found by cylindrical electrodes system due to short polymerization duration in the plasma compared to plane electrodes system. The feature of defects was also contributed by the location of the substrate in the plasma polymerization which the position after plasma glow zone is more difficult to initiate the deposition compared to continuously initiating the deposition in the plasma zone. Furthermore, air contamination and heat produced by small electrodes were enhanced the oxygen content in the deposition which may be over polymerized the chemical structure before
deposited on substrate towards the non-continuous deposition. Therefore, improvements for pre-treatment, chamber sealing, and configuration of electrodes will effectively enhance the formation of the film to overcome the gaps between polymerization.

In addition, the degree of crosslinking was not yet studied by controlling the functionalized POSS nano-particles in the plasma deposition for nano-composite thin film preparation due to the difficulty of yield for functional groups on octamethyl POSS nano-particles. Limited duration of sample preparation at Bari University (Italy) cannot support the proper study on purchased functionalized POSS nano-particles by parallel plane electrodes system. The study of interaction in POSS nano-composite was limited by non-continuous deposition in parallel cylindrical electrodes system which both non-functionalized and functionalized POSS nano-particles were not applied to the demonstration. Impact of POSS nano-particles in nano-composite for mixed solvents and PV performances was also not yet studied due to the insufficient number of samples prepared at Bari University (Italy) and non-selected deposition at Deakin University.
Chapter 6 Summary and Conclusions

6.1 General outcomes

The development for the fabrication of POSS nano-composite thin film membranes by atmospheric pressure plasma deposition was the primary objective of this Thesis. Plasma technologies were introduced for (i) the functionalization of POSS nano-particles by plasma gas activation and (ii) the design of POSS nano-composite membranes through aerosol-assisted plasma polymerization.

In the low-pressure gas plasma system, nitrogen-containing functional groups were successfully introduced across the POSS nano-particles but the production rate was limited to less than 10 mg per run, due to the need to expose a large surface area of POSS. In the low-pressure stirring plasma system, oxygen-containing functional groups were successfully introduced across the POSS nano-particles with over 60 mg of POSS functionalized per run. To control the number of functional groups and maintain the cage-like structure after functionalization, the power and duration were tuned to control the efficiency of the functionalization. The low-pressure plasma gas functionalization was reported in “Grafting of N-moieties onto octa-methyl polyhedral oligomeric silsesquioxane microstructures by a sequential continuous wave and pulsed plasma” published in Plasma processes and Polymers in volume 14, issue 10, October 2017 [105].

POSS nano-composite thin film membranes were prepared by atmospheric pressure aerosol-assisted plasma deposition in a single-step process with HMDSO monomer. The first batch of membranes was processed at Bari University (Italy) in the plasma lab within the Department of Chemistry. These membranes provided selective
ideal separation capabilities for ethanol from water. The presence of the POSS nanoparticles in the polymerized matrix was determined by composition analysis and the stability of the cage-like structures confirmed. The hydrophobic surfaces were generated and the degree of crosslinking was controlled by tuning the amount of POSS nano-particles. The nano-composite membranes exhibited a Janus behaviour which was reported in “Single Step Synthesis of Janus Nano-composite Membranes by Atmospheric Aerosol Plasma Polymerization for Solvents Separation” and published in Science of the Total Environment, volume 645, December 2018 [215].

The summary of the POSS nano-composite membranes were reviewed in the literature review for different separation applications includes pressure-driven separation, desalination, solvent separation, gas separation and proton exchange fuel cell. The comparison between commercial and POSS incorporated membranes provided benefits and limitations from the membrane performance which was reported in “Polyhedral Oligomeric Silsesquioxane (POSS) Nano - Composite Separation Membranes – A Review” and published in Advanced Engineering Materials, volume 21, issue 2, November 2018 [122].

6.2 Shortcomings of the studies

Plasma modifications are usually only performed at nano-scale depth for effective modifications of the exposed side. Therefore, the agglomeration of POSS nano-particles in micro-sized particles shall affect the functionalization process. Hence, although evidence of the plasma functionalization was demonstrated by the direct plasma treatment on POSS nano-particles, the yield of functional groups formation across the POSS nano-particles is still limited.
To overcome this shortcoming, a stirring plasma gas system was applied at low-pressure. The POSS nano-particles were however still aggregated and difficult to physically break down even if the stirring motion, which led to a reduction of functionalization yield compared to the conventional low-pressure process. Furthermore, nitrogen-containing functional groups were not successfully introduced due to sealing issues, leading to oxygen gas intake, and to a lower quality of vacuum in the stirring plasma system.

In the second phase of the Thesis, a homemade aerosol-assisted atmospheric pressure plasma system by Bari University with He gas carrier was successfully used to develop octamethyl POSS nano-composite thin films across commercial PSf UF membrane supports. Due to limitations related to the size of the system and to the design of the precursor flow inlet, uniform depositions were achieved only across small surface areas on the order of $40 \times 40$ mm$^2$.

A system including an X-Y moving stage was built at Deakin University with an Ar gas inlet flow system to tentatively tackle these challenges. However, the difference between the dimension of electrodes in two systems and the effect from air oxidation in the Deakin system which could not be as efficiently sealed as the Bari system led to different deposition mechanisms. The deposition at Deakin became very non-uniform and spotty despite the averaging of the system with the overlapping layers generated with the X-Y stage. Composition characterizations suggested that the influence from air affected the monomer aerosolization and the crosslinking of the deposited layers. The separation performance for the Deakin synthesized membranes was found to be lower than those obtained in Bari, and lower selectivities for ethanol from the water were achieved. Analysis of the membrane surface suggested crack formations which could not be resolved unless developing a new system. The main
limitation of the deposition was attributed to the electrodes geometry and substrate location for deposition as well as the air influence due to a large chamber. The parallel cylindrical electrodes may have induced plasma reactions prior to the monomer reaching the substrate, therefore polymerizing prematurely the monomers compared to parallel plate electrodes. In addition, the large chamber affected the polymerization by increasing the amount of air present despite degassing, which enhanced the network formation and oxidation reactions prior to the substrate surface, leading to crack-like features formation across the surface of the deposition.

6.3 Future works and research directions

To further improve the number of functional groups across the POSS nanoparticles for future polymerizing cross-linked structure with polymers, highly vacuum environment should be applied to avoid the oxidation from air. The degree of functionalization can be also improved by feeding highly reactive gas such as NH₃ or amine based monomers for amine formation or carboxylic based monomer for carboxylic functional groups introduction. A new strategy for preparing nano-scale POSS nano-particles in solid state will be considered to enhance the contact area of nano-particles with plasma eventually improve the degree of functionalization.

To further improve the homogeneity of the deposition, pre-treatment of the substrate PSf membranes with Ar plasma can activate the surface of substrate which initiate the deposition in the plasma polymerization. Therefore, gaps between deposited domains can be effectively reduced by uniform activation on the surface of the substrate towards the continuous thin film.
A key feature to be modified across the system may be the type of discharges and the geometry of the glow, allowing for smoother activation or else more controlled deposition if polymerization was to be performed after-glow.

Therefore, alternative pathways for nano-composite thin film formation would be considered including plasma initiated dip-coating and UV curing to demonstrate a comparison in membrane performance compared to plasma polymerization. Thus, a better understanding of the interaction between nano-particle and matrix in the plasma can be obtained towards the more specific control of cross-linked structure. New recipes of POSS nano-composite thin film by plasma deposition should be developed by possible plasma polymerized PVA or potentially designable NaAlg which suggested promising performance on separating solvent mixture. Future development on smart design of the plasma configuration should also be focused on the adjustment of location for substrate which in the plasma zone should lead better bridging between each polymerized units and with substrate. Reduction of gaps between precursor inlet and electrodes and sample holder would effectively enhance the formation of the dense film due to less chance of aggregation from plasma polymerized species before they arrived the substrate. Therefore, Figure 6-1 presents a possible design to improve the deposition compared to the current system. The distance between precursor inlet and electrodes can reduce from 32.5 mm to less than 10 mm, while the distance between electrodes and the sample holder also can reduce from 10 mm to less than 5 mm. In addition, the ground electrode could move to the bottom of the sample holder or work as the sample holder. Hence, the plasma reaction area becomes close to the substrate and suggests the relatively stronger plasma on the sample substrate compared to the original design. Therefore, the aerosol of HMDSO monomer would be smaller as small droplets before they excited by plasma and polymerization compared to original design.
Furthermore, the continuously curing by plasma above the substrate could bring a dense coating from the polymerized HMDSO. The increase of nozzle size for the inlet design would also effective bring more precursors to the plasma reaction area which reduce the pressure of carrier gas for monomer lead a less waste of gases and monomers.

Figure 6-1 plasma configuration of a) current setup, b) future development for thin film deposition
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