Graphene Based Membranes for Osmosis Applications

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A thesis submitted for the degree of Doctor of Philosophy

August, 2020
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Sevilay Akca

25-08-2020
ABSTRACT

Graphene Based Membranes for Osmosis Applications

Sevilay Akca

With the discovery of two-dimensional hexagonal graphene (single layer of graphite), a tremendous interest has grown due to its remarkable properties. Apart from all other properties, its superior thickness (one-atom thick) enabled to discover many opportunities in membrane science by being functionally active layers of separation membranes. Besides, graphene nanosheets provide fast transport of water molecules through its unhindered channels and offers high selectivity which can be controlled by highly ordered graphene laminates. The main goal of this research was to demonstrate the feasibility of fabricating thin-film composite membranes with stacked graphene nanosheets as selective layer for utilization in osmosis applications such as waste water treatment, desalination, power generation, food industry etc.

Despite the fact that there are several ways to produce graphene from bulk material graphite, the widely used liquid phase exfoliation technique (LPE) was used in this research as it is mass-scalable and low-cost technique for industrial fabrication of graphene. Various solvents were studied to test the dispersibility of graphite via LPE since suitable solvent is essential to decrease the potential energy between adjacent layers in the bulk material in order to overcome the van der Waals interactions between layers. Seven reproducible dispersion methods have been established to fabricate multi-layer graphene from graphite with the help of high boiling point solvent NMP, low boiling point solvent ethanol and water-sodium cholate mixture, which provided a broad possibility of selection with respect to concentration, flake size and thickness, number of layers and type of solvent used in the dispersion. A high yield of up to 7.2% was achieved by revealing a highest concentration of 0.36 mg mL$^{-1}$ in one of the NMP based dispersions. Furthermore, the concentration of graphene dispersion in ethanol-based systems was successfully increased up to 0.08 mg mL$^{-1}$ with the assistance of potassium sodium tartrate salt (KNaC$_4$H$_4$O$_6$). The characterization results provided graphene made of large number of multi-layers with lateral size less than micron, mostly ≤500 nm. Except for residual solvents (NMP and sodium cholate) on silicon substrate, no oxygen related groups were found in the resultant dispersions which can be explained by the fabrication of pure graphene. By simply assembling millions of graphene flakes together onto a porous support membrane via pressure-assisted filtration technique, graphene-based membranes which included graphene composite membranes (assembled graphene onto support membrane) and graphene-polymer hybrid membranes (assembled...
graphene with or without cross linker in between two polyethylenimine (PEI) layers onto support membrane) were fabricated. Here, the aim of using two PEI layers was to create a positively charged membrane surface to obtain a strong attachment of graphene layers and thereafter to improve selectivity further by 2nd layer of PEI after graphene assembly. Using a cross-linker (ethylene diamine, EDA) was proposed as a method to enhance the stability of nanosheets in aqueous systems.

High-water permeability varied from 80 – 366 L/m².h.bar and improved selectivity with 48% rejection for dextran 2000 kDa rejection was observed in some of the best graphene composite membranes. Ultrafiltration membrane made from polyethersulfone (PES) showed better performance compared to microfiltration membranes from Nylon or polytetrafluoroethylene (PTFE) due to its smooth surface morphology. After a huge effort had been made in order to improve the quality of graphene-based membranes, significant achievement came from the graphene-polymer hybrid membranes fabricated via ethanol-based dispersion E2 and PES porous support membrane. Highly compact graphene layer assisted by the polymer provided a selective layer with a thickness of ~1 μm. Filtration results for the graphene-polymer hybrid membrane without cross-linker provided that increasing graphene amount from 0.06 mg/cm² to 0.2 mg/cm² led to superior rejection of dextran 2000 kDa from 53% with 77 L/m².h.bar water permeance up to 96% with 33 L/m².h.bar water permeance. This meant that average pore sizes of the graphene-polymer/PES hybrid membranes with 0.2 mg/cm² graphene were smaller than 50 nm which is defined as average molecular size of dextran 2000 kDa.

Therefore, the filtration results from the graphene-polymer hybrid membrane with cross-linker provided that contribution of EDA on membrane separation performance was not so pronounced compared to graphene content, but cross-linker definitely enhanced membrane stability in aqueous medium. The highest dextran 2000 kDa rejection of 94% with 23 L/m².h.bar water permeability was achieved from graphene-cross-linker modification. Additionally, by testing the resultant graphene-polymer hybrid membrane under forward osmosis experiments which included solution of polyacrylic acid sodium salt (PAA-Na) as draw and water as feed solutions, it has been also achieved 2.1 L/m².h water flux with 0.6 g/m².h reverse solute flux in active layer facing with draw solution mode while 1.4 L/m².h water flux with 0.4 g/m².h reverse solute flux were obtained in active layer facing with feed solution mode.

Keywords: exfoliated graphene, multilayer graphene, liquid phase exfoliation, pressure-assisted filtration technique, graphene composite membranes, graphene-polymer hybrid membranes, forward osmosis, polyacrylic acid sodium salt, polyethyleneimine, ethylene diamine.
DEDICATION

This thesis is dedicated

To all people who live this world for others.

And to my dear sister, half-mother Đondü Akca Dinç who has been always a role model, supportive, and a good mentor during my life.

And also, to my beloved parents, Ulfet Akca and Ali Akca who has been always source of my encouragement, inspiration and love.
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Ph.D. is a long journey which mainly takes 3-4 years. It seems to contain mostly research, long hours in the lab and later spending time for analyzing data in PC. However, it is also a part of a whole life. There are other vital things which are happening during Ph.D. period. One should also manage those other things aside at the same time. It has been a challenge for me, both in my academic life and personal life. I had to deal with many obstacles internally or externally. I sometimes thought to give up and do something else. But I could not. Because there was only thing that pushed me to continue my career on this way whatever happened. It was my hope that one day I could enlighten someone who really need assistance, guidance. Be able to give hope and create an opportunity with full of life to someone else without expecting anything in return could be priceless joy. It is almost impossible to deny the contribution of some people who helped me to come to this stage materially and morally.

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Sevilay Akca
Dublin, August 2020
“Nothing in life is to be feared, it is only to be understood. Now, it is the time to understand more, so that we may fear less.”

-Marie Curie-
TABLE of CONTENTS

ABSTRACT ......................................................................................................................................................... iii

ACKNOWLEDGEMENTS ................................................................................................................................. vi

TABLE of CONTENTS ........................................................................................................................................ ix

LIST of ABBREVIATIONS ................................................................................................................................... xii

LIST of SYMBOLS ........................................................................................................................................... xiii

LIST of FIGURES ........................................................................................................................................... xv

LIST of TABLES ................................................................................................................................................ xxi

Foreword – Objective of the Thesis and Outline .............................................................................................. 1

Objective of the Thesis ..................................................................................................................................... 1

Outline ................................................................................................................................................................. 3

Chapter 1 - Fundamentals ............................................................................................................................... 4

1.1 Introduction to Graphene .......................................................................................................................... 5

1.1.1 Graphite and Its Discovery .................................................................................................................... 5

1.1.2 Properties of Graphene .......................................................................................................................... 5

1.1.3 Structure of Graphene ............................................................................................................................ 8

1.1.4 Fabrication of Graphene ........................................................................................................................ 9

1.1.4.1 Liquid Phase Exfoliation Technique .................................................................................................. 12

1.1.4.1.1 Solubility Parameters & Exfoliated Graphene in Organic Solvents ......................................................... 16

1.1.4.1.2 Exfoliated Graphene in Aqueous System Assisted by Surfactant ......................................................... 20

1.1.5 Characterization Techniques of Graphene Dispersion ......................................................................... 22

1.2 Introduction to Membrane Technology ..................................................................................................... 33

1.2.1 Membrane Processes ............................................................................................................................ 33

1.2.2 Membrane Applications ......................................................................................................................... 36

1.2.3 Graphene Based Membranes ................................................................................................................. 36

1.2.3.1 Fabrication Methods of Stacked Graphene Composite Membranes ....................................................... 38

1.2.3.2 Transport Mechanism Through Nanochannels ............................................................................... 41

1.2.3.3 Separation Mechanism Through Nanochannels ............................................................................... 42

1.2.4 Osmosis Processes .................................................................................................................................. 43

1.2.4.1 Selection of Draw Solute ................................................................................................................... 45

1.2.4.2 Concentration Polarization ............................................................................................................... 47

1.2.5 Equations used in Filtration Characterization ....................................................................................... 50

1.2.6 Equations used in Forward Osmosis Characterization ......................................................................... 51

Chapter 2 – Experimental Section .................................................................................................................... 52

2.1 Materials, Methods and Experimental Procedures .................................................................................... 53

2.1.1 Materials .................................................................................................................................................. 53

2.1.2 Methods ................................................................................................................................................ 53

2.1.2.1 Preparation of Graphene Dispersions ............................................................................................... 53
Chapter 3 – Exfoliated Graphene Dispersion in Various Solvents

3.1 Introduction ................................................................. 72
3.2 Results and Discussion ................................................. 74
3.2.1 UV-Vis Spectroscopy ............................................... 74
3.2.2 Dynamic Light Scattering ............................................ 78
3.2.3 Raman Spectroscopy .................................................. 81
3.2.4 Atomic Force Microscopy ............................................ 85
3.2.5 Transmission Electron Microscopy ............................ 88
3.2.6 X-ray Photoelectron Spectroscopy ............................ 90
3.2.7 Comparison of Flake Size Results from Different Techniques ............................. 92
3.3 Conclusion ..................................................................... 93

Chapter 4 – Graphene Based Membranes .................................................. 96
4.1 Introduction ................................................................... 96
4.2 Graphene Composite Membranes ..................................... 98
4.2.1 Introduction .............................................................. 99
4.2.2 Results and Discussion ............................................... 99
4.2.2.1 Gas Flow/Pore De-wetting Permporometry ................ 99
4.2.2.2 Contact Angle Analysis ........................................... 101
4.2.2.3 Study of Membrane Surface Properties .................... 102
Chapter 5 – Forward Osmosis Characterization .......................................................... 150

5.1 Introduction ........................................................................................................... 151
5.2 Results and Discussion ......................................................................................... 153
5.2.1 Viscosity Analysis of PAA-Na ........................................................................ 153
5.2.2 Forward Osmosis Characterization ............................................................... 156
5.3 Conclusion ............................................................................................................. 167

Chapter 6 – Summary and Outlook ............................................................................ 168

6.1 Summary .............................................................................................................. 169
6.2 Outlook ................................................................................................................. 176

Appendices .................................................................................................................. 177

List of Presentations and Publications ..................................................................... 198

References .................................................................................................................... 200
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl alcohol</td>
</tr>
<tr>
<td>C_{60}</td>
<td>Fullerene</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half-maximum</td>
</tr>
<tr>
<td>G</td>
<td>Graphene</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon wafer</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>LPE</td>
<td>Liquid phase exfoliation</td>
</tr>
<tr>
<td>C_G</td>
<td>Concentration of graphene</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>WS\textsubscript{2}</td>
<td>Tungsten disulphide</td>
</tr>
<tr>
<td>MF</td>
<td>Microfiltration</td>
</tr>
<tr>
<td>UF</td>
<td>Ultrafiltration</td>
</tr>
<tr>
<td>NF</td>
<td>Nanofiltration</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>PRO</td>
<td>Pressure Retarded Osmosis</td>
</tr>
<tr>
<td>FO</td>
<td>Forward Osmosis</td>
</tr>
<tr>
<td>PES</td>
<td>Polyethersulfone</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethyleneimine</td>
</tr>
<tr>
<td>EDA</td>
<td>Ethylenediamine</td>
</tr>
<tr>
<td>LbL</td>
<td>Layer by layer</td>
</tr>
<tr>
<td>DS</td>
<td>Draw solution</td>
</tr>
<tr>
<td>FS</td>
<td>Feed solution</td>
</tr>
<tr>
<td>ICP</td>
<td>Internal concentration polarization</td>
</tr>
<tr>
<td>ECP</td>
<td>External concentration polarization</td>
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<td>CP</td>
<td>Concentration polarization</td>
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# LIST of SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>C</td>
<td>Concentration</td>
</tr>
<tr>
<td>I</td>
<td>Intensity</td>
</tr>
<tr>
<td>I₀</td>
<td>Intensity of the incident light</td>
</tr>
<tr>
<td>ε</td>
<td>Molar extinction coefficient</td>
</tr>
<tr>
<td>l</td>
<td>Optical path length</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>d</td>
<td>Spacing between diffracting planes</td>
</tr>
<tr>
<td>θ</td>
<td>Incident angle</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>β</td>
<td>Peak width</td>
</tr>
<tr>
<td>L</td>
<td>Crystallite size</td>
</tr>
<tr>
<td>k</td>
<td>Constant related to crystallite shape</td>
</tr>
<tr>
<td>Eₚ</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>Eₘₘ</td>
<td>Binding energy</td>
</tr>
<tr>
<td>ν</td>
<td>Frequency</td>
</tr>
<tr>
<td>h</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>w</td>
<td>Work function of spectrometer</td>
</tr>
<tr>
<td>d(H)</td>
<td>Hydrodynamic diameter</td>
</tr>
<tr>
<td>D</td>
<td>Translational diffusion coefficient</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann’s constant</td>
</tr>
<tr>
<td>L</td>
<td>Crystallite size</td>
</tr>
<tr>
<td>T</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>η</td>
<td>Viscosity</td>
</tr>
<tr>
<td>ΔGₘixe</td>
<td>Free energy of mixing</td>
</tr>
<tr>
<td>ΔHₘixe</td>
<td>Enthalpy of mixing per unit volume of solvent</td>
</tr>
<tr>
<td>ΔSₘixe</td>
<td>Entropy of mixing per unit volume of solvent</td>
</tr>
<tr>
<td>δ</td>
<td>Solubility parameter</td>
</tr>
<tr>
<td>δ₉</td>
<td>Solubility parameter of dispersion force</td>
</tr>
<tr>
<td>δₚ</td>
<td>Solubility parameter of polar intramolecular force</td>
</tr>
<tr>
<td>δ₅</td>
<td>Solubility parameter of hydrogen bonding</td>
</tr>
<tr>
<td>m</td>
<td>Ground vibrational energy level</td>
</tr>
<tr>
<td>n</td>
<td>Higher vibrational energy level</td>
</tr>
<tr>
<td>hVₘ, hVₙ</td>
<td>Excited state energy level</td>
</tr>
<tr>
<td>J</td>
<td>Flow between laminar graphene membranes</td>
</tr>
<tr>
<td>d</td>
<td>Distance between adjacent graphene layers</td>
</tr>
<tr>
<td>L</td>
<td>Average lateral size of the nanosheets</td>
</tr>
<tr>
<td>π</td>
<td>Osmotic pressure</td>
</tr>
<tr>
<td>πₑff</td>
<td>Net osmotic pressure difference</td>
</tr>
<tr>
<td>Δπ</td>
<td>Osmotic pressure difference</td>
</tr>
<tr>
<td>πₚ₉,b</td>
<td>Osmotic pressure at the bulk feed side</td>
</tr>
<tr>
<td>πₚ₉,m</td>
<td>Osmotic pressure on the feed side of the active layer</td>
</tr>
<tr>
<td>πₙₙ</td>
<td>Osmotic pressure on the draw side of the active layer</td>
</tr>
</tbody>
</table>
\( \pi_{D,b} \)  
Osmotic pressure at the bulk draw side

\( \pi_{D,i} \)  
Osmotic pressure of the draw solution within the support

\( \pi_{F,i} \)  
Osmotic pressure of the feed solution within the support

\( n \)  
Number of moles of species

\( M_w \)  
Molecular weight of the solute

\( R \)  
Gas constant

\( D_s \)  
Diffusion coefficient

\( K \)  
Solute resistance

\( \tau \)  
Tortuosity

\( \varepsilon \)  
Porosity

\( t \)  
Support layer thickness

\( J_w \)  
Water flux

\( A_m \)  
Membrane active layer area

\( \Delta V \)  
Permeate volume

\( \Delta t \)  
Testing duration

\( A \)  
Water permeability

\( \Delta P \)  
Applied pressure

\( R \)  
Rejection (\%)  

\( C_p \)  
Permeate concentration

\( C_f \)  
Feed concentration

\( m_1 \)  
Wet membrane weight

\( m_2 \)  
Dry membrane weight

\( \rho_w \)  
Density of the water

\( \rho_p \)  
Density of the substrate

\( J_s \)  
Reverse solute flux

\( C_0 \)  
Initial concentration of feed solution

\( V_0 \)  
Initial volume of feed solution

\( C_1 \)  
Measured concentration of feed solution

\( V_1 \)  
Measured volume of feed solution
LIST of FIGURES

Figure 1.1: (a) Image of natural graphite, (b) schematic of graphite and (c) arrangements of how the carbon atoms are oriented.................................................................6

Figure 1.2: a) Atomic structure of a carbon atom. (b) Energy levels of outer electrons in carbon atoms. (c) The formation of sp2 hybrids. (d) The crystal lattice of graphene, where A and B are carbon atoms belonging to different sub-lattices, a1 and a2 are unit-cell vectors. (e) Sigma bond and pi bond formed by sp2 hybridization.................................................................8

Figure 1.3: Step by step description of Scotch tape method to produce graphene................................................. 10

Figure 1.4: Several methods of mass graphene production which provide a broad selection with regards to production cost, final graphene quality and size................................................................. 11

Figure 1.5: Concentration of graphene dispersed in NMP after centrifugation as a function of sonication time................................................................. 14

Figure 1.6: Schematic illustration of graphite exfoliation mechanism................................................................. 15

Figure 1.7: Schematic description of LPE process for graphene exfoliation and stabilization in a solvent medium................................................................. 16

Figure 1.8: The concentration of graphene dispersion in various solvents after centrifugation as a function of solvent surface tension. The concentrations were calculated using absorbance value at 660 nm and absorption coefficient taken as 2460 Lg·m⁻¹................................. 17

Figure 1.9: Model of Hildebrand (a) and Hansen (b) solubility theory................................................................. 19

Figure 1.10: Molecular structures of ionic surfactant of sodium cholate (a), cationic surfactant (cetyltrimethylammonium bromide) CTAB (b) and non-ionic Pluronic 123 (c)...................................................... 21

Figure 1.11: The typical UV-vis spectroscopy of graphene and graphene oxide (GO)...................................................... 23

Figure 1.12: Simplified version of the description of AFM technique................................................................. 25

Figure 1.13: Schematic description of main types of Raman scattering................................................................. 26

Figure 1.14: Schematic diagram of XRD and Bragg’s law................................................................. 28

Figure 1.15: The typical XRD patterns of graphite, graphene and graphene oxide...................................................... 28

Figure 1.16: Schematic diagram of XPS working process which is describing the ejection of a 1s electron by photoionization................................................................. 30

Figure 1.17: Schematic description of change in hydrodynamic diameter with changing electric double layer’s thickness (Debye length)........................................................................................................... 31

Figure 1.18: TEM images of graphene flakes of monolayer (a) and diffraction pattern produced from the monolayer (a, inset), (b) edges of the individual flakes in a multilayer flake and (c) a wide-field image showing the large quantities of flakes observed................................................................. 32

Figure 1.19: Schematic description of two phases which are separated by a selective membrane. \( \Delta C \), \( \Delta P \), \( \Delta T \), \( \Delta E \) are (concentration, pressure, temperature and electrical potential gradient, respectively) the source of driving force of the flow from feed to permeate side................................................................. 33

Figure 1.20: Types of graphene-based membranes, (a) porous graphene layer (b) assembled stacked graphene laminates and (c) graphene based composites................................................................. 38

Figure 1.21: Schematic of composite GO/mPAN membranes produced via pressure assisted filtration, vacuum filtration and evaporation method................................................................. 39

Figure 1.22: Schematic description of molecular transport through interlayer channels of graphene oxide (a) and inter-layer channels laminates of GO and holes on graphene nanosheets (b)................................................................. 42

Figure 1.23: Schematic description of separation mechanism for monolayer graphene membrane (a) and multilayer graphene membrane (b)................................................................. 43

Figure 1.24: Schematic description of osmosis processes................................................................. 44

Figure 1.25: Schematic description of osmotic pressure gradient in symmetric membranes under FO orientation (active layer faces with feed solution) and PRO orientation (active layer faces with draw solution) \( \pi_{F,b} \) is the osmotic pressure at the bulk feed side, \( \pi_{F,m} \) is the osmotic pressure of the feed solution on the feed side of the active layer, \( \pi_{D,b} \) is the osmotic pressure of the draw solution on the draw side of the active layer, \( \pi_{D,m} \) is the osmotic pressure at the bulk draw side, \( \pi_{F,j} \) is the osmotic pressure of the draw solution within the support layer close to the active layer, \( \pi_{F,i} \) is the osmotic pressure of the feed solution within the support layer close to the active layer................................................................. 48
Figure 2.1: Schematic of fabrication of graphene dispersion at various solvents ........................................ 54
Figure 2.2: Schematic describing the fabrication of graphene dispersion via methods N1 (red arrows), N2 (black arrows) and N3 (green arrows) ................................................................. 56
Figure 2.3: Schematic describing the fabrication of graphene dispersion via methods E1 (blue arrows) and E2 (yellow arrows) ................................................................. 57
Figure 2.4: Schematic describing the fabrication of graphene dispersion via method S1.5 ........................................ 58
Figure 2.5: Image (a) and schematic (b) of dead-end filtration cell with a 9.07 cm² filtration area. Stirrer is on mode at 300 rpm during graphene coating in each experiment ................................. 58
Figure 2.6: Schematic diagram of (a) G/support membrane, (b) (PEI/G/PEI)/support membrane (c) (PEI/G+EDA/PEI)/support membrane ................................................................. 59
Figure 2.7: Schematic of the graphene composite membrane fabrication via procedure 1 (undiluted graphene dispersion) and Procedure 2 (diluted graphene dispersion) ........................................... 60
Figure 2.8: Schematic of the graphene-polymer hybrid membrane fabrication via Procedure 3 .................................................................................................................. 60
Figure 2.9: Schematic of the graphene-polymer hybrid membrane fabrication via Procedure 4 .................................................................................................................. 61
Figure 2.10: Forward osmosis U-tube test apparatus (a), membrane unit together with graphene membrane in two orientations (AL-DS and AL-FS) (b) and schematic of test system (c,d) ........................................................................ 62
Figure 2.11: Schematic of cross cell FO test system .............................................................................................. 63
Figure 2.12: Image of UV - Vis spectroscopy to measure absorbance spectra of exfoliated graphene ................................................................. 65
Figure 2.13: Image of dynamic light scattering (DLS) to analyse particle size of graphene flakes ...................... 65
Figure 2.14: Image of contact angle system ........................................................................................................ 68
Figure 2.15: Capillary flow porometer to analyse pore diameter of membranes .................................................. 69
Figure 3.1: UV-vis absorption spectra of graphene dispersions exfoliated in different solvents (A). As mentioned in experimental work section, N1, N2 and N3 are graphene dispersions in NMP; E1 and E2 are graphene dispersions in ethanol; S1 is graphene dispersion surfactant assisted, sediment and supernatant part of the dispersion. Spectra of graphene dispersion in ethanol (E1, E2) and in aqueous surfactant (sodium cholate) (S1 Se, S1 Su) is enlarged in (B) to identify maximum absorbance peak ...................................................................................................................... 75
Figure 3.2: Absorption coefficient spectra for graphene flakes dispersed in NMP and ethanol at concentrations from 2 to 35 µg/mL. Optical absorbance (λ = 660 nm) divided by cell length (A/l) as a function of concentration for graphene showing Lambert–Beer behaviour with an average absorption coefficient of 3786 and 3780 Lg⁻¹m⁻¹ for in NMP and 3542 and 3520 Lg⁻¹m⁻¹ for in ethanol. The data were converted from absorbance (660 nm) using A/l = (λ₆₆₀)/C formula ...................................................................................................................... 77
Figure 3.3: Hydrodynamic size distribution (number based) of graphene dispersions in NMP (A), in ethanol (B) and in aqueous sodium cholate (C). Measurements were recorded with diluted graphene dispersion (5 µg/mL) ...................................................................................................................... 78
Figure 3.4: Raman spectra of graphene sheets in the dispersion. Disorder related Ih/I₀ value is calculated by dividing the intensity of D band to the intensity of G band. Graphene dispersion in NMP via procedure N1, N2 and N3. Graphene dispersion in ethanol via procedure E1 and E2. Graphene dispersion in aqueous sodium cholate via procedure S1Se and S1Su (a) .......................................................................................... 82
Figure 3.5: Enlarged Raman spectrum of D (a), G (b) and 2D (c) peaks of exfoliated graphene dispersions ...................................................................................................................... 85
Figure 3.6: Atomic force microscopy (AFM) images together with thickness and lateral flake size histograms of graphene dispersion in NMP via procedure N2 (a) and N3 (b) ........................................................................ 86
Figure 3.7: Atomic force microscopy (AFM) image together with thickness and lateral flake size histograms of graphene dispersion in ethanol via procedure E1 (a) and E2 (b) ........................................................................ 87
Figure 3.8: Transmission electron microscopy (TEM) image of graphene dispersion in NMP via procedure N2 (a), N3 (b) and in ethanol via procedure E1 (c), E2 (d) ........................................................................ 88
Figure 3.9: TEM images of graphene dispersion fabricated via method N3 ........................................................................ 89
Figure 3.10: XPS analysis of graphene dispersion in NMP via procedure N2 (a) and in aqueous sodium cholate via procedure S1 Se (b), S1 Su (c). Contribution of the components used in fitting of C 1S peak is also listed in each of graph ........................................................................ 91
Figure 4.1: Chemical structure of PEI (a) and EDA (b).…………………………………………………………………………………………………………………………..98

Figure 4.2: Gas flow measurement as a function of applied pressure in bar (a) and pore size distribution of N02 and G/N02_1mg_05 membranes (b). Black and red lines represent support and graphene composite membranes, respectively. Membranes were fabricated via graphene dispersion N2. …………………………………………………………………………………………………………………99

Figure 4.3: Gas flow measurement as a function of applied pressure in bar (a) and pore size distribution of P02 and G/P02_1mg_08 membranes (b). Blue and red lines represent support and graphene composite membranes, respectively. Membranes were fabricated via graphene dispersion N2.………………………………………………………………………………………………………………100

Figure 4.4: Contact angle of graphene/N02 membranes (a), graphene/N045 membranes (b) and graphene/P02 membranes (c) with different graphene loadings. Orange colour and black colour represent the graphene membranes prepared via method N1 and N2, respectively. Amount of graphene over deposited area varied 0.06, 0.11 and 0.16 mg/cm²………………….101

Figure 4.5: Zeta potential of N02, N045 and P02 membrane without any surface modification (left) and graphene composite membranes fabricated via dispersion of method N2 (right)……………………103

Figure 4.6: Water permeability (L/m².h.bar) of graphene/N02 membranes prepared via dispersion N1 (left) and N2 (right) with various graphene loadings (0.5-1.4mg) prepared as a function of operation time. Average water permeability of unmodified Nylon 0.2 membrane is 7338 ± 168 L/m².h.bar. Membrane active area is 9.07 cm²……………………………………………………………………………………………………………………104

Figure 4.7: Water permeability (L/m².h.bar) of graphene/N045 membranes prepared via dispersion N1 (left) and N2 (right) with various graphene loadings (0.5-1.4mg) as a function of filtration time. Average water permeability of unmodified Nylon 0.45 membrane is 7656 ± 636 L/m².h.bar. Membrane active area is 9.07 cm²……………………………………………………………………………………………………………………105

Figure 4.8: Water permeability (L/m².h.bar) of graphene/P02 membranes prepared via dispersion N1 (left) and N2 (right) with various graphene loadings (0.5-1.4mg) as a function of filtration time. Average water permeability of unmodified PTFE 0.2 membrane is 11520 ± 563 L/m².h.bar. Membrane active area is 9.07 cm²……………………………………………………………………………………………………………………106

Figure 4.9: Average water permeability (L/m².h.bar) of G/N02, G/N045 and G/P02 membranes fabricated via dispersion N1 (black) and N2 (blue) under 0.5 bar and 0.8 bar pressure with various graphene loadings such as 0.5 mg, 1 mg and 1.4 mg. Membrane active area is 9.07 cm²……………………………………………………………………………………………………………………………107

Figure 4.10: Comparison of average water permeability (L/m².h.bar) and dextran 4kDa rejection of graphene/N02 membranes prepared via dispersion N2 with various concentrations. (a) 160 µg/mL, (b) 1.6 µg/mL and (c) 0.16 µg/mL. Active area of membranes: 9.07 cm². Filtration pressure: 0.5 bar…………………………………………………………………………………………………………………109

Figure 4.11: Schematic description of stability problem. Either graphene layer completely peels off from the membrane surface after first touch with water or partly delamination occurs in membrane surface……………………………………………………………………………………………………………………………………….113

Figure 4.12: Surface morphology change of graphene composite membranes (after sonication) fabricated via dispersion method of S1 with anionic (SC), cationic (CTAB), non-ionic (Pluronic 123) surfactants (a, b, c, d) and via method of E1 (e and f)………………………………………………………………………………………………………………………………………………………………………………….113

Figure 4.13: XRD analysis of G/P02 composite membranes fabricated via dispersion N1 and N2 in dry phase (a), G/N02 composite membranes fabricated via dispersion N2 (b) and fabricated via dispersion S1-Se (c) in both dry and wet phases……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………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modified PES membrane and graphene/polymer hybrid membranes (a). Zeta potential of Nylon 0.2 m membrane (unmodified), 0.5 mg/mL PEI and 3 mg/mL PEI modified nylon membrane and graphene/polymer hybrid membranes (b) PES (PEI/G/PEI) and Nylon (PEI/G/PEI)………

**Figure 4.21:** FTIR spectra of unmodified PES membrane and various concentration of PEI modified PES membranes. .............................................................................................................. 122

**Figure 4.22:** FTIR spectra of an unmodified PES membrane and various concentration of PEI modified PES membranes and graphene-polymer/PES hybrid membranes (a) and and enlarged FTIR spectra of graphene-polymer/PES hybrid membranes (b). .................................................. 123

**Figure 4.23:** FTIR spectra of an unmodified Nylon 0.2 (N02) membrane and various concentration of PEI modified Nylon membranes ........................................................................................................................................... 124

**Figure 4.24:** FTIR spectra of an unmodified Nylon 0.2 membrane and various concentrations of PEI modified Nylon 0.2 membranes and graphene-polymer/N02 hybrid membranes (a) and and enlarged FTIR spectra of graphene-polymer/N02 hybrid membranes (b).…………………… 125

**Figure 4.25:** XRD analysis of PES/(PEI/Go06/PEI) fabricated via dispersion E1 in both dry and wet phases (a) and PES/(PEI/Go06+EDA 1200/PEI) fabricated via dispersion E1 in both dry and wet phases (b).…………………….. 127

**Figure 4.26:** XRD analysis of PES/(PEI/Go16/PEI) fabricated via dispersion E2 in both dry and wet phases (a) and PES/(PEI/Go16+EDA 1200/PEI) fabricated via dispersion E2 in both dry and wet phases (b).…………………….. 127

**Figure 4.27:** Water contact angle measurement of graphene-polymer/PES hybrid membranes fabricated via dispersion E2 (M14 – M37) and E1 (PES 15, PES 17) (a), and graphene-polymer/N02 hybrid membranes fabricated via dispersion N3 (M6, M8, M9, M12, M13) and E2 (M30 and M32) (b). Specifications of membranes were shown in below table................................................................. 129

**Figure 4.28:** Gas (dry) flow measurement as a function of applied pressure (a) and pore size distribution (b) of graphene-polymer/Nylon hybrid membranes fabricated via dispersion N3. Unmodified Nylon 0.2 and 0.5/3 mg/mL of PEI modified Nylon 0.2 membrane were also added to the graphs. ............................................................................................................................ 131

**Figure 4.29:** Gas (dry) flow measurement as a function of applied pressure (a) of pore size distribution (b) graphene-polymer/Nylon hybrid membranes fabricated via dispersion E1. Unmodified Nylon 0.2 and 3 mg/mL of PEI modified Nylon 0.2 membrane were also added to the graphs............................................................................................................................ 131

**Figure 4.30:** Gas (dry) flow measurement as a function of applied pressure (a) and pore size distribution (b) of graphene-polymer/PES hybrid membranes fabricated via dispersion E1. Unmodified PES and 0.5/3 mg/mL of PEI modified PES membrane were also added to the graphs. G content: 0.06 mg/cm² .................................................................................................................... 132

**Figure 4.31:** Gas (dry) flow measurement as a function of applied pressure (a) and pore size distribution (b) of graphene-polymer/Nylon hybrid membranes fabricated via dispersion E1. Unmodified Nylon 0.2 and 0.5/3 mg/mL of PEI modified Nylon 0.2 membrane were also added to the graphs. G content: 0.06 mg/cm² .................................................................................................................... 133

**Figure 4.32:** Average water permeability (L/m².h.bar) and rejection for PES membranes without any surface modifications (a), rejection tests for PES 1 and PES 4, which were dried at 60 °C for 2 hours after water flux measurements before rejection tests. With PEI surface modifications at various concentrations (0.2, 0.5 and 1 mg/mL) and various operating times on a hot plate at 70°C (b) and PES 9 membrane, PES-graphene and PES_(PEI/G(001))(c) ................................................................. 134

**Figure 4.33:** Performance of average water permeability (L/m².h.bar) and dextran 4kDa and 200kDa rejection of graphene-polymer/Nylon hybrid membranes prepared by dispersion N3. Specifications of membranes were shown in below table ................................................................................................................................. 135

**Figure 4.34:** Performance of average water permeability (L/m².h.bar) and dextran 4kDa and 200kDa rejection of graphene-polymer/Nylon and graphene-polymer/PES hybrid membranes prepared by dispersion E1 in two different support materials, Nylon 0.2 and PES. Specifications of membranes were shown in below table ................................................................................................................................. 137

**Figure 4.35:** Top (right) and cross section (left) SEM images of membrane graphene-polymer/Nylon hybrid membrane. Nylon/(PEI 0.5/G(006)+EDA 1200/PEI 0.5) ................................. 138

**Figure 4.36:** Particle size (nm) change of Graphene + EDA mixture during a certain of time. Graphene dispersion was fabricated via method E1. Particle size of Graphene + EDA mixture peaked at 289 nm (37%), 486 nm (31%), 687 nm (41%) after 5,7 and 12 h respectively………………………………... 139
Figure 4.37: Performance of average water permeability (L/m².h.bar) and dextran rejection of graphene-polymer/PES hybrid membranes without cross-linker (EDA) as a function of various graphene amount (mg/cm²) (%), with cross-linker as a function of various graphene-EDA weight ratios (b), with cross-linker ratio of 1-15 (c) and 1-1200 (d) as a function of various graphene amount (mg/cm²). ................................................................. 140

Figure 4.38: Relative water flux (L/m².h) decline of graphene-polymer/PES hybrid membranes M43 as a function of time. J is the permeate flux (L/m².h) and J0 is the initial flux (L/m².h). .................................................................................. 141

Figure 4.39: Cross section SEM images of PES support membrane (a), membrane 43 (b), membrane 35 (c) and membrane 34 (d). ........................................................................................................... 142

Figure 4.40: Average water permeability (L/m².h.bar) and dextran 4 kDa and 2000 kDa rejection (%) of graphene-polymer/PES (a) and graphene-polymer/Nylon (b) hybrid membranes which were dried for 12 h in vacuum oven. ................................................................................. 143

Figure 4.41: SEM top images of Nylon and PES membrane without any surface modification. 144

Figure 4.42: SEM top (a, b, c) and cross section (d, e, f) images of PES/PEI3. ............................................. 144

Figure 4.43: SEM top (a, b) and cross section (c, d) images of PES/PEI0.5. .................................................. 145

Figure 4.44: SEM top (a, b) and cross section (c, d) images of N02/PEI4. .................................................. 145

Figure 4.45: SEM top (a, b) and cross section (c, d) images of N02/PEI1. .................................................. 145

Figure 4.46: SEM top (a, b, c) and cross section (d, e, f) images of M14 (PES (PE1/Go.06/PEI3)). Membrane is fabricated via dispersion E2. ................................................................. 146

Figure 4.47: SEM top (a, b, c) and cross section (d, e, f) images of M16 (PE1/0.11/PEI3). Membrane is fabricated via dispersion E2. ................................................................. 146

Figure 4.48: SEM top (a, b, c) and cross section (d, e, f) images of M28 (PES (PE1/Go.16+EDA3/PEI3)). Membrane is fabricated via dispersion E2. ................................................................. 146

Figure 4.49: SEM top (a, b) and cross section (c, d) images of M6 (Nylon (PEI3/Go.06/PEI3))(left) and M8 (Nylon (PEI3/Go.11/PEI3))(right). Membranes were fabricated via dispersion N3. ........................................ 147

Figure 4.50: Schematic description of Nylon (a) and PES (b) support membrane surface morphology. The thickness of selective layer is shown as x and y. ............................................. 148

Figure 5.1: The viscosity of 0.5 mM and 2 mM of PAA-Na 5kDa, 8kDa and 30kDa as a function of temperature. .................................................................................................................. 154

Figure 5.2: The average viscosity of 0.5 mM and 2 mM of PAA-Na 5kDa, 8kDa and 30kDa draw solutions in between 33 °C – 45 °C temperature .......................................................... 154

Figure 5.3: Gel permeation chromatography (GPC) analysis of PAA-Na solution prepared by using 5 kDa, 8 kDa and 30 kDa molecular weights ................................................................. 155

Figure 5.4: Average water flux (L/m².h) and reverse solute flux (g/m².h) as a function of 0.2 mM, 0.5 mM and 2 mM PAA-Na 5kDa, 8kDa and 30kDa. Test system is U-tube. .............................. 157

Figure 5.5: Average water flux (L/m².h) and reverse solute flux (g/m².h) as a function of 2mM PAA-Na 5kDa, 8kDa and 30kDa as draw solute. Two orientations: active layer faces with feed solution (AL-FS) or active layer faces with draw solution (AL-DS). Test system is the cross cell. ....... 158

Figure 5.6: FO results of 0.2 mM of PAA-Na (Mw 5kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr). ........................................... 160

Figure 5.7: FO results of 0.5 mM of PAA-Na (Mw 5kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr). ........................................... 160

Figure 5.8: FO results of 2 mM of PAA-Na (Mw 5kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr). ........................................... 161

Figure 5.9: FO results of 0.125 mM of PAA-Na (Mw 8kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr). ........................................... 161

Figure 5.10: FO results of 0.5 mM of PAA-Na (Mw 8kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr). ........................................... 162

Figure 5.11: FO results of 2 mM of PAA-Na (Mw 8kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr). ........................................... 162

Figure 5.12: FO results of 0.033 mM of PAA-Na (Mw 30kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period
Figure 5.13: FO results of 0.5 mM of PAA-Na (Mw 30kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr) .......................................................... 163

Figure 5.14: FO results of 2 mM of PAA-Na (Mw 30kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr) .......................................................... 163

Figure 5.15: Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa)//AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr) .......................................................... 164

Figure 5.16: Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa)//AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr) .......................................................... 165

Figure 5.17: Forward osmosis experimental results of 2mM of PAA-Na (Mw 8kDa)//AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr) .......................................................... 166

Figure 5.18: Forward osmosis experimental results of 2mM of PAA-Na (Mw 5kDa)//AL-DS Water flux and reverse salt flux (a), net driving force estimated from calculated draw and feed osmotic pressures (b) as a function of operation period (hr) .......................................................... 166

Figure A.1: Top and cross section images of M18 (PES/PEI3/G0.06+EDA1200/PEI3)) ........................................ 177

Figure A.2: Top and cross section images of M20 (PES/PEI3/G0.06+EDA15000/PEI3)) ........................................ 177

Figure A.3: Top and cross section images of M22 (PES/PEI3/G0.06+EDA15/PEI3)) ........................................ 178

Figure A.4: Top and cross section images of M9 (Nylon (PEI3/G0.06+EDA1200/PEI3)) ........................................ 178

Figure A.5: Top and cross section images of M12 (Nylon (PEI3/G0.06+EDA15000/PEI3)) ........................................ 179

Figure A.6: Top and cross section images of M16 before and after filtration (PES/PEI3/G0.11/PEI3)) ............. 179

Figure A.7: Top and cross section images of M18 before and after filtration (PES/PEI3/G0.06+EDA2000/PEI3)) .......................................................... 180

Figure A.8: Top and cross section images of M20 before and after filtration (PES/PEI3/G0.06+EDA15000/PEI3)) .......................................................... 180

Figure A.9: Top and cross section images of M22 before and after filtration (PES/PEI3/G0.06+EDA15/PEI3)) .......................................................... 181

Figure A.10: Top and cross section images of M6 before and after filtration. Nylon (PEI3/G0.06/PEI3). .......................................................... 181

Figure A.11: Top and cross section images of M8 before and after filtration. Nylon (PEI3/G0.11/PEI3). .......................................................... 182

Figure A.12: Top and cross section images of M9 before and after filtration. Nylon (PEI3/G0.06+EDA2000/PEI3). .......................................................... 182

Figure A.13: Top and cross section images of M12 before and after filtration. Nylon (PEI3/G0.06+EDA15000/PEI3). .......................................................... 183

Figure A.14: Top and cross section images of PES(PEI0.5/G). .......................................................... 183

Figure A.15: Top and cross section images of M4_PES(PEI5/G/PEI3). .......................................................... 183

Figure A.16: Top and cross section images of PES(PEI0.5/G/PEI0.3). .......................................................... 184

Figure A.17: Top and cross section images of PES(PEI0.5/G+EDA). .......................................................... 184

Figure A.18: Top and cross section images of PES(PEI0.5/G+EDA/PEI0.3). .......................................................... 184

Figure A.19: Top and cross section images of N02(PEI3). .......................................................... 185

Figure A.20: Top and cross section images of N02 (PEI4.3/G). .......................................................... 185

Figure A.21: Top and cross section images of N02 (PEI4.3/G/PEI0.5). .......................................................... 185

Figure A.22: Top and cross section images of N02 (PEI4.3/G+EDA). .......................................................... 186

Figure A.23: Top and cross section images of N02 (PEI4.3/G+EDA/PEI0.3). .......................................................... 186

Figure A.24: TEM images of dispersion of N2, E1 and E2 .......................................................... 187

Figure A.25: Water flux decline of graphene composite membranes during filtration ........................................ 188

Figure A.26: FO results of 0.2mM of PAA-Na (Mw 5kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e) .......................................................... 189

Figure A.27: Forward osmosis experimental results of 0.5mM of PAA-Na (Mw 5kDa) Water and
reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.28:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 5kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.29:** Forward osmosis experimental results of 0.125mM of PAA-Na (Mw 8kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.30:** Forward osmosis experimental results of 0.5mM of PAA-Na (Mw 8kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.31:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 8kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.32:** Forward osmosis experimental results of 0.033mM of PAA-Na (Mw 30kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.33:** Forward osmosis experimental results of 0.5mM of PAA-Na (Mw 30kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.34:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.35:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) // AL-FS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.36:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) // AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.37:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 8kDa) // AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.38:** Forward osmosis experimental results of 2mM of PAA-Na (Mw 5kDa) // AL-DS Water flux and reverse salt flux (a), net driving force estimated from calculated draw and feed osmotic pressures (b), experimental fluctuation (water flux/Net driving force and reverse solute flux/Net driving force) (c), volume change in feed and draw compartments (d) and TOC value in feed side and reverse solute transport (e).

**Figure A.39:** Porosity (%) measurement G/P02, G/N02 and G/N045 membranes with various graphene loadings. Black color represents the graphene dispersion N1 and blue color represents the graphene dispersion N2.
**LIST of TABLES**

- **Table 1.1:** Membrane categories based on their nature, structure and configuration ........................................35
- **Table 1.2:** Characteristics of pressure driven membranes .................................................................36
- **Table 1.3:** GO membrane performance ..............................................................................................40
- **Table 2.1:** Dispersion pathways with various diversity in terms of different solvents (i.e. NMP, ethanol and surfactant based) and mechanical force factors (i.e. ultrasonic probe and bath). N1, N2, N3, E1, E2 and S1 are the name of the methods which were used to disperse graphite in NMP, ethanol and surfactant-based systems, respectively .......................................................... 55
- **Table 2.2:** Key parameters of membrane fabrication procedures .......................................................... 59
- **Table 2.3:** Summary of exfoliated dispersion techniques .......................................................................... 64
- **Table 2.4:** Summary of membrane characterization techniques ............................................................ 67
- **Table 3.1:** Effects of different factors (i.e. solvent, centrifuge speeds) on the yield of graphene dispersions. Absorption coefficient was taken as 3620 Lg^−1m^−1 for NMP and ethanol-based dispersions and 1390 Lg^−1m^−1 for water-surfactant dispersion. Concentration was calculated from the Lambert-Beer equation ........................................................................................................... 76
- **Table 3.2:** Average Polydispersity index (PDI) of each graphene dispersion ........................................... 81
- **Table 3.3:** Raman spectra peaks of three characteristic bands D, G and 2D in each of graphene dispersions ..................................................................................................................................... 82
- **Table 3.4:** Ratios of intensity and integrated area of D, G and 2D peaks ..................................................... 83
- **Table 3.5:** Flake lateral dimension (L) and thickness (W) obtained from DLS, TEM and AFM .................................................................................................................................. 92
- **Table 4.1:** Performance of average water permeability (L/m^2.h.bar) and dextran 4kDa and 2000kDa rejection (%) under 0.15, 0.25 and 1 bar pressures. Defect density experiment .......................................................................................................................... 108
- **Table 4.2:** Compaction test of SX membrane (Table. 4.3) with dextran 4kDa and 2000kDa rejection (%) under 0.25 and 1 bar pressures ........................................................................................................ 110
- **Table 4.3:** Performance of average water permeability (L/m^2.h.bar) and dextran 4kDa and 2000kDa rejection of G/N02 membranes prepared via dispersion N2, E1, S1_Se and S1_Su with dilution factor of 100 times (B1 and B2), 1000 times (C1 and C2) as a function of various graphene loadings. Active area of membranes: 9.07 cm^2. Filtration pressure: 0.5 bar .......................................................................................................................... 110
- **Table 4.4:** Comparison with respect to key parameters, including pure water permeability and rejection values between the performance of the graphene composite and graphene-polymer hybrid membranes prepared in this work and GO membranes reported in the literature ............................................. 174
- **Table 4.5:** Comparison of water flux, reverse solute flux and specific flux (Js/Jv) of forward osmosis membranes reported in the literature under FO test system .............................................................................. 175
Objective of the Thesis

In this project, it has been aimed to increase the efficiency of the current commercial symmetric membranes by using two-dimensional layered material graphene as it provides fast transport of water molecules through their unhindered channels and offer exceptional high rejection capability and also to add functionality to existing membranes to enhance efficiency and to break the bottleneck of limited efficiency and unfeasible costs of osmotic membranes for osmosis applications. The choice of the membranes for a specific application is typically determined by the separation properties of the membranes such as water permeability value and rejection capacity which varies depending on the solute and its particle size to be separated. It would be desirable to have the both values in optimum level which refers to achieve as much as high-water permeability by gaining considerable selectivity. In this study, the graphene-based membranes were aimed to provide water permeability higher than 20 L/m².h.bar (if the support membrane is a nanofiltration membrane) and higher than 100 L/m².h.bar (if the support membrane is a microfiltration membrane) and the over 90% rejection for dextran 2000 kDa.

The following tasks have been carried out in order to achieve the goal of this research:

1) Preparation of exfoliated graphene dispersed in various solvents like NMP, ethanol and water-sodium cholate mixture by using LPE method. In the end of this task, it has been aimed to have seven graphene dispersions which were all exfoliated via a unique fabrication path. By doing so, various parameters of liquid phase exfoliation technique like sonication energy, rotational speed, solvent effect etc. and their effect on the quality of graphene nanosheets has been examined accordingly. Afterwards, characterization of graphene dispersions using certain techniques like UV-Vis Spectroscopy, dynamic light scattering, Raman spectroscopy, atomic force microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy.

2) Fabrication of graphene-based membranes via pressure-assisted filtration technique and characterization of the membranes using gas flow/pore de-wetting permoporometry, zeta potential, Fourier transform infrared spectroscopy, X-ray diffraction, contact angle analysis, scanning electron microscopy, filtration characterization using a dead-end filtration cell.
3) Study the effect of using diluted or undiluted graphene dispersion on the quality of selective layer of graphene nanosheets. Within this task, it has been aimed to provide mainly two types of graphene-based membranes; one type of the membranes has only included the combination of graphene which was the major element for the selectivity and support membrane and the second type of the membranes were composed of graphene and polymer (polyethylenimine and ethylenimine) onto support membrane. Thus, contribution of graphene alone and graphene with polymer to the membrane performance has been investigated with these two types of membrane. Later, characterization of the membranes via various membrane characterization methods have been carried out in order to obtain information about pore size, surface morphology, chemical morphology, surface charge properties, interlayer distance of nanosheets, filtration performance of obtained membranes.

4) Test one of the best membranes obtained from task 2 under forward osmosis experimental conditions to see the feasibility of using such membranes for osmosis applications. Forward osmosis is considered as the emerging technology for many applications such as waste water treatment\(^1\), water purification\(^2\), seawater desalination\(^3\), food processing\(^4\), pharmaceutical industry\(^5\) and osmotic power\(^6\). In the current study polyelectrolytes of a series of polyacrylic acid sodium salt (PAA-Na) were used as the draw solute in forward osmosis experiments.
Outline

This thesis was organized into six chapters which describe main points of this work as summarized in the following:

**Chapter 1** provides a brief introduction about the journey from graphite to graphene, fabrication methods of graphene and key aspects of LPE technique and an overview of membrane science and technology, graphene application on membrane science and osmosis process, specifically forward osmosis processes.

**Chapter 2** describes the details of fabrication methods and characterization of all materials used in this research.

**Chapter 3** covers and discusses the characterization results of exfoliated graphene dispersions in various solvents. It has been established seven different fabrication methods for exfoliated graphene in different solvents. Obtained dispersions have been analysed in terms of distinguishing between single-layer, few-layers (< 10 layers) or multi-layers of graphene and graphite by Raman analysis, final concentration of the dispersion via absorption spectra, hydrodynamic size of flakes via DLS analysis, flake lateral size and thickness via AFM and TEM, chemical composition via XPS analysis.

**Chapter 4** presents the characterization results of graphene composite membranes and graphene-polymer hybrid membranes. Average pore sizes by PMI, surface wetting by contact angle measurement, surface charge properties by zeta potential, filtration performances (water permeability, rejection) via dead-end filtration cell, surface morphology and graphene selective layer quality by SEM of the membranes were mainly studied in this chapter.

**Chapter 5** presents the results of forward osmosis test by using one the best graphene-polymer hybrid membranes fabricated in Chapter 4. Draw solute (PAA-Na) was characterized to obtain information about viscosity (rheology measurement) and average molecular weights (GPC).

**Chapter 6** presents the overall conclusions of this work as well as recommendations for future work.
CHAPTER 1

FUNDAMENTALS
1.1 Introduction to Graphene

1.1.1 Graphite and Its Discovery

There are various types of carbon structures which sustain the same physical states in the nature. They are called as allotropes of carbon element such as diamond, graphite, fullerenes and nanotubes\(^7\).

One of the most well-known carbon allotropes is the graphite which has a long history going back to 16\(^{th}\) century and was discovered in a mine by locals\(^8\). Even though it looked like coal, people noticed later that it could not burn. A large amount of solid graphite was found in Borrowdale, near Keswick in the Lake District of England. In the early days of this exciting discovery, graphite was used in different purposes like marking and drawing, also in military as a lining for cannonball moulds\(^9\). Later on; after first attempts to make graphite sticks from powder graphite, today’s good quality pencil production had blossomed into the range of various graded levels of pencils\(^10\). Apart from this purpose of usage of graphite, an essential need occurred to use graphite as bulk material since nanomaterials attracted great attention over the past 20 years\(^11\).

1.1.2 Properties of Graphene

Layered materials are known as the solids which have strong in-plane chemical bonds and weak out-of-plane, van der Waals bonds\(^12\). These materials show new characteristics, completely different from those of the bulk material, when they are nanometre thin or atomically thin\(^12\). Graphene is the most sensational\(^13\) material discovered in the layered materials world. A Canadian theoretical Physicist Philip Russell Wallace was the first to explore the graphene theoretically and defined it as the single building block of graphite in his paper in 1947\(^14\). Then, two researchers from the Manchester University were able to remove some flakes from a bulk of graphite by using scotch tape\(^15, 16\). By the aid of analysing the thickness of flakes each time, after a long series of tests, they successfully achieved monolayer graphene flakes. This research carried their work to the Nobel prize award in 2010. Since this time, graphene has been widely studied 2-dimensional crystal due to its extraordinary properties of the high values of its Young’s modulus \(~1,100 \text{ GPa}\)\(^17\), strength \(130 \text{ GPa}\)\(^17\), thermal conductivity \(~5,000 \text{ Wm}^{-1}\text{K}^{-1}\)\(^18\), mobility of charge carriers 200,000 \(\text{ cm}^2\text{V}^{-1}\text{S}^{-1}\)\(^19\), specific surface area \(2,630 \text{ m}^2\text{g}^{-1}\)\(^20\).
Graphene is the thinnest and strongest material that we ever have known so far and due to being its flexibility, graphene can also get shaped as in Fig. 1.1c. A wrapped up version of it is called a zero-dimensional (0D) structure, i.e. fullerenes, $C_{60}$; if it is rolled, it can be formed into a one-dimensional (1D) structure, i.e. nanotubes.

Graphene is one-atom thick, an individual layer of three-dimensional (3D) graphite which consist of covalently bonded carbon atoms arranged in a honeycomb lattice. Each carbon atom is bonded to each other by $sp^2$ bonds with a length of 1.42 Å. Graphite consists of graphene sheets which stacked on each other into a three-dimensional structure and connected by weak van der Waals interaction. The interlayer distance of these sheets is approximately 3.4 Å. Considering the bond length of each atom in graphene and interlayer distance of graphene sheets, it can be concluded that interatomic bonding is much stronger than the interlayer bonding\(^7\).

![Figure 1.1](image)

**Figure 1.1** (a) Image of natural graphite, (b) schematic of graphite and (c) arrangements of how the carbon atoms are oriented\(^{21-23}\).

In literature, there is very broad definition of “graphene”. However, this broad use brings some drawbacks such as generalization about abilities and restraints of graphene-based materials\(^{24}\). There is remarkable amount of work which has been devoted to build a consistent system which provides rational scientific nomenclature for the graphene-based materials\(^{24-27}\). The confusion in naming mainly comes of two-dimensional (2D) sheet-like or flake like carbon structures\(^{25}\). Alberto et al.,\(^{25}\) proposed a methodology which includes some of the definitions and characteristics for graphene and graphene-based materials. Some of the morphological descriptors\(^{24, 25, 28}\) of graphene were chosen as the set parameters in order to build this model. For example, thickness (number of layer), lateral dimension and carbon to oxygen content ratio are considered as the fundamental properties. The number of layers defines the thickness, surface area\(^{29}\) while the lateral dimension illustrates deformability degree\(^{30}\) of the material. These variables should be critically studied for each type of material to understand its feasibility for different types of application because specific
size and thickness is required for the most cases. Here, some of those terms are discussed in the following.

**Graphene** – a single-atom thick sheet of hexagonally packed, sp2 carbon atoms which might be free or sticked onto a substrate. The lateral dimensions of graphene can differ in between nanometres to the macrometers.

**Graphene layer** – a single-atom thick sheet of hexagonally packed, sp2 carbon atoms which forms in carbon material. The structure of this material is not an important aspect, whether it is 3D form (graphitic) or not.

**Bi-layer graphene, tri-layer graphene** – two dimensional (sheet-like) materials which contains 2-3 well-defined, numerable, stacked graphene layers.

**Few-layer graphene** – two dimensional (sheet-like) materials which contains 2-5 well-defined, numerable, stacked graphene layers.

**Multi-layer graphene** – two dimensional (sheet-like) materials which contains 2-10 well-defined numerable, stacked graphene layers.

**Graphite nanoplatelets; graphite nanosheets; graphite nanoflakes** – 2D graphite materials. Stacking registration is specified as ABA or ABCA stacking. These materials have a thickness and/or lateral dimension less than 100 nm.

**Graphene nanosheet** – a single-atom thick sheet of hexagonally packed, sp2 carbon atoms which might be free or sticked onto a substrate. The lateral dimension for graphene nanosheet is mainly less than 100 nm.

**Graphene nanoplatelets** – 1 to 3 nm thick and 100 nm to 100 μm in size[31].

**Graphene microsheet** – a single-atom thick sheet of hexagonally packed, sp2 carbon atoms which might be free or sticked onto a substrate. The lateral dimension for graphene nanosheet is mainly in between 100 nm and 100 μm.

**Graphene oxide (GO)** – chemically modified graphene which is fabricated by oxidation and exfoliation processes. Oxidative modification is applied to the basal plane of graphene. GO is typically single layer and it is rich with oxygen content and it is characterized by carbon to oxygen (C/O) ratios, typically less than 3.0.

**Graphite oxide** – a bulk solid material which is prepared by oxidation of graphite by functionalizing the basal planes and enlarge the interlayer spacing. It is possible to exfoliate graphite oxide to fabricate monolayer or few-layer graphene oxide.

**Reduced graphene oxide (rGO)** – graphene oxide that has been reductively modified by various methods like chemical, thermal, microwave, photo-chemical, photo-thermal etc. in order to reduce its oxygen amount.
1.1.3 Structure of Graphene

The electron configuration of a carbon atom, sixth element, is 1s²2s²2p²(2pₓ²2pᵧ²) as can be seen in Fig. 1.2b. In carbon atoms, 1s electrons, the electrons in the inner shell Fig.1.2(a), do not make any bonding. However, the other four electrons are called as valence electrons which are responsible to contribute to chemical bonding. 2s, 2pₓ, 2pᵧ atomic orbitals form sp² hybridization in Fig.1.2(c). Strong covalent sigma (σ) bonds are formed by the s-, pₓ- and pᵧ- orbitals and it is directly linked to mechanical robustness of graphene structure. σ bonds are oriented in xy-plane with 120° angles\(^{[32]}\). Left pₓ- orbital form weak π bonding which is perpendicular to the plane (Fig. 1.2e). It is responsible for van der Waals force between graphene layers in graphite\(^{[33]}\). So, there are 6 sigma (σ) bonds and 3 pi (π) bonds in a graphene with three neighbours\(^{[7]}\). If carbon atoms share sp² electrons with other carbon atoms, monolayer graphene is formed as a layer of honeycomb planar structure. In Fig. 1.2d, the unit cell of a graphene is shown with purple dashed line, which includes 2 carbon atoms. In the x, y coordinate system, the unit vectors \(a_1\) and \(a_2\) can be defined as

\[
a_1 = \frac{a_{c-c}}{2} (3, \sqrt{3}), \quad a_2 = \frac{a_{c-c}}{2} (3, -\sqrt{3})
\]

Where the bond length of carbon to carbon (\(a_{c-c}\)) is nearly 1.42 Å\(^{[32]}\).

![Figure 1.2](image-url) (a) Atomic structure of a carbon atom. (b) Energy levels of outer electrons in carbon atoms. (c) The formation of sp² hybrids. (d) The crystal lattice of graphene, where A and B are carbon atoms belonging to different sub-lattices, \(a_1\) and \(a_2\) are unit-cell vectors. (e) Sigma bond and pi bond formed by sp² hybridization, image adapted from\(^{[34]}\).
1.1.4 Fabrication of Graphene

Graphite is known as a layered material which consists of individual graphene crystals that stacks on top of each other\cite{31}. The reason behind formation of stacking is attractive covalent and van der Waals forces\cite{35} in between graphene crystals. It is necessary to break the bond between graphene crystals by providing energy such as mechanical, thermal, chemical, etc. to the stack in order to distinguish the individual crystals from each other\cite{35}.

Despite the graphene is accepted as the first two-dimensional material\cite{36} discovered in the laboratory conditions the predictions which were made about the dispersion of nanotubes were applied to the graphene dispersion laterly. So, the dispersion mechanism of carbon nanotubes (CNTs) was an inspirational journey for the graphene production. CNTs are tubular structures which are made up of rolled-up graphene sheets. They can be classified into two categories, single-walled carbon nanotubes (SWCNTs) with less than 1 nanometer (nm) diameter or multi-walled carbon nanotubes (MWCNTs) which consist of several joint nanotubes with more than 100 nm diameter\cite{37,38}. Like graphene, CNTs have also amazing mechanical\cite{39}, electrical\cite{40} and thermal\cite{41} properties, but many of those are correlated with the individual nanotubes. Liquid phase exfoliation and stabilization of CNTs\cite{42} is considered as the efficient technique in order to separate CNTs from their bundles. Carbon nanotubes have been dispersed and stabilized by various assistances like solvents\cite{43}, surfactants\cite{44}, acids\cite{45} etc. in order to prevent aggregation because of attractive van der Waals interactions. It has been concluded with several findings after studying of CNTs dispersion mechanism. Solubility parameters, i.e., Hildebrand and Hansen, which are dissociated with cohesive energies and the solubility parameter based on surface energy (ideal solvents were those with surface tension close to 70 mJ m$^{-2}$) were used to determine the solvent quality for such systems. Noted that the idea solvents for the dispersion of functionalized nanotubes must have Hildebrand solubility parameters which match with the solubility parameter of the functional group of nanotubes. Furthermore, for surfactant assisted nanotubes dispersions, it has been found that successful surfactants were described as small molecules which pack firmly on the nanotube surface\cite{42}.

Addition to discovery of graphene’s superior properties and being the most promising layered material for many industrial applications, enormous effort has been put on to the production of graphene with a cost-effective method which will provide defect-free graphene in a large scale. Writing with a pencil (graphite) onto a paper is a simple and easy way of producing graphene sheets\cite{46}. When you write somethings over the paper, you basically exfoliate bulk graphite and create thin graphite with various thicknesses and lengths onto the
However, this way is far from commercially applicable due to its difficulty of controlling the number and size of sheets.

A serious improvement could not be achieved in this regard until 2004 when the research community impressed with the exciting news coming from two researchers at the University of Manchester, Professor Andre Geim and Professor Kostya Novoselov. A very first attempt was done with the help of an adhesive tape which was used to stick graphitic crystals onto a substrate. The process took many times until reaching to the thinnest flakes on the surface. Finally, residual thin flakes were transferred by rubbing the tape onto the substrate (an oxidized silicon wafer) where optical image was performed to analyse the quality of the graphene flakes. It can be seen the steps in Fig. 1.3. It is possible to produce high quality graphene which has a slightly low defect density by this method. However, it is a time-wasting approach and also the yield is still not enough for mass production.

**Figure 1.3** Step by step description of Scotch tape method to produce graphene, image adapted from[48].

There is still on-going research on this field to extend the feasibility of using other methods to produce desired graphene which will have the required characteristics. There are various types of graphene production methods which can classified into two categories as top-down and bottom-up approaches. Each of these methods has some advantages and disadvantages with itself. Many of those are aimed to produce graphene with various dimensions, shapes and quality[49]. In bottom-up methods, graphene can be synthesized by methods such as chemical vapor deposition [50, 51], growth on SiC [52] and chemical conversion[53].

Most well-known graphene production techniques are listed in Fig 1.4 according to desired application with specific characteristics which will show quality of the product and price of the production.
A very versatile way to produce graphene is chemical vapor deposition (CVD) which enables growth of large area uniform polycrystalline on copper films and films. By using CVD techniques, it has been successful in the roll-to-roll production of squares meters of graphene copper substrates. Nevertheless, CVD is still accepted as an expensive method to grow graphene as it requires large energy consumption; moreover, current used substrates, commonly copper foils or films, may not be suitable for each industrial application. In order to consider CVD as widely used technique, there should be some improvements and optimization on the transfer process which might cause contamination on graphene, and also alter graphene electrochemical properties. Additionally, due to the fact that final product of graphene in CVD is polycrystalline, it is crucial to control of the number and relative crystallographic orientation of the graphene layers because this will pave the way for many applications which will be in need of single, double or even thicker graphene layers.

Synthesis on SiC is another growth method has been gaining great attention for mass production of graphene. It has been shown that graphene can be grown on the silicon or carbon faces of SiC wafer. Findings showed that it is feasible to produce high quality of graphene with hundreds of micrometres in size. Two disadvantages of this techniques, the high cost of SiC and high temperatures > 1000°C, make essential it to do further optimization.

Top-down processes consist of (i) scotch tape method (explained in Fig. 1.3), the first production method of graphene, (ii) chemically converted graphene, (iii) electrochemical exfoliation and most well-known method is (iv) liquid phase exfoliation which is
considered as mass-scalable and cost-effective method for many applications. Because other approaches were not employed in our project so they are not further discussed.

Although graphene has a perfect 2D crystal structures with excellent physical and chemical features, some defects, disorders and impurities in the crystalline materials might be occurred during production process. These defects can alter the properties of graphene\(^{[61]}\), Generally, atomic level (lattice) defects in graphene can be classified into various types: The first group defects are intrinsic defects i.e., stone-wales defects\(^{[62]}\), single vacancy defects\(^{[63]}\), multiple vacancy defects\(^{[64]}\), line defects\(^{[65]}\) and carbon adatoms\(^{[66]}\), which consist of non-sp\(^2\) orbital hybrid carbon atoms. Non-hexagonal rings which are surrounded by hexagonal rings are formed in this type of defects. The second group defects are extrinsic defects which are caused by non-carbon atoms which are bonded or replaced with the nearest carbon atoms in graphene\(^{[67]}\), i.e., foreign adatoms\(^{[68]}\), substitutional impurities\(^{[68]}\). Individual graphene layer is surrounded by the edge which consist of either free or passivated (with hydrogen atoms) edge carbon atoms. Edge structures are mainly divided into armchair or zigzag orientations\(^{[69]}\). In general, defects can be caused by edge or basal planes for multilayer graphene\(^{[70]}\). Defective edges can occur, for instance by removing one of carbon atom from a zigzag edge and led to reconstructed edge. This results in formation of one pentagon of a row of hexagons at the edge\(^{[63]}\). To produce defect-free graphene from graphite, liquid phase exfoliation technique will be used in this research. In the following section, there will be more details on this method.

1.1.4.1 **Liquid Phase Exfoliation Technique**

LPE technique has been considered as the most versatile method for graphene production due to being capable of producing mass production of graphene. Due to being straightforward and scalable process it has gained enormous attraction over the last decades by researchers. There are different types of exfoliation process which includes two popular examples\(^{[71]}\). One example is oxidation of graphite to give graphene oxide (GO)\(^{[72-75]}\)the other example is sonication-assisted exfoliation of graphite that is stabilized by using special solvents or surfactants\(^{[76, 77]}\). As an advantage of graphene oxide dispersion, it mainly consists of monolayer flakes. However, the presence of oxidation process would be disadvantage due to introducing the structural defects\(^{[78, 79]}\) that alters the physical properties of graphene. Exfoliated graphene assisted by a solvent provides comparatively low monolayer content with defect-free nature\(^{[71]}\).

In LPE technique, pristine graphite is directly mixed with a suitable solvent, by doing so it is aimed to weaken van der Waals attractive forces between the graphene layers held within a
π-π stacking distance of 3.35-3.4 Å by applying ultrasonication or high shear, then followed by a stabilization process with an appropriate medium.

Liquid phase exfoliation contains three major steps. First, it is essential to choose an appropriate solvent to disperse pristine graphite, which will overcome van der Waals interaction between adjacent layers through sonication energy. Suitable solvents might be either non-aqueous or aqueous assisted by various agents like surfactants. Then, the second step is to exposure this mixture to ultrasonication process by either sonic probe provides high energy or sonic bath provide low energy in order to separate into individual platelets from pristine graphite. In the third step, since produced dispersion after sonication is expected to be highly poly-dispersed[80], a size selection process is performed by mild centrifugation[49], unexfoliated large graphitic structures in the suspension is removed from the exfoliated thin flakes by centrifugation.

In this fabrication technique, there is one big limitation which effects the quality of final result of graphene. For instance; the yield of the dispersion might be so low typically 0.01 mg/mL[81] or even less than this concentration. It is a very vital parameter one should consider the concentration carefully by optimizing the processing parameters such as solvent type, sonication time, centrifugation rate and speed. With the purpose of improving the yield efficiency and facilitate graphene mass production, a large number of research groups focused on possible solutions. It has been reported [82] that increasing sonication time resulted in increased dispersion concentration with reduced flake dimensions (Fig. 1.5). Long sonication times are required to achieve high concentration of graphene according to previous research findings, i.e., with a low power sonication about 460 h[82] for about 1.2 mg/mL dispersion in high boiling organic solvent (NMP) and 48 h[83] for about 0.5 mg/mL dispersion in low boiling organic solvent. However, such a process including longer times is not time-effective which makes it impractical for industrial applications and also requires high energy which has an influence on the electronic structure of graphene, leading partial damage of the graphene sheets[84]. Graphite sonication is accepted as a safe process in terms of not being destructive for graphite, thus defects can be found at the flake edges and basal-plane of the flakes are comparatively free of defect[70]. Because small flakes makes the defect mapping by various characterization techniques like Raman spectroscopy very difficult, defect locations whether on the edge or in the basal place might not be easily identified[85]. Raman spectra of graphene deposited films showed a disorder related D peak but it was comparably small with defective graphene[86]. This was an indication that measured D band here was caused by flake edges.
Based on the work done by Coleman et al.,\textsuperscript{[87]} it has been found that graphene concentration is related to square root of sonication time: $C_G \approx \sqrt{t}$\textsuperscript{[82]} and in addition to this, mean flake length and size showed $t^{1/2}$ behaviour\textsuperscript{[88]}. The input energy to disperse graphite in suitable solvent is also critically important, which might be performed by bath sonication or tip sonication. Schematic description of exfoliation mechanism of graphite was shown in Fig. 1.6. Ultrasonic waves create shear forces or captivation bubbles which produce high amount of energy by collapsing of the bubbles in the solvent that can convert graphite from layered structure to mono-, single- or few-layered graphene\textsuperscript{[89, 90]}. In detail, the ultra-sonic waves spread into graphite suspension and create high pressure and low pressure simultaneously. When the low-pressure happens, small vacuum bubbles are generated in the suspension by the waves. Afterward, the energy is absorbed by the bubbles which collapse during high pressure cycle. This ultrasonic cavitation causes high-speed micro liquid jets and intense shock waves which will create shear forces on the graphite, resulting in diminishing the size of nanosheets. Graphite is exfoliated into separate layers known as graphene under the effect of forces and wedge action\textsuperscript{[91, 92]}. 

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{graph.png}
\caption{Concentration of graphene dispersed in NMP after centrifugation process as a function of sonication time. Adopted from reference\textsuperscript{[87]}.}
\end{figure}
Figure 1.6 Schematic illustration of graphite exfoliation mechanism (modified from \cite{92}).

The attractive van der Waals forces between the adjacent graphene layers can be significantly diminished by increasing the $\pi-\pi$ stacking distance ($r$) greater than 5 Å, as the van der Waals force is proportional to $1/r^6$ \cite{93}. Ultrasonication or shear force are greatly useful the intercalation of solvent molecules into bulk graphite layers; thereby effectively increase the interlayer spacing for the benefit of successful graphene exfoliation into mono- and/or multi-layered graphene sheets \cite{94}.

Reproducibility of the dispersion via sonic bath is a critical parameter that should be considered carefully. Sonic energy input depends on the water level of the bath, the exact position of the sample in the bath, the dispersion volume, shape of the container etc. Besides, output power of sonic baths might be also different from the rated one, resulting in providing different result from the identical baths. Changing water at a certain time or using an external cooler system will prevent water evaporation and keep the temperature at constant. By doing that, solvent degradation can be inhibited \cite{82}.

The dispersion after sonication contains flakes with a broad size distribution, which also includes thick- unexfoliated graphitic like structures which can be separated based on the separation technique, so called centrifugation. It is a technique which applies the centrifugal force generated by rotation of the rotor about a central axis in order to separate particles from a suspension according to their size, shape etc \cite{95}. It has been reported that flake size after centrifugation depends on rotational speed ($w$). Small size graphene flakes separates from thick material at higher rotation speed \cite{82}. In addition to that Backes et al. have reported that a selection of various size and thickness of graphene nanosheets can be obtained by applying repetitive centrifugation cascade system \cite{96}. It has been found based on the TEM
results that graphene dispersion obtained with 3000 rpm centrifugation compose of much smaller flakes rather than in that with the 500 rpm one\textsuperscript{[97]}.

### 1.1.4.1.1 Solubility Parameters & Exfoliated Graphene in Organic Solvents

The successful LPE process requires using only organic solvents which has same or close surface energy with that of graphene. The idea of using the solvents with matched surface energy comes from the rule of “like dissolves like” in chemistry\textsuperscript{[42]} which was firstly tried on carbon nanotubes successfully\textsuperscript{[60]}. Based on the free energy of mixing formula given in the following equation:

\[
\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}
\]  

(1.2)

\(\Delta H_{mix}\) and \(\Delta S_{mix}\) are defined as enthalpy and entropy of mixing per unit volume of solvent. The systems includes small size solutes has a large entropy (negative free energy of mixing) which drives the system (entropy driven processes). However, since exfoliated graphene consist of mostly big size flakes, ranging in sub-micron range, its entropy of mixing becomes generally small. In that case, it is significant to reduce the enthalpy of mixing to make the free energy negative. This can done by achieving stronger solute-solvent interaction rather in that of inter-solute and inter-solvent interactions. In the case of stronger inter-solute and inter-solvent interactions, then graphite flakes tends to stick back to each other due to energetically favourable aggregation. Contrarily, if the solute-solvent interaction is stronger than the solute, dispersion in the solvent successfully occurs\textsuperscript{[42, 98]}.

Additionally, since graphene flakes tend to aggregate within a certain of waiting time (Fig. 1.7), solvent-solute (nanosheets) interaction stabilize the graphene nanosheets for a long time in the dispersion by balancing inter-sheet attractive forces\textsuperscript{[81]}.

![Figure 1.7](image)

Figure 1.7 Schematic description of LPE process for graphene exfoliation and stabilization mechanism in a solvent. Reprinted from reference\textsuperscript{[99]}. 

16
After a number of investigations in the search for possible organic solvents, it has been concluded that solvents which have a surface tension (the property of the surface of a liquid that allows it to resist an external force, due to the cohesive nature of its molecules) $\sim 40 \text{ mJ m}^{-2}$\cite{81} are considered as the best candidates for the dispersion of graphene and graphitic flakes, because they minimize the interfacial tension between solvent and graphene. In addition, the surface energy of graphene is known as $68 \text{ mJ m}^{-2}$ and it is defined as the energy per unit area (energy/area, J/m$^2$) required to overcome the van der Walls attractions when separating two sheets apart$^{[100]}$. Surface energy can be defined as the work per unit area done by the force which creates new surface while surface tension (N/m$^2$ or J/m$^2$) is the net intermolecular force on the surface of material$^{[101]}$. However, the most of best solvents with a surface energy of $\sim 40 \text{ mJ m}^{-2}$ such as N-methyl-2-pyrrolidone (NMP $-40 \text{ mJ m}^{-2}$), N,N-dimethylformamide (DMF $-37.1 \text{ mJ m}^{-2}$), and ortho-dichlorobenzene (o-DCB $-37 \text{ mJ m}^{-2}$)\cite{85} have crucial drawbacks. For instance, they are not user-friendly for many organs due to being toxic, which is easily absorbed by the skin and not eco-friendly. As can be seen in Fig. 1.8, the concentration of graphene dispersed in various solvents reached its maximum value at around $40 \text{ mJ m}^{-2}$ which provides $\sim 70 \text{ mJ m}^{-2}$ surface energies$^{[81,102]}$. Even though surface energy-based model as a solubility criterion provides well-fitting data for such dispersion combinations, it might not be enough to understand details of the interaction between solvent and graphite. As an alternative, Hildebrand and Hansen solubility theory has been proposed to investigate the dispersibility of such nanomaterials by the researchers$^{[103,104]}$.

![Figure 1.8](image.png)

**Figure 1.8** The concentration of graphene dispersion in various solvents after centrifugation as a function of solvent surface tension. The concentrations were calculated using absorbance value at 660 nm and absorption coefficient taken as 2460 Lg$^{-1}$m$^{-1}$$^{[100]}$. 
Hildebrand theory\cite{105} was proposed by Joel H. Hildebrand in 1936. The Hildebrand solubility parameter $\delta_i$ is described as the square root of the cohesive energy density, which is an indication of the energy of vaporization to determine if a solvent is suitable or not for a polymer. Cohesive energy density can be calculated by following equation\cite{106} $C_i = \delta_i^2 = \frac{(\Delta_{cap}H)}{V_i}$ where $\Delta_{cap}H$ is the ratio of the energy of vaporization and $V_i$ is the molar volume. However, the type of interaction whether it is polar or non-polar interaction is not differentiated clearly in this theory and this is accepted as the drawback of Hildebrand theory. Therefore, Hansen theory proposed by Charles M. Hansen\cite{107} described the solubility parameter with three components: dispersion force ($D$), polar intermolecular force ($P$) and hydrogen bonding ($H$) as the square root of each $\delta_D$, $\delta_P$ and $\delta_H$ components ($\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$). Compared to Hildebrand theory, Hansen theory provides a more detailed, differentiated model in three regions.

As shown in Fig. 1.9a, According to Hildebrand theory, a good solvent should have a solubility parameter $\delta$ in between $\pm 2$ MPa$^{0.5}$ of the solute/polymer $\delta$ value. The value 2 MPa$^{0.5}$ is used in this theory as the basis of experimental considerations. If $\delta$ value of a solvent is found in the outer side of $\pm 2$ MPa$^{0.5}$ of the solute $\delta$ value, then this solvent is considered as non-appropriate for such solute/polymer\cite{108}. Whereas, in Hansel theory, three axes are used to represent the dispersion ($\delta_D$), polar ($\delta_P$) and hydrogen bonding ($\delta_H$). Radius of the sphere is defined as $R= 8$ MPa$^{0.5}$ where solute/polymer is placed at the centre of this sphere. A solvent is presumed to be a good candidate for related solute/polymer if its solubility parameter ($\delta$ value) locates within this sphere radius, corresponding $R< 8$ MPa$^{0.5}$ which is defined as the basis of experimental considerations. Hansen theory provided a wide range of published databases including 1200 solvents. It protects its usefulness together with surface energy based theory. It has been found that $\delta_D$ (it is primarily more pronounced to control the dispersion concentration\cite{83}) should be in the range of $15$ MPa$^{1/2} < \delta_D < 21$ MPa$^{1/2}$ \cite{104} for a successful graphene dispersion. Hansen parameter of organic solvents DMF, NMP, cyclohexanone, IPA, chloroform, acetone were found 17.4, 18, 17.8 15.8 17.8 and 15.5 respectively. These results confirmed that these solvents fitted very well with the specified region except chloroform due to showing very low $\delta_P$ value.
Figure 1.9 Model of Hildebrand (a) and Hansen (b) solubility theory[108].

Overall, both surface energy based model and Hansen model described NMP and DMF as the best possible solvents which has a capability of producing defect-free graphene in a high concentration and assisting stabilization of the dispersion for the long time. Whereas, one should make sure that the complete removal of those organic solvent from the substrate (silicon, mica etc.) occurred successfully as the existence of remaining organic solvents on the substrate’s surface for instance is not preferable because it may cause overestimation of flake size, thickness. High boiling point (202 °C for NMP and 153 °C for DMF) causes difficulties in complete evaporation or removal for characterization process.

Herein, low-boiling point organic solvent based dispersions was considered as an alternative to those good organic solvent with a problematic high boiling point. But it is well-known that their performance in terms of solubility of graphene is so low, resulting in very low concentration. Alcohol like ethanol, isopropyl alcohol (IPA) was noted as a suitable candidate due to being cheap, non-toxic and green. Hansen solubility parameters for ethanol is calculated as in the following $\delta_D=15.8$, $\delta_P=8.8$, $\delta_H=19.4$ [109]. According to previous
published works, graphene can be fabricated via exfoliation of graphite in pure ethanol or water-ethanol mixture with a concentration about only 0.002 mg/mL in pure ethanol, and 0.014 mg/mL in water-ethanol mixture\textsuperscript{[110, 111]}. This increment of dispersion concentration can be explained by the steric repulsive force between nanosheets provided by the ethanol-water hetero-associate molecules\textsuperscript{[112-114]}. It has been achieved to improve the dispersion efficiency via ethanol up to 0.5 mg/mL of few layered graphene after a drastically long sonication process, nearly 300 h\textsuperscript{[83]}.

Numerous investigations have been devoted in this region in order to search for a method which will lead to improve dispersion efficiency in ethanol based systems. For instance, solvent exchange was suggested to transfer graphene dispersion from high boiling point solvents to low boiling point solvents. Graphite was exfoliated in NMP, then it was filtered through a porous substrate and washed the dispersion to remove residual NMP. The achieved nanosheets were re-dispersed in ethanol\textsuperscript{[115, 116]}. Nevertheless, filtering about 100 ml dispersion took more than 1h, besides iterative washing is required to completely remove NMP. These points make it unpractical for large production of graphene dispersion\textsuperscript{[117]}

Regarding to improve the solubility of ethanol with graphite, a promising exfoliation method has been proposed assisted with salts, i.e. it can either organic or inorganic salts, as intercalator. Here, the function of salt in the dispersion is to be intercalated into graphite interlayer spaces and expand the spacings of the graphitic layers, resulting in weaken van der Waal forces and improving the electrical repulsion between the sheets.

It has been reported that exfoliation efficiency increased up to 40 times in ethanol-KNaC\textsubscript{4}H\textsubscript{4}O\textsubscript{6} (0.062 mg/mL) (potassium sodium tartrate) compared to that in pure ethanol (0.0015 mg/mL) \textsuperscript{[110]} by 2 hr sonication. In salt-assisted exfoliation technique, there is no requirement of solvent exchange, any treatment for chemical functionalization or toxic solvents. Besides, because of low boiling temperature (78°C), the membrane surface can be easily removed without exposing high heat treatment.

\textbf{1.1.4.1.2 Exfoliated Graphene in Aqueous System Assisted by Surfactant}

Water is a natural solvent with a surface energy of 72.8 mJ m\textsuperscript{-2} for exfoliation purposes due to its environmentally friendly nature and almost no cost, contrary to organic media\textsuperscript{[118]}. However, water alone is not sufficient to disperse graphite due to the hydrophobic nature of graphene. Surfactant-assisted exfoliation has allowed the use of water as a solvent, which is attractive from an environmental standpoint as well as for applications that are not compatible with organic solvents. Surfactants can be divided into four main categories; (1) aromatic (2) non-aromatic and small molecules (3) ionic liquids and (4) polymers\textsuperscript{[94]}
Surfactants are usually known as organic compounds which compose of a hydrophobic groups (tail) which absorbs onto the graphene basal plane by van der Waals interaction and a hydrophilic head group which assists prohibit re-stacking of nanosheets through electrostatic repulsion or steric effect\textsuperscript{[102, 119]}.

The surfactant plays a dual role in the aqueous dispersion. First, it reduces the liquid– vapor interfacial energy of the solution to an optimum range that in relation to the energy required to separate the sheets beyond the range of the van der Waals forces. That is, the work of cohesion of the aqueous phase and the sheets of graphene within the graphite solid are comparable. When the surfactant concentration is too high, then the surface tension is hence reduced to such an extent that exfoliation does not occur because the energies are no longer matched. In addition to that, each surfactant has been identified a critical micelle concentration (CMC) which is the characteristic parameter of a surfactant. It is described as the concentration of surfactant above micelles (aggregation) form and after exceeding CMC, all additional surfactants contribute to the micelle formation. When the concentration is lower than CMC then the surface tension is strongly dependent on surfactant concentration while surface tension does not change anymore or relatively constant after reaching CMC. Second, the surfactant improves the stabilization of the dispersion by adsorbing onto the exfoliated graphene sheets, generating an extra repulsive term prohibiting the reaggregation of the sheets post-sonication\textsuperscript{[120-122]}.

![Molecular structures of surfactant](image)

**Figure 1.10** Molecular structures of ionic surfactant of sodium cholate (a), cationic surfactant (cetyltrimethylammonium bromide) CTAB (b) and non-ionic Pluronic 123 (c).

In this current work, sodium cholate (C\textsubscript{24}H\textsubscript{39}NaO\textsubscript{5}), CTAB and Pluronic 123 were used as surfactants in order to produce aqueous graphene dispersion. Lotya et al. presented that an aqueous dispersion stabilized by the surfactant sodium cholate, showed the concentration reached to 0.3 mg/mL. Based on the TEM results, the obtained flakes had an average length \~1 \textmu m and width \~400 nm. Additionally they pointed out that increasing sonication time led to stable dimensions but increasing centrifugation from 500 rpm to 5000 rpm resulted in reducing mean flake length from \~1 \textmu m to \~500 nm\textsuperscript{[123]} Moreover, Backes et al. reported\textsuperscript{[96]}

21
a method which consists of WS$_2$ dispersion in surfactant based aqueous system and iterative centrifugation cascade system. By applying repetitive centrifugation with sequentially increasing rotation speed it was aimed to separate exfoliated nanosheets by size. The most significant advantage of this method is that can be designed to create the desired size and thickness. This method was modified and used to produce surfactant assisted aqueous graphene dispersion for fabrication graphene composite membranes. Guardia et al.\textsuperscript{[78]} studied a wide range of surfactants (18) including non-ionic surfactants (i.e. Pluronic 123, Tween 80, Brij 700) and ionic surfactants (i.e. propane sulfonate, sodium deoxycholate, sodium dodecylbenzene-sulfonate). Dispersion were produced by 2 h sonication followed by centrifuged at 5000 h for 5 min and collecting supernatant as the final dispersion. A significant trend in terms of dispersion concentration was that non-ionic surfactants outperformed ionic ones, specifically Tween 80 and Pluronic 123 providing concentration up to 1 mg/mL for 2 h and reached up to 1.5 mg/mL for 5 h. sonication. Flakes composited of mostly few layer graphene $\sim$5 layers. The obtained results concluded that non-ionic surfactants worked better than ionic ones in regards to their suspending ability for graphene. This suggests that steric repulsion is more influential than electrostatic repulsion corresponding to the stabilization of nanosheets in water. Steric stabilization with non-ionic surfactants is procured by their hydrophilic chains which can easily disperse into water. The hydrophilic moieties compose of linear or branched polyethylene oxide (PEO), and those which has higher molecular weight proved enhanced stabilization in the dispersion. Like ionic sodium cholate and polymer based surfactant (Pluronic 123), cationic surfactants have been also gained attention as stabilizer agents for graphene dispersion. According to the results obtained by the group of Vadukumpully\textsuperscript{[124]} the hydrophobic part of the long alkyl chains can be absorbed by the graphene surface, resulted in hydrophobic interaction. Additionally, restacking and agglomeration can be inhibited by the electrostatic charge of hydrophilic chains. The obtained results suggested that produced graphene flakes had the thickness of 1.18 nm, length and width 0.7 $\mu$m and 0.5 $\mu$m respectively, and mostly less than 4 layers.

1.1.5 Characterization Techniques of Graphene Dispersion

The resultant graphene dispersion has a broad distribution of flake in size and length and these values depend on the conditions applied. So, in order to get a detailed understanding of the final product characterization of graphene dispersion is vital in LPE. To do that, there are of course various techniques which will be discussed in the following section.
(i) **UV-Vis Spectroscopy**

It is a useful technique which has been available since 1943\(^{[125]}\) and it is based on relation of the interaction of light with matter. UV-Vis spectroscopy is a well-known technique which can be used to determine the concentration of graphene dispersion. The transmission of light from one medium to another one, with different densities, results in bending of the beam because the speed of the traveling wave varies, this phenomenon is known as refraction. Here, current work focused on the interaction of light with graphene nanosheets dispersed in an appropriate solvent or in a surfactant assisted aqueous system. There are mainly two significant events occurring when a light beam passes through a liquid which includes particles in it, the light beam is relatively scattered or absorbed by the particles. In the case of the light beam propagates through a sample, absorption of scattering effect reduces the intensity of the beam. This intensity change is explained by the Lambert-Beer law\(^{[126]}\) which describes that the absorbance at a certain wavelength is proportional to the cuvette length, \(l\) and the concentration, \(C\) of the absorbing particles. \(I_0\) is the intensity of the incident light and \(I\) is the intensity of the transmitted light.

\[
A = \log \left( \frac{I_0}{I} \right) = \mathcal{E} l C
\]

\(\mathcal{E}\) is the extinction coefficient for the material, which is mainly affected by the intrinsic property of the molecules. This value can be calculated experimentally by filtering a certain volume of dispersion through a porous substrate and then weighing the resultant mass via a microbalance\(^{[82, 123]}\). Various extinction coefficient values have been reported in the literature for both aqueous\(^{[127]}\) and non-aqueous\(^{[81]}\) dispersion, ranged from 1390 to 6600 \(Lg^{-1}m^{-1}\)\(^{[85, 99, 128, 129]}\).

![Figure 1.11](image.png) The typical UV-vis spectroscopy of graphene and graphene oxide\(^{[130, 131]}\).
A typical UV-Vis for graphene and graphene oxide shown in Fig. 1.11. Graphene oxide (GO) is one of the important derivatives of graphene. It contains oxygen functional groups, such as epoxy, hydroxyl, carbonyl and carboxyl groups which decorates the basal plane and edges of GO[132]. The characteristic absorption peak was found at 235 nm for GO owing to π-π* transitions of the remaining sp² C=C bonds whereas it was shifted to a longer wavelength of around 267 nm (due to restoration of electronic conjugation) which is an indication reduction of GO to graphene. The reduction process from GO to obtain graphene increased the π-conjugation[133]. As the π-conjugation increases, less energy is needed for the transition, which corresponds to the observed shift of the absorption to the longer wavelength region[130]. There is also a small shoulder at around 300 nm for GO due to n-π* transition of C=O bonds. However, this shoulder is removed in graphene case confirming the absence of oxygen related groups.

(ii) Atomic Force Microscopy

Atomic force microscopy technique is used to get information about the sample geometry and determine thickness of the material/nanosheet by measuring height profile which is divided by the interlayer distance of single layer graphene which is usually less than 0.8 nm[134]. An extremely sharp tip which is placed at the end of cantilever moves across the sample surface vertically and this movement is detected by the reflection of laser on a photodiode. In this technique, there are mainly three operating modes: tapping, non-contact and contact mode. The use of purpose of these modes depends on the properties of the sample. For example, for graphene investigations, tapping mode is commonly preferable since contact mode might damage the sample surface by dragging or tearing[99].

In tapping mode, the tip oscillates at a certain resonance frequency and screen the sample surface as it moves across from right to left. When the cantilever gets close to the surface, the oscillation amplitude is decreased. Further decrease in separation between the tip and sample causes sample deformation due to van der Waals force[135]. Variations of the deflection or oscillation of the cantilever caused by attractive and repulsive interactions from the interaction of the tip and surface can be converted into topography map of the sample. AFM images provide a topographical contrast of the sample. However, it is not possible to know whether it consists of pure graphene or oxidized graphene or graphene together with solvent residual exist on the surface. The thickness profile depends on the preparation conditions of the sample, for instance; the type of substrate (SiO₂, mica or glass etc.).
The samples for AFM characterization were fabricated by drop casting a certain volume of diluted graphene dispersion (~20-30 μl) was dropped onto silicon wafer which was freshly cleaned with ethanol, IPA and water. When the solvent is NMP then the drop casting was operated with silicon wafer onto hot plate at 150°C to make sure complete solvent removal by evaporating. If it is an aqueous system or ethanol-based graphene dispersion to be characterized then silicon wafer was cleaned and pre-heated, followed by performing drop casting in fume hood. Afterward, drop-casted silicon wafers were left in vacuum overnight. Deposited flakes showed a shape on the wafer like ‘coffee ring formation’.

An ideal surface to be analysed is supposed to be a region with low density of deposited flakes. Otherwise, it might cause inaccurate estimation of thickness Additionally, to make sure that no residual solvent left on the surface, repeatedly washing process of silicon after drop-casting was applied here in this work.

(iii) Raman Spectroscopy

If a molecule is irradiated by an electromagnetic radiation, then the energy will be in three forms, absorbed, transmitted or scattered. Raman scattering was discovered by an Indian scientist Chandrasekhera Venkata Raman and Russian scientists G. S. Landsberg and L. I. Mandelstam simultaneously in 1928. Later, C.V Raman received the Nobel Prize in 1930. Raman spectrometry is based on the detection of the photons which are scattered inelastically by the sample owing to interaction of electron-phonon. A sample is lightened by a light source with a certain wavelength, and then interaction of incident radiation with the sample causes scattering which is detected by the spectrometer.
Main types of scattering are Rayleigh and Raman scattering. In Rayleigh scattering, the incident light interacts with a molecule and results in moving of an electron from a ground vibrational energy level $m$, to an excited state $(hV_m)$. Then, after relaxing it goes back to the initial vibrational energy level $(hV_m)$. So, during Rayleigh, no energy transfer occurs, emitted photon frequency and incident photon frequency have the same energy (no change in the frequency or energy). This type of scattering is also defined\textsuperscript{[142]} as elastic scattering.

In Raman scattering, the electron moves from the ground vibrational energy level $(hV_m)$, to the excited state, then it relaxes back to a higher vibrational energy level $n$, compared to initial energy level of electron $(hV_m - hV_n)$. This process is described as \textit{Stokes scattering}, in which photon loses energy. Therefore, if an electron moves from a vibrational energy level to an excited energy level, then it relaxes back to ground vibrational energy level which has a lower energy level than the initial energy level $(hV_m + hV_n)$. This scattering is known as \textit{Anti-Stokes scattering} which includes loss of energy from to the molecule and the transfer of energy to the scattered photon. Commonly used scattering is Stokes because the amount of the molecules in the ground state is higher than in that of excited vibrational state. In addition to the excitation occurring to virtual states, if the incident photon energy and electronic vibrational energy is the same or close, then excitation to electronic excited state can happen\textsuperscript{[143-146]}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic.png}
\caption{Schematic description of main types of Raman scattering\textsuperscript{[139]}.}
\end{figure}

By Raman spectrum of graphene, various amounts of information can be provided such as layer number, the type/quality of edges, disorder related peaks etc.\textsuperscript{[147, 148]} There are three main characteristic features in Raman spectrum of graphene; G peak at $\sim 1580$ cm$^{-1}$, 2D peak at $\sim 2700$ cm$^{-1}$ and D peak at $\sim 1350$ cm$^{-1}$. The G-band result in the vibration of neighbouring carbon-carbon bond and it is found at $\sim 1582$ cm$^{-1}$ in graphite. The 2D peak is caused by second-order two phonon processes, and the shape, width, position of this band can change with the increasing number of graphene layers which can influence the electronic
band structure of graphene. Hence, it is a significant to probe to determine the resultant graphene whether it is single-, bi- or few-layers. It has been reported by Graf. et al.\cite{149} and Lee et al.\cite{150}, that full width at half maximum (FWHM) of the 2D band in the case of single layer, few layer, multilayer graphene can be found in 25-30 cm\(^{-1}\), 39-65 cm\(^{-1}\), greater than 65 cm\(^{-1}\) respectively. For single layer graphene, 2D band intensity is much higher compared to G band, whereas the spectrum, is dominated by the G band in graphite\cite{151}. In addition, D peak is also important for graphene characterization, mostly described as the disorder related band. It can occur that (not Raman active in pure graphene) when the graphene’s symmetry is broken by the defects in the lattice. Intensity ratios of D and G peaks can be used to quantify the disorder and defects in graphene.

\(\text{(iv) X-ray Diffraction}\)

Physicists Sir W.H. Bragg and his son Sir W.L. Brag proposed a relationship in 1913, which was based on the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample\cite{132}. X-ray diffraction (XRD) can be used as a significant characterization tool in order to explore the crystal structures and atomic spacing. X-ray diffraction relies on constructive interference of monochromatic X-rays and a crystalline sample. Those X-rays are produced by a cathode ray tube and filtered by the lens to generate monochromatic radiation which are directed to sample. The interaction of the atoms in the sample and incident X-ray with specific angle \(\theta\) result in the diffraction of X-rays which will be collected by the X-ray detector and they are processed and counted. Diffraction peaks are converted into d-spacings and providing information for the identification of the material since each material has a unique d-spacing. A diffraction pattern is usually generated by the scattering of X-rays from the atoms which are arranged in a periodic array as shown in Fig 1.14. According to the Bragg’s Law, the relationship with the wavelength (\(\lambda\)) of the X-ray beam, the incident angle with respect to the diffracting planes (\(\theta\)), and spacing between diffracting planes (\(d\)) could be described as in the following formula:

\[
2d \sin \theta = n\lambda
\]  
(1.4)
Figure 1.14 Schematic diagram of XRD and Bragg’s law[133].

The d-spacing is the distance between planes of atoms which causes diffraction peaks. So, each peak in XRD pattern corresponds to a d-spacing which is usually defined in Angstroms (Å)[154]. During X-ray experiments, the X-ray beam irradiates each atom in the crystal structure and diffraction in all directions is created due to the interaction between the incoming X-ray beam and the oscillating electrons within each atom. The scattered X-ray beams from all Miller indices provide different spots. The diffraction pattern of the crystal is represented by the diffraction spots[155].

Fig. 1.15 provides typical XRD peaks for graphene and graphene oxide dispersions. The characteristic peak for graphitic like structures is at 26.5° (2θ) which is related to the (002) graphite reflection. This peak is strong and narrow in graphite while weak and broad in graphene[156, 157]. The peak at 11° can be seen in GO, indicating the presence of functional groups.

Figure 1.15 The typical XRD patterns of graphite, graphene and graphene oxide[130].
Johra et al. reported XRD patterns of graphite and its derivatives, graphene, and graphene oxide (GO) as can be seen in Fig. 1.15. Noted that GO was fabricated via improved Hummers’ method\cite{150}. Interlayer distance (d-spacing) of GO was found 8.33 Å which is a typical distance for GO while the d-spacing was 3.36 Å for graphite. Higher d-spacing in the case of GO compared to that in graphite is caused by the existence of oxygen-containing groups on the edge of each layer, which increased the distance between the layers. After the reduction process via hydrothermal treatment to remove functional groups to produce graphene, resultant d-spacing was monitored as 3.70 Å. From the observed peak broadening, it was concluded that the stacking of graphene was not well ordered\cite{130}.

In order to obtain the crystallite size (L), i.e., out of plane crystallite size which is the perpendicular dimension within graphitic ordering\cite{159} the full widths at half-maximum of the (002) peak (FWHM) were measured by using the Debye-Scherrer’s Equation:

\[
L = \frac{k\lambda}{\beta(2\theta)\cos\theta}
\]  

(1.5)

where \( \lambda \) is the X-ray wavelength in nanometre (nm), \( \beta(2\theta) \) is the peak width of the diffraction peak profile at half maximum height in radians, \( \theta \) is the scattering angle in radians and \( k \) is a constant related to crystallite shape, taken as 0.9 for the (002) Bragg reflection\cite{160}. The average number of graphene layers for each flake can be estimated from the combination of equation 1.4 (Bragg’s equation) and 1.5 (Debye-Scherrer’s equation) which provides the estimated graphene layer (n) for each domain as in the following:

\[
n = \frac{L}{d} + 1
\]

(1.6)

(v) **X-ray Photoelectron Spectroscopy**

XPS is a surface analysis technique which provides information about the chemical state of the material being studied. The XPS technique relies on the photoelectric effect\cite{161}. Kinetic energy of electrons which are ejected from a core level by an X-ray photon of energy \( hv \), usually (Mg K\(_\alpha\), 1254 eV or Al K\(_\alpha\), 1487 eV monochromatic radiation) The kinetic energy of the electron can be expressed by the following equation:

\[
E_k = hv - E_b
\]

(1.7)

where \( hv \) is the energy of incident radiation and \( E_b \) is the binding energy or ionization potential. When a sample is hit by an X-ray beam, core electron of an atom absorbs the energy of X-ray beam. In case the photon energy is adequate, the core electron can leave from the atom and be ejected from the sample surface. This ejected electron can be described as the *photoelectron* which is a kinetically energetic electron.
The binding energy of the inner electron can be defined by the following formula\cite{161}:

\[ h\nu = E_k + E_b + w \] (1.8)

where \( E_k \) is the photoelectron’s kinetic energy and \( w \) is the work function of spectrometer.

**Figure 1.16** Schematic diagram of XPS working process which describes the ejection of a 1s electron by photoionization\cite{129, 161}.

The energy of the emitted photoelectrons is measured by an electron energy analyser. The elemental composition, chemical state, and quantity of a detected element can be identified by analysing the binding energy and intensity of a photoelectron peak.

**Dynamic Light Scattering**

DLS is a useful light scattering technique to characterize particle size and particle size distribution of the material that is being studied. The diffusion coefficient \( (D_t) \) which is related to hydrodynamic size of particle can be obtained by monitoring the variations in intensity of light which is scattered from a suspension. The hydrodynamic radius is defined as the radius of sphere which moves with the same speed as the particle. Dynamic light scattering, (also known as photon correlation spectroscopy or quasi-elastic light scattering) measures the Brownian motion of particles in suspension which is described as the random movement of particles because of bombardment caused by the solvent molecules. By using Stokes Einstein equation, the hydrodynamic size of particle can be calculated from the translational velocity for spherical particles.

\[ d(H) = \frac{kT}{3\pi \eta D} \] (1.9)

Where \( d(H) \) is hydrodynamic diameter, \( D = \) translational diffusion coefficient, \( k = \) Boltzmann’s constant, \( T = \) absolute temperature, \( \eta = \) viscosity.

However, it is necessary to generate another equation rather than Stokes Einstein’s equation in order to estimate the lateral size of nanosheets for such layered compounds which are not
spherical. For this purpose, Lotya et al[162], provided an in-situ method by using primary peak position from intensity PSD \( a_{\text{DLS}} \) from DLS. The expression is given by as in the following form:

\[
<L>, \text{ nanosheet lateral length} > = (0.07 \pm 0.03) a_{\text{DLS}}^{1.5(0.13)}. \]

It is suggested that there is a strong correlation between the peak of the particle size distribution which is obtained from DLS instrument and the nanosheet lateral length measured by TEM. By this method, the lateral size of any 2-dimensional nanosheets which is dispersed in a liquid can be estimated easily.

Such a motion is dependent to various parameters such as temperature, solvent viscosity (as it is directly present in the formula) and also particle size and shape. Moreover, concentration of the suspension, type of ions and surface structure of a particle in the solution are also significant parameters which has influence on the translational diffusion coefficient. An ionic medium with a low concentration generates an external ions layer around the particle, resulting in decreasing diffusion speed and larger hydrodynamic diameter (Fig. 1.17a). However, an ionic medium with high concentration presses the electrical double layer and causes increased diffusion speed and reduced hydrodynamic diameter (Fig. 1.17b). Surface modifications effects the size by further increasing the hydrodynamic diameter. Electrical double layer[163] which was proposed in the 1850’s by Helmholtz[164] is defined as a structure which occurs on the surface of particle in a liquid medium. The electrical double layer consists of two parallel layers of charge surrounding the particle. The first layer consists of ions which are adsorbed onto the particle because of chemical interactions. The second layer is composed of ions which are attracted to the surface charge via the Coulomb force. This second layer is loosely connected with the particle due to free ions which float in the fluid under the influence of electric attraction and thermal motion. It is thus called the "diffuse layer".

![Figure 1.17 Schematic description of change in hydrodynamic diameter with changing electric double layer’s thickness (Debye length) \(^{163}\).](image)
It should be critically considered that the particle size is measured by DLS because it is hydrodynamic diameter which describes how a particle diffuses within a suspension and it is the diameter of a sphere which has the same translational diffusion coefficient as the particle that is being measured\textsuperscript{[166]}. Large particles diffuse slowly whereas small particles diffuse faster.

(vii) **Transmission Electron Microscopy**

Transmission electron microscopy provides atomic scale resolution\textsuperscript{[167, 168]}. Because of its high sensitivity, TEM provides deeper understanding by assisting to identify the atomic features of graphene, so it is used for characterizing thickness and size distribution of graphene nanosheets by counting the layer number at the flake edges\textsuperscript{[169]}. By analysing a large number of TEM images, paying close attention to the uniformity of the flake edges, flake thickness statistics can be produced. Besides, lateral dimension of flakes can be also calculated by measuring length and width of each layer to be screened. In this thesis, length (L) is referred to dimension along the long axis, and width (w) is defined as the dimension perpendicular to the long axis. The lateral size of each flake was determined by taking the mean of length and width.

In order to prepare samples for TEM characterization, The simple drop-casting method can be used by a few drops of diluted graphene dispersion onto holey carbon grid, followed by a waiting time for evaporation of the residual solvent from the surface. It should be noted here that smaller flake might be lost through the carbon grid during drop-casting, and this results in over-estimation of lateral flake size\textsuperscript{[82]}.

![Figure 1.18 TEM images of graphene flakes of monolayer (a) and diffraction pattern produced from the monolayer (a, inset), (b) edges of the individual flakes in a multilayer flake and (c) a wide-field image showing the large quantities of flakes observed\textsuperscript{[82]}.]
1.2 Introduction to Membrane Technology

1.2.1 Membrane Processes

Membrane separation technology has gained enormous attention owing to many advantages such as being energy-efficient, environmentally benign, its easiness in continuous mode operation and requiring less space\textsuperscript{[170]}. Membranes can be described as the selective (semi-permeable) barrier which allows the permeation of certain species while rejecting others. Mulder (1996) describes the membrane as, “selective barrier between two phases, the term ‘selective’ being inherent to a membrane or a membrane process”\textsuperscript{[171]}.  

![Figure 1.19](image_url)

**Figure 1.19** Schematic description of two phases which are separated by a selective membrane. ΔC, ΔP, ΔT, ΔE are (concentration, pressure, temperature and electrical potential gradient, respectively) the source of driving force of the flow from feed to permeate side (adopted from \textsuperscript{[171]}).

As shown in Fig 1.19, the membrane is a key material in between two phases. Phase 1 is a place where feed solution with a broad size particle can be found. Large sized particles compared to membrane’s pore size are rejected while small ones pass through to the other side of membrane which is known as permeate side (phase 2). The driving force for this transport of particles from one side to the other side might be caused by various factors such as gradients of concentration, pressure, temperature and electrical potential\textsuperscript{[172]}.
Because of a huge interest in the membrane separation field since the discovery of membrane as a selective material, a lot of membranes which has various specifications has been produced. It is possible to categorize membranes according to some certain parameters like nature, morphology and application, as shown in Table 1.1 \cite{171-174}. With regards to nature, membranes can be classified into two major categories: synthetic which includes organic, inorganic, hybrid and liquid, and natural which consists of biological and non-biological membranes. Another classification is based on the structure which is determinative for membrane’s selectivity and this can be subdivided into two as symmetric (i.e. porous or dense membranes) and asymmetric (i.e. integral and composite membranes). Also, membranes can vary according to their configurations, for instance; flat sheets, tubular, spiral wound and hollow fibre.
A variety of materials are available to make membranes, for example; polymers, inorganic, metals, glass and liquids\textsuperscript{173}. Appropriate materials should be chosen according to fulfill desired specifications for membrane since the membrane material has a significant influence on chemical, thermal stability, wettability etc. Due to being flexible, cost-effective and easiness to process, polymers are the most employed membrane material. Polymers which are high molecular weight components compose of repeated basic units that are connected together to build the long chain molecule\textsuperscript{171}.

**Table 1.1** Membrane categories based on their nature, structure and configuration \textsuperscript{171, 172, 174}.

<table>
<thead>
<tr>
<th>Nature</th>
<th>Synthetic</th>
<th>Natural</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Organic</td>
<td>Biological</td>
</tr>
<tr>
<td></td>
<td>Inorganic</td>
<td>Non-biological</td>
</tr>
<tr>
<td></td>
<td>Hybrid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Structure</th>
<th>Symmetric</th>
<th>Asymmetric</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Porous</td>
<td>Integral asymmetric</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Flat sheet</th>
<th>Tubular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Spiral wound</th>
<th>Hollow fibre</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In the current work, the following commercial symmetric porous membranes were used as support membranes; polyethersulfone (PES) which is an amorphous polymer from the thermoplastic family, nylon and polytetrafluoroethylene (PTFE) which is a synthetic fluoropolymer of tetrafluoroethylene, also known as Teflon.

### 1.2.2 Membrane Applications

Membranes can be classified in various categories based on membrane’s pore structure, and particle size of the solute to be filtrated/separated or ionic. For instance, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) are pressure driven membranes, except for forward osmosis (FO), which can be seen from the characteristics shown in Table 1.2. However, FO is a novel process, in which the driving force is the osmotic pressure gradient. Osmotic pressure is the hydrostatic pressure applied to the draw solute side (high solute concentration) of the membrane. It is essential to stop water transport through the membrane\(^{[173]}\).

If a particle to be rejected has a size >100 nm, then a membrane from microfiltration group can be used. High fluxes can be obtained in such application with a small pressure as driving force due to low hydrodynamic resistance. By increasing applied pressure, it is also possible to separate particles with a size in the range of 2-100 nm\(^{[176]}\). In that case, membrane resistance is greater than that in microfiltration owing to denser membrane’s structure. This process is known as ultrafiltration. From microfiltration to reverse osmosis, average pore size of membranes decreases and membrane’s hydrodynamic resistance increases, so these situations require high driving forces as can be seen in Table 1.2. Applied pressure should be increased with increasing resistance\(^{[171]}\). A highly permeable membrane\(^{[177]}\) is described as a thin membrane with high pore density (pores/µm\(^2\)), which is defined as the number of the pores per membrane area\(^{[178]}\), and large-diameter pores.

**Table 1.2** Characteristics of pressure driven membranes\(^{[176]}\).

<table>
<thead>
<tr>
<th></th>
<th>Microfiltration (MF)</th>
<th>Ultrafiltration (UF)</th>
<th>Nanofiltration (NF)</th>
<th>Reverse Osmosis (RO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeability (L/m(^2)hbar)</td>
<td>&gt;1000</td>
<td>10-1000</td>
<td>1.5-30</td>
<td>0.005-1.5</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>0.1-2</td>
<td>0.1-5</td>
<td>3-20</td>
<td>5-120</td>
</tr>
<tr>
<td>Pore size (nm)</td>
<td>100-10,000</td>
<td>2-100</td>
<td>0.5-2</td>
<td>&lt;0.5</td>
</tr>
</tbody>
</table>
1.2.3 Graphene Based Membranes

There are some important limitations in the current membrane world such as not able to tune water and solute permeability, low fouling/chemical resistance etc\cite{173, 179}. It has been underlined that there is a significant necessity of designing new generation membranes with solid and engineered pore structure, scalable for practical modules\cite{180, 181}. Graphene is a promising material for fabricating size selective membranes due to its unique atomic thickness, 2D structure and high mechanical strength. Graphene membranes are mainly categorized into three types; single layer (nano-porous) graphene membrane, stacked graphene membranes and graphene mixed matrix membranes as can be seen in Fig. 1.20. In this current work, stacked graphene membranes were studied and fabricated via a pressure assisted filtration technique.

Nano porous graphene membrane: This type of membrane is also known as free-standing graphene membrane. It is the simplest graphene membrane that can be generated by a single layer of graphene. The most promising feature of a graphene nanosheet is its extremely thin nature (one atom thick) which makes graphene wander membrane material due to the fact that permeance is inversely proportional to the membrane thickness\cite{170, 182} due to mass transfer resistance\cite{183} which increases with the increased membrane thickness. It has been studied selectivity of monolayer graphene membrane, and found that it is impermeable to even small gases like helium. According to Berry\cite{184}, geometric pore size of graphene was calculated as 0.064 nm, smaller than the diameter of helium (0.28 nm) or hydrogen (0.314 nm). However, it has been reported that it is possible to adjust the ultra-small nanopores and create hydroxylated pores of diameter around 0.45 nm by employing various methods like ion bombardment, oxygen plasma etching\cite{175, 185, 186}, electron beam\cite{187} and ionic etching\cite{186}. By producing nanopores with controlled geometry, density and chemistry\cite{188}, these membranes can be used as desalination membranes which allows water to pass through while rejecting water pollutants, salt ions etc. In addition to this, graphene can resist high pressure differences (6 atm)\cite{189}, caused by its mechanical strength.

Stacked graphene composite membrane: The surface morphology and transport mechanism are different in these membranes compared to monolayer graphene membrane. To form this type of membranes, graphene nanosheets are assembled into highly ordered, stacked graphene laminates onto a porous substrate via various fabrication techniques. Multilayer, well-packed graphene laminates allows water to pass but reject other molecules. In further parts, transport and separation mechanism and fabrication methods of this type of membranes will be discussed in detail.
Graphene mixed matrix membranes: These membranes were produced by directly mixing graphene with functional material, for instance polymer solution during fabrication process in order to obtain multi-functional membranes[182].

![Types of graphene-based membranes](image)

**Figure 1.20** Types of graphene-based membranes, (a) porous graphene layer (b) assembled graphene laminates and (c) graphene based composites.

### 1.2.3.1 Fabrication Methods of Stacked Graphene Composite Membranes

Graphene composite membranes can be assembled via various fabrication techniques such as (i) filtration-assisted method including vacuum assisted filtration, pressure assisted filtration[190], (ii) casting/coating based on spin coating, drop casting, dip coating and spray coating[191], (iii) layer by layer (LbL) assembly technique[192] and (iv) some other methods including evaporation[193], shear alignment[194]. A desired graphene composite membrane can be fabricated by a suitable preparation technique which strongly influences the membrane structure and separation performance, so a well-optimized fabrication method is crucial. Since filtration assisted and LbL fabrication techniques were used in this study, a brief description of their operating conditions is included in the following.

Filtration assisted technique is divided into two main techniques; vacuum filtration and pressure assisted filtration (Fig. 1.21). In pressure assisted filtration, membrane is pressurized with a constant certain pressure during the formation of graphene laminates under a stirrer. Pressure has a key role of the being driving force which has a strong influence on the orientation and order quality of nanosheets[195]. Therefore, in vacuum assisted filtration technique, variable suction is applied to the suspension and the liquid is filtered through porous substrate while graphene nanosheets form a stacked layer structure. These two techniques contain downward driving forces. However, the deposition of graphene by the evaporation technique involves upward driving force which is associated with the vaporizing the liquid. The formation of graphene selective layer and the surface roughness are affected by these differences (constant or variable pressure and the direction of driving forces).
Graphene membranes fabricated by pressure assisted, vacuum-assisted and evaporation assisted methods provided highly ordered (due to the constant pressure results in overlaying of nanosheets orderly), random (as the deposited layer thickness grows with time, the layer resistance increase and vacuum decreases. This situation results in formation of compact graphene layer near the substrate, but loose away from the substrate) and highly random orientation of stacked nanosheets[195], respectively. Consecutive laminar graphene structure with tuneable nanosized inter-layer distance is responsible for providing molecular separation. Besides, the interlayer distance of graphene nanosheets were also studied in each type of fabrication methods. The d-spacing decreased from 11.5 Å in evaporation method to 9.7 Å in vacuum assisted and to 8.4 Å in pressure assisted filtration. These results also underlined the importance of driving force for fabricating highly ordered dense selective layers of graphene. It has been also noted that centrifugation and diluted graphene dispersion[196] are important parameters in order to achieve high quality graphene membranes since selectivity of these membranes are dominated by only high-quality graphene dispersion.

Figure 1.21 Schematic of composite GO/mPAN membranes produced via pressure assisted filtration, vacuum filtration and evaporation method[195].

In addition to filtration method, layer by layer (LbL) assembly of nanosheets can be used as a fabrication method which involves formation of multilayers by using various techniques like immersion with wash steps in between each deposition. In this technique, covalent bond or electrostatic interactions are two major forces for a stable graphene deposition[197]. In order to increase the smoothness of the surface and also seal possible big pores of porous substrate or macro defects which occur during the casting process, the substrate was pre-modified with a positively charged polymer, polyethyleneimine (PEI) solution at a certain concentration. PEI also assists to improve membrane surface charge properties in order to obtain high rejection and also enhance the adhesion between substrate and graphene layers. This fabrication technique will be also called as “sandwich model” which composes of two
versions; stacked graphene nanosheets in between two PEI layers or cross linked modified stacked graphene nanosheets in between two PEI layers. Thus, very diluted graphene with cross-linker modified and without was assembled onto PEI modified porous substrate via a pressure-assisted filtration technique. So, some results presented in this work were obtained from the membranes fabricated with covalently modified graphene with a type of cross-linker (ethylenediamine) and without modified graphene dispersion. Nan et al.[192] studied on the preparation of graphene-oxide/PEI modified nanofiltration membrane via layer-by-layer method. The results showed that composite membranes are highly positively charged due to PEI modification and superior multivalent salt rejections of 93% and 38% for Mg$^{2+}$ and Na$^+$, and permeability of 4.2 L/m$^2$.h.bar. Moreover, Hu et al.[198] reported a water purification membrane fabricated by this method. GO was introduced with a positively charged polymer called polyallylamine hydrochloride (PAH) via electrostatic interaction, then deposited onto support membrane, PAN. The results revealed that GO membranes maintained its stability in solutions and provided good selectivity. Table 1.3 shows the water permeability and rejection performance of EDA crosslinked GO composite membranes.

Table 1.3 GO membrane performance.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Fabrication method</th>
<th>d-spacing (Å)</th>
<th>Water Permeance (L/m².h.bar)</th>
<th>Rejection</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDA cross-linked GO/CA</td>
<td>Pressure-assisted self-assembly</td>
<td>9.1 (dry) 9.3 (dry)</td>
<td>~0.5</td>
<td>-</td>
<td>[199]</td>
</tr>
<tr>
<td>EDA cross-linked GO/CA</td>
<td>Pressure-assisted self-assembly</td>
<td>9.2 (dry) 9.4 (wet)</td>
<td>~10</td>
<td>34.3%</td>
<td>Natural organic matter (NOM)</td>
</tr>
<tr>
<td>EDA cross-linked GO/NF+HPEI</td>
<td>Pressure-assisted self-assembly</td>
<td>-</td>
<td>~5</td>
<td>96.3% MgCl$_2$</td>
<td>[200]</td>
</tr>
</tbody>
</table>

- CA: cellulose acetate; NF: nanofiltration; HPEI: hyperbranched polyethyleneimine

In both methods, graphene composite membrane thickness can be adjusted by controlling the volume of graphene dispersion and number of layer-by-layer deposition cycle. The thinnest membrane is preferable in terms of achieving high permeability. However, forming
thick graphene stacked layers might be beneficial since defects occurred from incomplete coverage of graphene nanosheets can be eliminated by increasing the thickness of graphene selective layer. There are some important parameters one should carefully consider such as modification duration of PEI and its concentration and reaction time to allow sufficient cross-linking process.

A desired membrane should fulfill the following characteristics: high flux and selectivity, mechanical stability, chemical and thermal stability, low fouling and good compatibility, being cost effective and defect-free fabrication. Membrane thickness is a vital tool which should be decreased in order to achieve improved membrane performance with high flux.

### 1.2.3.2 Transport Mechanism Through Nanochannels

By considering that water inside graphene nanochannels acts as a classical liquid, Geim et al.\[^{201}\] studied Hagen-Poiseuille’s law to explain the flow between laminar GO membranes as shown in the following equation:

\[
J = \frac{d^4 \Delta P}{121L^2 \eta h} \tag{1.10}
\]

where \(J\) is the water permeability (L/m\(^2\).h.bar) within nanochannels in stacked laminate, \(d\) is the distance between adjacent graphene layers, \(L\) is the average lateral size of the graphene sheets, \(\eta\) is the viscosity of water (889 mPa s), and \(h\) is the thickness of the graphene stacked laminate (selective layer of composite membrane). The calculations indicated that graphene oxide (GO) membranes provide fast water transport by a factor of a few hundred compared to classical laminar flow regime. Hagen-Poiseuille equation is based on laminar flow between two parallel plates which has a parabolic flow velocity regime, from zero velocity at the boundary layer to a maximum velocity at the centreline. The results suggested that liquid flow velocity was not zero at the graphene wall, with an estimated 10 – 100 nm slip length. In addition to the theoretical calculations based on Hagen-Poiseuille’s law, experimental results of filtration also showed 4-6 orders of magnitude higher water flux\[^{202}\]. The same trend was found by Han et al.\[^{203}\]. All these findings enabled to conclude that superior fast water transport through graphene nanochannels is caused by slip flow theory\[^{182}\]. The pure graphene without functional groups provides frictionless carbon walls, which are in charge of the fast transport of water (Fig. 1.22a). More hydrophobic solvents (isopropanol, ethanol, hexane, cyclohexane, and toluene) cause to decrease flux compared to that of water, owing to greater interaction between the more hydrophobic liquid and graphene walls, which matches with the slip flow theory. Additionally, another possible reason for high water flux
was proposed\textsuperscript{[182]} in which water molecules could flow through defects of the graphene nanosheets (shorter pathways for the transport), resulting in smaller $L$ and higher flux according to equation (1.9).

![Figure 1.22 Schematic description of molecular transport through interlayer channels of graphene oxide (a)\textsuperscript{[201]} and inter-layer channels laminates of GO and holes on graphene nanosheets (b)\textsuperscript{[203]}.](image)

Intrinsic defects (1-15 nm) i.e., holes, tears and wrinkles and extrinsic defects (100-200 nm)\textsuperscript{[181]} might be appeared during the fabrication of stacked graphene membranes. The presence of defects has an impact on the filtration performance of graphene-based membranes which suffer from intrinsic defects, grain boundaries, and wrinkles which contribute to defective pathways\textsuperscript{[204]}. The defects must be identified and eliminated for such stacked graphene nanosheet membranes in order to enhance the sufficient sieving properties. Sealing or blocking defects\textsuperscript{[205]} (holes, tears etc) is one way in order to enhance the membrane’s mass transport.

Two typical transport mechanism\textsuperscript{[206]} occur in such membranes: structural defects within graphene flake and interlayer channels between flakes. Existence of distance between graphene nanosheets and holes formed on the surface of graphene sheets create horizontal (channels) and vertical (holes) transport of the molecules as shown in Fig. 1.22b.

1.2.3.3 Separation Mechanism Through Nanochannels

In graphene based membranes, separation mechanism can be mainly classified into three groups\textsuperscript{[182]}; size exclusion, Donnan exclusion (electrostatic interactions) and ion adsorption (Fig. 1.23). Size exclusion occurs when large molecules are rejected from the membrane’s pores. Selectivity of graphene membranes according to size of desired molecule/ion to be blocked can be tuned by carefully controlling the interlayer spacing of graphene layers\textsuperscript{[197, 207]}. Hydrated diameter of ions in water was shown in the following\textsuperscript{[208]}; for example, Na$^+$ 0.72 nm, K$^+$ 0.66 nm, Ca$^{2+}$ 0.82 nm, Mg$^{2+}$ 0.86 nm and Cl$^-$ 0.66 nm. They are all larger than the effective size of a water molecule (0.26 nm). It has been reported by the molecular dynamics simulations that monolayer graphene membranes have a capability to fully reject
salt ions \cite{185}. Based on the findings from such studies, the critical nanopore diameter for rejecting NaCl is determined in between 0.6 and 0.8 nm \cite{209}.

In addition to size exclusion factor, electrical charge properties of membrane surface also has an influence on rejection. Thus, charged ions and small molecules can be blocked by the Donnan exclusion effect owing to negatively charged property of graphene \cite{192}. Apart from size exclusion and Donnan exclusion, some smaller hydrated ions are blocked by the adsorption due to coordination interactions of transition metal cations and oxygen-containing functional groups in oxidized regions of graphene \cite{210-212}.

**Figure 1.23** Schematic description of separation mechanism for monolayer graphene membrane (a) and multilayer graphene membrane (b) \cite{213}.

### 1.2.4 Osmosis Processes

Osmosis can be described as the water transport across a selectively permeable membrane, which is driven by an osmotic pressure difference, from a solution with high water chemical potential to a solution with low water chemical potential \cite{214-217}. Osmotic pressure difference ($\Delta \pi$) across the membrane is used as the driving force in forward osmosis, results in water passage from feed to draw side.

Solution with high water chemical potential is called the feed solution, while the solution with high solute chemical potential (low water chemical potential) is referred to as draw solution. The osmotic membrane allows water molecules to pass through while rejecting draw solute. During the osmosis tests, the concentration of draw solution decreases and becomes diluted draw solution within this time as water molecules permeates from feed to
draw side. This transport will proceed until the chemical potential across the membrane arrives at the equilibrium level.

Osmotic processes can be categorized into three main types: forward osmosis\(^{[214]}\) (FO) (referred also as osmosis or natural osmosis), reverse osmosis\(^{[218]}\) (RO) and pressure retarded osmosis\(^{[219]}\) (PRO) (Fig. 1.24). In FO, there is no applied hydraulic pressure, the system is driven by the osmotic pressure gradient of two solutions in different concentrations. These solutions are defined in such processes as feed solution with low solute concentration (i.e., pure water) and draw solution with high solute concentration (i.e., salt solution).

If a hydraulic pressure (\(\Delta P\)) is applied to the draw side which is the opposite direction of the osmotic pressure gradient, water flow is still in the direction from feed to draw solution (as in FO) when the case is \(0 < \Delta P < \Delta \pi\) (since the osmotic pressure gradient is still bigger than the applied external pressure). This process is known as PRO which has a reduced net driving force, \(\Delta \pi - \Delta P\). If hydraulic pressure, \(\Delta P\) applied to the draw side is greater than the osmotic pressure gradient, \(\Delta \pi\); then the water molecules are forced to flow from draw to feed solution side, resulting in changing the direction of water transport. This phenomenon is described as RO\(^{[214, 215]}\).

![Diagram of osmosis processes](image)

**Figure 1.24** Schematic description of osmosis processes\(^{[215]}\).
FO has some advantages compared to RO, for instance; it exhibits a stronger antifouling capability[216,220,221], higher water recovery and also is applicable to wide range of fields such as seawater desalination[222], agricultural irrigation[223], osmotic power generation[224], wastewater treatment[1], protein enrichment[225], drug industry[226] and food industry[227]. FO consists of two steps: the first step is an energy saving process which involves water permeating through to the other side of the membrane, where the concentrated draw solution gets diluted. Furthermore, the second step is to re-concentrate diluted draw solution (DS) for reuse and purify water (concentrated feed solution due to reverse solute leakage during FO tests) by using other technologies like ultrafiltration (UF) separation in the end of the process. Even though FO is considered as the energy efficient process, additional energy is required for the regeneration after FO run, which might increase relevant energy costs of this process. From that point of view, selection of draw solution is a highly critical parameter of FO run.

It is expected from an ideal FO membrane that it should allow water passage while blocking solute molecules completely. However, in real systems, reverse solute diffusion occurs, resulting in passage of some solute from the draw solution side to feed solution side. This is a major technical challenge in FO which should be solved, otherwise it results in flux decline by reducing the net osmotic pressure across the membrane.

1.2.4.1 Selection of Draw Solute

A remarkable amount of effort has been made on discovering appropriate draw solutions for FO processes. Many draw solute candidates have been proposed by researcher in the literature, i.e., commercially available compounds such as, inorganic salts[228, 229], organic salts[230] and polymers[231] etc. A suitable draw solute for FO processes has to fulfil following requirements; it must have the capability of generating high osmotic pressure since the osmotic pressure gradient between feed solution and draw solution across the membrane is the driving force of the forward osmosis process. Osmotic pressure of the draw solution must be higher than that of feed solution in order to provide high flux from feed to draw side[232].

Then, it has to diminish internal concentration polarization which would be minimized by selecting a draw solute with high diffusion coefficient (minimize ICP by diffusion quickly through the support layer); it should have a low viscosity to allow easy circulation within the FO loop, small ion/molecule size[216, 233]. Besides, reverse solute transport from draw solution to feed solution must be minimal. Otherwise, high solute transport to feed solution might be reduced net driving force in the process, which is not favourable. Furthermore, it has to be cost-effective, non-toxic, be easy to re-concentrate and provide low reverse solute
permeability, and have good bio fouling resistance. Another important criteria is the recovery of diluted draw solution in the end of FO. This should be done via cost-friendly process to consume less energy, otherwise it might not be applicable for industrial scale implementation. Various techniques have been discussed in literature such as reverse osmosis\cite{234, 235}, nanofiltration process\cite{236}, distillation\cite{237}, ultrafiltration\cite{238}, heating magnetic field separators\cite{239}.

\[ \pi = n \left( \frac{c}{M_w} \right) RT \quad (1.11) \]

Osmotic pressure of the draw solution can be calculated by using Van’t Hoff equation\cite{240} shown in eqn1.10. Where \( n \) is the number of moles of species, \( c \) is the solute concentration in g/L of solution, \( M_w \) is the molecular weight of the solute, \( R \) is the gas constant (\( R = 0.0821 \)), \( T \) is the absolute temperature of the solution. As can be seen from the equation 1.11, it is obvious that the osmotic pressure is also strongly dependent on solute concentration, molecular weight (\( M_w \)) of the solute and temperature. Therefore, the type of species dissociated in the solution is not important in that case. Furthermore, FO performance is also affected by other properties of draw solution, such as diffusion coefficient of DS as shown in the following equation 1.12. Small \( M_w \) of draw solute exhibits higher osmotic pressure compared to large \( M_w \)\cite{241, 242}.

\[ K = \frac{t \tau}{\varepsilon D_s} \quad (1.12) \]

Where, \( D_s \) is solute diffusion coefficient in water \( (m^2/s) \), \( K \) is the solute resistance to diffusion within the membrane, \( t \) is the support layer thickness, \( \tau \) is the tortuosity and \( \varepsilon \) is the porosity of the support membrane. It can be concluded from the above equation that solutes which has higher diffusion coefficient will exhibits lower resistance and can more readily transport through the membrane support layer and result in therefore lower ICP effects. Solutes with lower \( M_w \) usually have higher diffusion coefficient compared to those with higher \( M_w \); however, many studies have reported that DS very small \( M_w \) exhibited higher reverse solute diffusion\cite{229, 241, 243-246} which could have an unfavourable influence on the FO performance, especially when high-quality product water is required. Solutes of higher \( M_w \) have lower diffusion coefficients, resulting in high resistance and higher ICP effects\cite{241}.

The concentration of the draw solution also has a remarkable impact on the FO process. It has been revealed by many studies\cite{247-249} that increases in DS concentration led to increase in water flux. Therefore, this increment was linear at lower concentration but showed a non-
linear behaviour (logarithmic) at higher DS concentrations. This can be explained by the internal concentration polarization (ICP) effect which occurred in the support layer.

Apart from all those mentioned above, the temperature of draw solution also has an impact on FO performance due to changing osmotic pressure, viscosity and diffusivity by temperature variance. The studies reported\cite{250-253} that increasing DS temperature led to increase in water flux and this was explained by the decreased water viscosity and therefore improved mass transfer. With the increase of DS temperature, the diffusion coefficient ($D_s$) increases and results in decreased solute resistance, $K$ (refer to Eq. 1.12) and therefore increased water flux\cite{250, 252}. On the other hand, the relationship between water flux and DS temperature has not been clarified yet. Since some others claimed that increasing DS temperature is only valid until a critical point where water flux increase can be observed, but after this point a decline trend in water flux is observed.

### 1.2.4.2 Concentration Polarization

Osmotic pressure difference ($\Delta \pi$) across the active layer of the membrane is found to be much lower than the bulk osmotic pressure difference between draw and feed solution ($\Delta \pi \leq \pi_D - \pi_F$). Reverse solute diffusion from the draw solution side to the feed solution side leads to increase in the concentration of the feed solution and a reduction in the concentration of the draw solution close to the membrane. Lower water flux can be related with this phenomenon\cite{254-257} which is commonly associated with concentration polarization (CP), and depends on the membrane orientation. CP might be referred to the accumulation of the solutes close to the membrane surface\cite{233}. There are mainly two type of CP that can occur in such processes; external concentration polarization (ECP) and internal concentration polarization (ICP), and two subcategories; concentrative and dilutive. Solute concentrations can change considerably at the boundary layer of the membrane as shown in Fig. 1.25.
Figure 1.25 Schematic description of osmotic pressure gradient in symmetric membranes under FO orientation (active layer faces with feed solution) and PRO orientation (active layer faces with draw solution). $\pi_{F,b}$ is the osmotic pressure at the bulk feed side, $\pi_{F,m}$ is the osmotic pressure of the feed solution on the feed side of the active layer, $\pi_{D,m}$ is the osmotic pressure of the draw solution on the draw side of the active layer, $\pi_{D,b}$ is the osmotic pressure at the bulk draw side, $\pi_{D,i}$ is the osmotic pressure of the draw solution within the support layer close to the active layer, $\pi_{F,i}$ is the osmotic pressure of the feed solution within the support layer close to the active layer.

If CP arises at the active layer of the membrane, it is called external CP (ECP) and CP in the support layer of the membrane is called internal CP (ICP) caused by the solute flow within the porous layer of the membrane.

**Formation of ECP:**

ECP occurs at the surface of the membrane’s active layer.

- If the membrane is placed in FO orientation, solutes are concentrated at the membrane surface due to the rejection of solutes by the membrane, resulting in rise of concentrative ECP ($\pi_{F,m} > \pi_{F,b}$) on the active layer of the membrane. Feed osmotic pressure increases from $\pi_{F,b}$ to $\pi_{F,m}$.
- If the membrane is placed in PRO orientation, draw solution concentration is reduced by the convective flow of fluid through the membrane, causing dilutive ECP ($\pi_{D,m} < \pi_{D,b}$) occurs on the active layer of the membrane. Osmotic pressure of draw solution decreases from $\pi_{D,b}$ to $\pi_{D,i}$.

It is possible to eliminate ECP by various methods such as increasing cross-flow velocity on the external surface of the membrane, improving mixing (magnetic stirring) or modification.
of feed spacers\cite{258, 259} Because there is no applied hydraulic pressure in FO, ECP can rarely be observed compared to RO.

Formation of ICP:
ICP takes place in the porous support layer of the membrane.

- When the active layer faces with the feed solution (FO mode); the water molecules passing through the support layer dilutes the draw solution and resulting in rise of dilutive ICP \( (\pi_{D,b} > \pi_{D,i}) \) which is the biggest problem in FO applications.

- When the active (dense) layer faces with the draw solution (PRO mode); because water molecules permeate through the membrane, draw solution inside the support layer gets more concentrated and results in the rise of concentrative ICP \( (\pi_{F,i} > \pi_{F,b}) \).

It has been reported that the existence of ICP is considered as the major reason for the considerable reduction of osmotic driving force (resulting in decreasing water flux and power density) rather than ECP\cite{253, 260}. Dilutive ICP causes a reduction of draw solute concentration within the porous support. In order to get rid of it, another suggestion proposed as in the ECP cannot be applied here since it happens inside the porous support layer. Solute accumulation near to membrane depends on diffusion rate. Decreasing support layer thickness and selection of an appropriate draw solute with low diffusion rate were suggested by the researches to eliminate dilutive ICP in FO\cite{261}. 
1.2.5 Equations used in Filtration Characterization

Permeate flux, given in units of liters per square meter per hour \( J_W \), \( \text{Lm}^{-2}\text{h}^{-1} \), \( \text{LMH} \) of a membrane can be identified as the flow rate of permeate produced per unit area of membrane surface per unit time (volume/unit area/time). Permeability \( A, \text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}, \text{LMH/} \text{bar} \) can be determined from the Eq. (1.13).

\[
J_W = \frac{Q_p}{A_m} = \frac{\Delta V}{A_m \Delta t} \quad (1.13)
\]

\[
A = \frac{Q_p}{\Delta P A_m} = \frac{J_W}{\Delta P} \quad (1.14)
\]

Where \( J_W \) is the permeate flux (L/m\(^2\).h), \( Q_p \) (L/h) is the permeate flow, \( \Delta V \) is the permeate volume (L), \( \Delta t \) is the operation period (h), \( A_m \) is the effective membrane active area (m\(^2\)) and \( \Delta P \) is the filtration pressure (bar), \( A \) is the water permeability (L/m\(^2\).h.bar).

\[
R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \quad (1.15)
\]

\( R \) is the rejection of solute across membrane, \( C_p \) and \( C_f \) are the concentrations of permeate and feed solutions in g/L, respectively. These values were recorded during and at the end of each run in order to measure rejection ratio.

\[
\varepsilon = \frac{(m_1 - m_2)/\rho_w}{(m_1 - m_2)/\rho_w + (m_2 - m_3)/\rho_p} \quad (1.16)
\]

Membrane porosity \( \varepsilon \) was measured by using gravimetric analysis using equation 1.15 where \( m_1 \) and \( m_2 \) are the wet and dry membrane’s mass, \( \rho_w \) is the density of the water, 1 g cm\(^{-3}\), \( \rho_p \) is the density of the substrate.
1.2.6 Equations used in Forward Osmosis Characterization

Osmosis water flux, given in units of liters per square meter per hour \( J_w \), can be calculated based on the volume change of the feed solution using Eq. (1.17).

\[
J_w = \frac{\Delta V}{A_m \Delta t}
\]  

Where, \( \Delta V \) is the volume of water permeated from draw solution to feed solution (L) over a certain of time \( \Delta t \) (h) during forward osmosis testing period; \( A_m \) is the effective membrane active area (m²).

Since draw solute, polyacrylic acid sodium salt (PAA-Na) used in the current work dissociates in its aqueous solution, some ions can transfer from draw solution to feed solution. The reverse solute leakage, given in units of grams per square meter per hour \( J_s \), can be determined from concentration change of the feed solution at a certain time interval. \( J_s \) is calculated by Eq. (1.18).

\[
J_s = \frac{C_1 V_1 - C_0 V_0}{A \Delta t}
\]  

Where, \( J_s \) is the solute flux, \( C_0 \) (g/L) and \( V_0 \) (L) are the initial concentration and initial volume of feed solution, respectively. \( C_1 \) (g/L) and \( V_1 \) (L) are the solutes concentration and measured volume of feed solution at time of \( t \).

\[
\pi = \mu cR T
\]  

Where, \( \pi \) is the osmotic pressure, \( \mu \) is the van’t Hoff factor, \( c \) is the molar concentration, \( R \) is the gas constant (8.31441 Jmol⁻¹K⁻¹), \( T \) is the absolute temperature.

\[
\pi_{\text{eff}} = \pi_{D,t} - \pi_{F,t}
\]  

Where, \( \pi_{\text{eff}} \) is the net osmotic pressure difference between draw osmotic pressure at given \( t \), \( \pi_{D,t} \) an feed osmotic pressure \( \pi_{F,t} \) at given time \( t \).
CHAPTER 2

EXPERIMENTAL SECTION
EXPERIMENTAL SECTION

2.1 Materials, Methods and Experimental Procedures

2.1.1 Materials

Solvents used in this project were ethanol and N-Methyl-2-pyrrolidone (NMP), respectively. Ethanol (absolute, 99%) was purchased from Fisher Scientific (Acros Organics, UK) and NMP was obtained from Merck Milipore, KGaA, Germany. Potassium sodium tartrate KNaC₄H₄O₆·4H₂O (ACS reagent, 99%) was acquired from Sigma-Aldrich. Poly(acrylic) acid, sodium salt (PAA-Na, Mw ~5100), PAA-Na (Mw ~8000, 45 wt% in H₂O) and PAA-Na (Mw ~30000, 40 wt% in H₂O) were supplied by Sigma-Aldrich. Poly(ethyleneimine) solution ~ 50% in H₂O was obtained from Sigma-Aldrich. Graphite flakes (+100 mesh ≥ 75%) was purchased from Sigma-Aldrich. Membranes used as support in this project are Nylon (0.2 μm and 0.45 μm, diameter 47 mm), was ordered from Supelco. PTFE (polytetrafluoroethylene) membrane (0.2 μm, diameter 47 mm) was bought from Sterlitech and polyethersulfone (PES) membrane was supplied from Sartorius. Cross linker monomer; ethylenediamine (EDA) was purchased from Sigma-Aldrich. Surfactants used in this project are Pluronic 123, Sodium cholate and CTAB were supplied from BASF, Sigma Aldrich and Acros Organics, respectively. The U-Tube used for osmosis experiments were purchased from PASCO. Silicon wafers (single side polished) were purchased from Sigma-Aldrich. Holey carbon grids (400 mesh) were bought from Agar Scientific Ltd., UK.

2.1.2 Methods

2.1.2.1 Preparation of Graphene Dispersions

In order to fabricate exfoliated graphene dispersion from graphite, a series of graphene dispersions were prepared by sonicating mixtures of graphite with various solvents in order to explore solvent dispersibility and their effect on quality of graphene flakes. Liquid phase exfoliation technique was used in this project to fabricate graphene from graphite. Flowcharts of each dispersion pathways were shown below Fig. 2.1.
Figure 2.1 Schematic of fabrication of graphene dispersion at various solvents.

By proposing the various graphene fabrication, it has been aimed to provide pure graphene (free of functional groups) with as much as small (typically, less than 1 μm) and thin flakes (few layers) dispersed in a range of solvents which gives a valuable choice according to the requirements of further membrane application. Sonication time (h) and energy, solvents, centrifugation rotational speed (rpm) are control parameters of the procedures. In the end as shown in Table 2.1, three NMP based dispersions which differed in centrifugation speed and further centrifugation exposure, two ethanol dispersions which differed in further centrifugation exposure and two surfactant assisted aqueous based dispersions were produced and characterized.

Fabrication tools which were mainly used to produce graphene dispersions are listed as in the following: ultrasonic bath (Elmasonic Transsonic, TI-H-10), ultrasonic probe (Sonopuls HD 2200 ultrasonic laboratory homogenizer, Bandelin), centrifuge (Hettich Universal 320) and ultrahigh centrifuge (Thermo electron corporation, SORVALL WX Ultra Series).
Table 2.1 Dispersion pathways with various diversity in terms of different solvents (i.e. NMP, ethanol and surfactant based) and mechanical force factors (i.e. ultrasonic probe and bath).

<table>
<thead>
<tr>
<th>Method Name</th>
<th>Solvent</th>
<th>Starting Concentration (mg/mL)</th>
<th>Sonic Probe 1</th>
<th>Sonic Bath 1</th>
<th>Centrifuge 1</th>
<th>Sonic Probe 2</th>
<th>Sonic Bath 2</th>
<th>Centrifuge 2</th>
<th>Centrifuge 3</th>
<th>Centrifuge 4</th>
<th>Final Part</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>NMP</td>
<td>5</td>
<td>4 hr, 4 sec on/off, 60% amplitude</td>
<td>-</td>
<td>1.5 krpm</td>
<td>45 min</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N2</td>
<td>NMP</td>
<td>5</td>
<td>4 hr, 4 sec on/off, 60% amplitude</td>
<td>-</td>
<td>4.5 krpm</td>
<td>45 min</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N3</td>
<td>NMP</td>
<td>5</td>
<td>4 hr, 4 sec on/off, 60% amplitude</td>
<td>-</td>
<td>4.5 krpm</td>
<td>45 min</td>
<td>-</td>
<td>4.5 krpm</td>
<td>45 min</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E1</td>
<td>Ethanol</td>
<td>10 - C&lt;sub&gt;G&lt;/sub&gt;, 30 - C&lt;sub&gt;sal&lt;/sub&gt;</td>
<td>-</td>
<td>4 hr, 45 kHz</td>
<td>3 krpm, 30 min</td>
<td>-</td>
<td>1 hr, 45 kHz</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Whole</td>
</tr>
<tr>
<td>E2</td>
<td>Ethanol</td>
<td>10 - C&lt;sub&gt;G&lt;/sub&gt;, 30 - C&lt;sub&gt;sal&lt;/sub&gt;</td>
<td>-</td>
<td>4 hr, 45 kHz</td>
<td>3 krpm, 30 min</td>
<td>-</td>
<td>1 hr, 45 kHz</td>
<td>3 krpm, 30 min</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
| S1          | Aqueous Surfactant | 20 - C<sub>G</sub>, 6 - C<sub>sal</sub> | 1 hr, 4 sec on/off, 60% amplitude | -            | 4.5 krpm, 90 min | 5 hr, 4 sec on/off, 60% amplitude | 1.5 krpm, 120 min | 7.5 krpm, 120 min | 10 krpm, 120 min | -          | Supernatant (Su)
|             |         |                                |               |             |              |               |             |              |              |              | Sediment (Se) |
In the case of method N1, N2 and N3 (*Table 2.1* and *Fig. 2.2*) graphene dispersions were prepared by using ultrasonic probe. Graphite was directly mixed with 80 mL NMP solvent (5 mg/mL). Then, this mixture was exposed to sonication for 4 h at 60% amplitude in an ice-cooled water bath. Here, two different centrifugation rotation speeds were applied to see the effects of using various speeds on flake size and thickness. Dispersions were placed into centrifugation for 45 minutes with 1500 rpm (method N1) and 4500 rpm (method N2). Then, the top 85% of supernatants from each set of experiments were collected for further analysis and the sediment was discarded. Dispersion N2 was exposed to further centrifugation for 45 minutes with 4500 rpm and the top 85% of supernatant was collected and labelled as N3.

**Figure 2.2** Schematic describing the fabrication of graphene dispersion via methods N1 (red arrows), N2 (black arrows) and N3 (green arrows).

Dispersion method E1 and E2 was re-modified from\cite{110} by making some changes in the fabrication procedure. In the case of method E1 (*Table 2.1* and *Fig. 2.3*), graphite flakes were mixed with potassium sodium tartrate KNaC\(_{4}\)H\(_{4}\)O\(_{6}\).4H\(_{2}\)O with a weight ratio of 1:3 and ethanol (10 mg/mL initial concentration of graphite and 30 mg/mL concentration of salt). Previous studies\cite{110,262-264} showed that salt assisted exfoliation was resulted in high efficiency of graphene dispersion in ethanol. This mixture was then exposed to sonication for 4 hours via ultrasonic bath with a frequency of 45 kHz, keeping the bath’s temperature as room temperature via changing the water in each 30 minutes. After completing sonication, since the resultant dispersion had a broad flake size distribution (highly poly-dispersed) and also included salt in the solution, the centrifugation process was applied to separate large unexfoliated graphitic like structures from the dispersion in order to have smaller thinner flakes in the dispersion.
Next, the mixture was placed into centrifugation for 30 minutes with 3000 rpm. Then, the top 85% of supernatant was collected for further analysis and the sediment was discarded. The supernatant was washed with water several times to remove possible salt residuals and re-dispersed in the same amount of ethanol for about 1 hour. In the end, dispersion E1 was obtained. Furthermore, E1 was exposed to another centrifugation for 30 minutes with 3000 rpm (Table 2.1 and Fig. 2.3). The supernatant gathered from this and labelled as the dispersion E2 which was used to prepare for making graphene based membranes.

**Table 2.1**

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Sonication</th>
<th>Centrifugation</th>
<th>Separation</th>
<th>Centrifugation</th>
<th>Separation</th>
</tr>
</thead>
<tbody>
<tr>
<td>240 mg Graphite 720 mg Potassium Sodium tartrate 24 mL Ethanol</td>
<td>4 hours sonic bath, 45kHz</td>
<td>3000 rpm for 30 min</td>
<td>Sediment</td>
<td>Re-dispense in 24 mL ethanol for 1 hr in sonic bath</td>
<td>Centrifugation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3000 rpm 30 min</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Supernatant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>E2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FINAL</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FINAL</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Remove salt</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>25 krpm, 15 min</td>
</tr>
</tbody>
</table>

**Figure 2.3** Schematic describing the fabrication of graphene dispersion via methods E1 (blue arrows) and E2 (yellow arrows).

Method S1 (Table 2.1 and Fig. 2.4) is based on a published procedure\(^\text{[96]}\). Graphite powder (20 mg/mL) was directly mixed with various aqueous surfactant solutions (i.e. Sodium cholate, CTAB and Pluronic 123) (6 mg/mL). Then, the mixture was sonicated via ultrasonic probe for 1 h at 60% amplitude. Then, the dispersion was centrifuged at 4.5 krpm for 1.5 h. The top 85% of the dispersion (supernatant) was discarded and the sediment was re-dispersed in fresh aqueous surfactant solution for 5 h at 60% amplitude. Centrifugation cascade with increasing rotation speeds was used in order to separate graphene flakes by size. Next, 1.5 krpm, 7.5 krpm and 10 krpm rotation speeds were applied respectively. After the final centrifuge step, (10 krpm), the dispersion was separated into two parts: 85% of the final dispersion was taken aside for later use with the name of S1_Su and the sediment was re-dispersed in a water-sodium cholate solution, labelled as S1_Se. The supernatant and sediment were collected and set aside for further analysis.
2.1.2.2 Preparation of Graphene Based Membranes

In all membrane fabrication processes, a dead-end filtration cell (Fig. 2.5) was used to deposit the exfoliated graphene dispersion onto the support membrane with the stirrer on mode (300 rpm) under a certain pressure, mainly less than 1 bar. Dead-end filtration\(^{265, 266}\) is known as the most basic form of filtration where fluid flow is applied perpendicular to the membrane surface. The fluid is forced through membrane by a certain pressure and the retained particles are accumulated with time on the surface of the membrane. In this filtration, stirring is typically used in order to decrease polarization effects.

**Figure 2.5** Image (a) and schematic (b) of dead-end filtration cell with a 9.07 cm\(^2\) filtration area. Stirrer is on a mode set at 300 rpm during graphene coating in each experiment.
A series of experiments were done in order to understand the working mechanism of the support membranes and graphene composite membranes. The fabrication process consisted of various preparation conditions with diverse parameters such as using the graphene dispersion as a coating solution with or without dilution before filtration, surface pre-treatment via polymer PEI and using cross-linker to increase selectivity. Basically, the fabrication process can be divided into two sections: only graphene (G) composite membrane (Fig. 2.6a) and layer by layer graphene composite membranes. Graphene layers forms in between two PEI layers like a sandwich model (Fig. 2.6b) or graphene flakes and cross linker forms a chemical bond and then they form a selective layer in between two PEI layers (Fig. 2.6c).

![Schematic diagram of (a) graphene/support membrane, (b) (PEI/G/PEI)/support membrane (c) (PEI/G+EDA/PEI)/support membrane.](image)

Key aspects of membrane fabrication pathways are briefly summarized in `Table 2.2`. Main differences between the procedures are listed according to the presence of surface treatment, using diluted or undiluted graphene dispersion as deposition solution, cross linker and applied pressure during deposition.

<table>
<thead>
<tr>
<th>Procedure Name</th>
<th>Membrane Surface Treatment</th>
<th>Dispersion Dilution</th>
<th>Cross Linker</th>
<th>Filtration</th>
<th>Drying Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>P.1</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>0.5 bar</td>
<td>Vacuum oven</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.8 bar</td>
<td></td>
</tr>
<tr>
<td>P.2</td>
<td>No</td>
<td>2 µg/mL - 0.2 µg/mL</td>
<td>No</td>
<td>0.5 bar</td>
<td>Vacuum oven</td>
</tr>
<tr>
<td>P.3</td>
<td>2 layers of PEI</td>
<td>5 µg/mL</td>
<td>No</td>
<td>0.2 bar</td>
<td>Vacuum oven</td>
</tr>
<tr>
<td>P.4</td>
<td>2 layers of PEI</td>
<td>5 µg/mL</td>
<td>EDA</td>
<td>0.2 bar</td>
<td>Vacuum oven</td>
</tr>
</tbody>
</table>
As shown in Fig. 2.7 any surface treatment was not applied to the support membrane before graphene coating. It was only washed with water and ethanol several times before starting graphene deposition in order to remove unbonded polymeric residuals. Then, a certain amount of graphene dispersion (varies from 3 mL to 7 mL) without any dilution was filtrated through support membrane (Nylon 0.2/Nylon 0.45 and PTFE 0.2) under 0.5 and 0.8 bar pressure via stirrer on the dead end filtration cell. Filtration continued until no liquid observed on membrane surface. Afterwards, wet membranes were dried in vacuum oven at 40 °C until the membranes were completely free of solvent. In procedure 2 (as can be seen in Fig. 2.7), the graphene dispersion was diluted up to 2 µg/mL - 0.2 µg/mL before starting the graphene deposition process to allow the graphene flakes enough time to make defect-free selective layer on support. The rest of the parameters were the kept same as it was as in procedure 1.

Figure 2.7 Schematic of the graphene composite membrane fabrication via procedure 1 (undiluted graphene dispersion) and Procedure 2 (diluted graphene dispersion).

Figure 2.8 Schematic of the graphene-polymer hybrid membrane fabrication via procedure 3.
In procedure 3 as shown in Fig. 2.8, firstly, in order to have a strong bond between support membrane and graphene flakes (due to negatively charged nature of the support membrane) and also increase membrane selectivity, the support membranes were coated with a positively charge polymer polyethyleneimine (PEI). Various protocols in terms of medium temperature, time and PEI's concentration were tried to analyse the effect of each set of conditions on membrane selectivity. So, from all experiments 3 mg/mL of PEI solution at 70 °C for 30 min was chosen as the reference protocol for further experiments. Secondly, a certain amount of diluted graphene dispersion (0.0052 mg/mL) was filtrated through PEI modified support membrane. After completing the graphene deposition, the wet membranes were immediately dried at 50 °C for 2 hours to improve the strength of graphene and PEI. Next, another PEI coating (with the same protocol mentioned above) was applied to prepared modified membrane followed by drying in a vacuum oven 50 °C for 1 hour. Then, composite membranes were soaked in water overnight to remove unbonded PEI before doing filtration experiments.

![Diagram](image_url)

**Figure 2.9** Schematic of the graphene-polymer hybrid membrane fabrication via procedure 4.

In procedure 4 as shown in Fig. 2.9, cross linker was used differently here from other fabrication procedures with the aim of enhancing the stability of graphene layers and stacking quality. All steps were the same as described in procedure 3 (Fig. 2.8), except a type of cross-linker, the monomer ethylenediamine (EDA) was mixed with graphene dispersion in a certain wt% ratio to introduce covalent bonds between graphene and EDA. Then this mixture was filtrated through PEI modified support membranes. Various mixing ratios were tried in order to find the best working conditions. G:EDA ratios wt/wt were 1:15, 1:1200; 1:15000. It is significant that enough reaction time is given to the graphene-EDA mixture. So, there are two reaction time parameters which have been used in this work, 7 h and 1 h.
After the reaction time had completed, the mixture was filtrated through a PEI modified membrane.

### 2.1.2.3 Experimental Work of Forward Osmosis Test

Two osmometer apparatus were used in this research. The first, shown in Fig. 2.10, apparatus tested was a PASCO Scientific Diffusion/Osmosis U-shaped osmometer which is specifically designed for osmosis experimentation. It consists of two separate graduated cylinders secured by four screw pins and bolts. The membrane support section, shown in Fig. 2.10c, contains a 19 mm hole over which the membrane is secured carefully. The o-rings aim to ensure a water tight seal around the membrane. The membrane was sealed between the two graduated cylinders, exposed screws and bolts ensure against any pressure leaks during testing.

![Forward osmosis U-tube test apparatus](image)

**Figure 2.10** Forward osmosis U-tube test apparatus (a), membrane unit together with graphene membrane in two orientations (AL-DS and AL-FS) (b) and schematic of test system (c,d).

The second test system, shown in Fig. 2.11, was a forward osmosis unit which consists of cross flow custom-built cell had an effective membrane area of 9.6 cm² on both sides of the membrane. The system was operated with a peristaltic pump (Cole Parmer) which were used in order to circulate feed and draw solutions in closed loop at a cross flow velocity of 80 cm/s. Using pump in such systems are beneficial in terms of reduced concentration polarization occurred near membrane surface. Water baths were used to control the temperature at 25°C. The volume of draw and feed solution were kept equal in both test systems. For the cross-flow test system, 300 mL of draw solution, and the feed solution container were placed on a digital scale (Precisa, XB 2200C) to measure the weight change at a certain time period.
For U-tube, about 40 mL of feed and draw solution were placed on both sides. Measurements were taken of the changes in liquid column height and volume over time.

**Figure 2.11** Schematic of cross cell FO test system.

There are two possible orientations in FO characterization that can be used to operate the system, i.e. active layer (graphene coated side) is facing with the draw solution and the active layer is facing with the feed solution. In this work, various molecular weight of polyacrylic acid sodium salt (PAA-Na) were chosen as the draw solute for FO experiments since it meets many essential criteria for the ideal draw solute for such systems. Commercially available PAA-Na molecular weights of 5 kDa, 8 kDa and 30 kDa were provided from Sigma Aldrich and dissolved in water with a certain concentration to use it later as draw solution. In order to keep constant pH of both draw and feed solutions, the pH value of each draw solution was adjusted to pH ~8 by carefully adding HCl or NaOH until the desired pH was achieved.

The water flux measurement was done by carefully monitoring volume change in feed solution. Regarding to reverse solute leakage transported from draw side to feed side, a certain volume of sample was taken out from feed for total organic carbon (TOC) analyser which was replaced with the same amount of fresh water. The amount of the sample removed was around 150 mL (half) since large volume change causes only small stepwise changes in terms of osmotic driving force which can be considered very well because the concentration of the solution is measured and it is known that at the moment, pure water is replaced with the sample removed so by that, the solution is again diluted to some extent but that is also something measurable later on. The net driving force was estimated from the calculated osmotic pressure difference between feed and draw solutions at a specific time.
during FO run and changes during course of experiment (appendices, Fig. 5A.26 - Fig. 5A.38) were calculated by dividing water flux and reverse solute flux to net driving force.

2.1.3 Characterization Techniques

2.1.3.1 Dispersion Characterization Techniques

To characterize exfoliated graphene in various solvents, various characterization tools were adopted in this study and those are summarized in Table 2.3. More detailed information for membrane characterizations can be found in the following part.

Table 2.3 Summary of exfoliated dispersion techniques.

<table>
<thead>
<tr>
<th>Key Parameter</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorbance, Concentration</td>
<td>UV Visible spectrophotometer (Varian Carry 50)</td>
</tr>
<tr>
<td>Particle size, hydrodynamic radius</td>
<td>Dynamic light scattering (DLS, Particle Metrix, ZetaSizer)</td>
</tr>
<tr>
<td>Elemental composition</td>
<td>X-ray photoelectron Spectroscopy (XPS, Bruker D8 Advance with Cu-Kα)</td>
</tr>
<tr>
<td>Flake length and thickness</td>
<td>Atomic force microscopy (AFM, Veeco Nanoscope-Illa, Digital Instruments)</td>
</tr>
<tr>
<td>Level of defect in exfoliated graphene</td>
<td>Raman spectroscopy (WITec Alpha 300R)</td>
</tr>
<tr>
<td>Shape, lateral dimension and thickness</td>
<td>Transmission electron microscopy (TEM, JEOL 2100)</td>
</tr>
</tbody>
</table>

2.1.3.1.1 UV-Vis Spectroscopy

For liquid phase exfoliation technique, ultrasonic bath (Elmasonic Transsonic, TI-H-10) and ultrasonic probe (Sonopuls HD 2200 ultrasonic laboratory homogenizer, Bandelin) were used in order to exfoliate the graphite with relevant solvents to produce graphene. The absorbance spectrum of graphene dispersions were performed via Varian Carry 50 UV Visible spectrophotometer using a glass cell with 1 cm length. Characteristic absorption spectra of exfoliated graphene dispersion were employed by using UV – vis spectroscopy. The absorbance at 660 nm wavelength was recorded in order to calculate the concentration of each dispersion. Dispersion were diluted with related solvents (i.e. NMP, ethanol or water) before measurement in order to eliminate possible errors due to high concentration.
2.1.3.1.2 Dynamic Light Scattering

The hydrodynamic particle size of graphene flakes was analysed by dynamic light scattering (DLS, Particle Metrix, Zeta Sizer). Dilution of solution is a critical tool in order to make a reasonable DLS measurement and obtain correct size. So, graphene dispersions were diluted to about 5 μg/mL beforehand and shake very well in order to make sure there was no aggregation in the solution. Then, measurements were employed in 3 runs which took 60 seconds each sequentially without non-stop. Hence, the average particle size was calculated as an averaged value of those three runs. The refractive index of graphite and viscosity values at certain temperature of solvents are necessary for this measurement and this information was added to the software as provided from the provider company.

Figure 2.12 Image of UV – Vis spectroscopy to measure absorbance spectra of exfoliated graphene.

Figure 2.13 Image of dynamic light scattering (DLS) to analyse particle size of graphene flakes.
2.1.3.1.3 **X-ray Photoelectron Spectroscopy (XPS)**

In order to characterize chemical composition of the graphene dispersion, X-ray photoelectron Spectroscopy (XPS) was employed with a VersaProbe II by Ulvac-Phi; Photon line: monochromatic Al-k alpha at 1486.6 eV; charge compensation using electron flood gun and Ar Ion-gun; beam diameter 100µm). In terms of sample preparation, a droplet on a Si wafer was dropped and let it lie for 1 1/2h and then the remaining droplet was dried by inserting it into vacuum. An SXI of a promising measurement position was recorded. An evaluation of the Auger C KLL line in terms of sp2 hybridization was not possible, because a possible graphite like signal is superimposed by the remaining NMP and C contamination auger signal.

2.1.3.1.4 **Atomic Force Microscopy**

Atomic force microscopy (AFM) analysis was carried out with a Veeco Nanoscope-Illa (Digital Instruments) in tapping mode after depositing a certain amount of diluted graphene dispersion (20 µL) onto pre-heated at 150 °C cleaned silicon wafer which was washed with ethanol, isopropanol and water beforehand.

2.1.3.1.5 **Raman Spectroscopy**

Raman spectra were performed by a spectrometer WITec Alpha 300R with 532 nm and 633 nm excitation lasers with a spectral grating of 1800 lines/mm and a 100× microscope objective (0.95 N.A., spot size ~0.3 µm) after depositing a certain amount of diluted graphene dispersion (20 µL) onto pre-heated at 150 °C cleaned silicon wafer which was washed with ethanol, isopropanol and water beforehand. Raman spectra for each graphene dispersions was formed by taking average of individual spectra from 10 different spots on each sample. The individual spectra have been normalized and stacked on top of each other.

2.1.3.1.6 **Transmission Electron Microscopy**

Transmission electron microscopy (TEM) analysis was performed using a JEOL 2100 at 200kV. The diluted dispersion was dropped onto pre-heated holey carbon (400 mesh) grids and let it dry in a vacuum to evaporate excess solvent.

2.1.3.2 **Membrane Characterization Techniques**

Various characterization techniques were used in order to analyze porous support membrane and graphene composite membranes. These methods are summarized in Table 2.4. More detailed information for the techniques of membrane characterization can be found in the following part.
Table 2.4 Summary of membrane characterization techniques.

<table>
<thead>
<tr>
<th>Key Parameter</th>
<th>Instrument</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface hydrophilicity/hydrophobicity</td>
<td>Contact angle measurement (OCA20 contact angles system, Data physics Co., Germany)</td>
</tr>
<tr>
<td>Inter layer spacing (d-spacing)</td>
<td>X-ray diffraction (Bruker D8 Advance with Cu-Ka)</td>
</tr>
<tr>
<td>Pore size measurement</td>
<td>Gas Flow/Pore De-wetting Permporometry (PMI, Porous Materials Inc.)</td>
</tr>
<tr>
<td>Membrane surface morphology</td>
<td>Scanning electron microscopy (SEM, Apreo-S by Thermo Fischer)</td>
</tr>
<tr>
<td>Chemical properties</td>
<td>Fourier transform infrared spectroscopy (FTIR, Bruker ALPHA-Platinum)</td>
</tr>
<tr>
<td>Surface charge properties</td>
<td>Zeta Potential measurement device (Anton Paar)</td>
</tr>
<tr>
<td>Membrane Performance</td>
<td>Permeability and Rejection Experiments (Dead End Cell, Sterlitech)</td>
</tr>
<tr>
<td>Water flux and reverse solute flux</td>
<td>Forward Osmosis Experiments (Setup 1:FO Unit; Setup 2: U-Tube)</td>
</tr>
</tbody>
</table>

2.1.3.2.1 Contact Angle

In order to study membrane wettability, water contact angles of graphene composite membranes were detected using an OCA20 contact angles system (Data physics Co., Germany). Samples were dried in a vacuum oven at 40°C before starting the measurement. Sessile drop was chosen as the measurement method in the software. Water was dropped onto the membrane surface with the help of a micro-syringe with a stainless steel needle. The software was adjusted accordingly, and the water contact angle was recorded just after the water droplet had met with the surface of membrane. An average value of at least three measurements from different locations on each membrane surface was calculated at the contact angle of the membrane to be analysed.
Figure 2.14 Image of contact angle system.

2.1.3.2.2 X-ray Diffraction

X-ray diffraction (Bruker D8 Advance with Cu-Ka) was measured in order to obtain d-spacing in both dry and wet phases (immerse membrane 2 h in water) of the composite membranes. All samples were fixed on a Si single crystal sample holder to avoid undesirable scattering. The average crystallite size can be calculated according to the Scherrer formula as shown in Eq. 1.21:

\[ L = \frac{K\lambda}{\beta \cos \theta} \]  

(1.21)

where \( \lambda \) is the X-ray wavelength in nanometre (Cu ka, 1.54056 Å), \( \beta \) is the peak width of the diffraction peak profile at half maximum height (FWHM in radian) and \( K \) is a constant (~0.89) which is related to crystallite shape, \( \theta \) is the diffraction angle.

2.1.3.2.3 Gas Flow/Pore De-wetting Permporometry

Pore size determination of graphene composite membranes were performed by a capillary flow porometer (Capillary flow porometer, CFP-34RTG8A-X-6-LA, Porous Materials Inc., Germany). Pore sizes can be measured by this method in the range of 0.013 – 500 microns. Required sample size is in between 12-60 mm diameter. Pore size was specified by analysing samples via dry up/wet up mode using a wetting agent called ‘galwick’ which has a surface tension 16 mJ/m². N₂ in the range of 0 to 20 bar was used as gas feed for the gas flow (L/min) measurement in dry membrane.

Capillary flow porometer analysis consist of mainly two parts including measurement of gas flow through pores in dry and wet membranes. The second part is just a de-wetting experiment where wetting liquid fills the pores in the membrane. Gas flow is replaced with the liquid from the pores by gas pressure applied. So, gas flow is used as an indicator to
determine which pressure the liquid is expelled from the pore and flow through the empty pores. That is transferred into pores size distribution. The differential pressure which is essential to extrude a pore is related to the diameter of the pore, as shown in Eq. (1.22)[268]

\[ D = 4.\gamma.\cos\theta/p \]  

(1.22)

where \( \gamma \) is the surface tension of wetting liquid, \( \theta \) is the contact angle and \( p \) is the differential pressure across the pore. Gas flow rates through dry and wet samples are measured as a function of differential pressure to figure out the pore diameter.

**Figure 2.15** Capillary flow porometer to analyze pore diameter of membranes.

### 2.1.3.2.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM, Apreo-S by Thermo Fischer) was employed to observe the surface morphology of composite membranes before or after filtration characterization by analysing cross section and top morphologies of the membranes. The SEM was performed at voltage of 5 kV and 10 mm working distance.

### 2.1.3.2.5 Fourier Transform Infrared Spectroscopy

Fourier transform infrared via FTIR, Bruker ALPHA-Platinum equipped with a diamond was used for chemical structural identification of functional groups in membranes.

### 2.1.3.2.6 Zeta Potential

The surface charge properties of composite membranes were employed by using a Zeta Potential measurement device (Anton Paar).

### 2.1.3.2.7 Porosity (%)

The membrane porosity (\( \varepsilon \)) of unmodified support membranes (Nylon, PTFE, PES) and graphene composite membranes was determined via gravimetric analysis using Eq. 1.15 given the density of water (\( \rho_w=1.00 \) g cm\(^{-3} \)) and each polymers (\( \rho_p \)). Dried samples were initially weighed (\( m_2 \), g) then were soaked in a wetting agent, known as ‘Galwick’ for 24 h at
30°C. Residual galwick was removed and then the wet samples were re-weighed ($m_1$, g).
Reported results are average values of at least five measurements.

2.1.3.2.8 **Membrane Performance Evaluation**

In order to measure the concentration of polyacrylic acid sodium salt (PAA-Na) and dextran solutions, a total organic carbon (TOC) analyser (ASI-V, SHIMATZU) was used. Conductivity measurement (SI Analytics Lab 865, Germany) was employed to calculate salt ion rejection.
CHAPTER 3

EXFOLIATED GRAPHENE DISPERSION IN VARIOUS SOLVENTS
EXFOLIATED GRAPHENE DISPERSION IN VARIOUS SOLVENTS

3.1 Introduction

What makes a good graphene dispersion favourable for this work’s aim?

Graphene has been known as a wonder material since it was isolated in 2004\cite{15} as many amazing properties have been revealed in terms of mobility\cite{269}, thermal conductivity\cite{270}, thickness\cite{271}, strength\cite{272} etc. Considering the feasibility of finding all these extraordinary characteristics in a single material, a tremendous interest has been attracted all over the world by researchers. Graphite is known as a crystalline layered structure. Each layer of graphite is a 2D carbon monolayer which consists of sp2-hybridised, hexagonally bonded carbon atoms. Each such layer constitutes graphene. Graphite can be defined as a stacked entity comprising of graphene sheets held together by the van der Waals forces between the π–π stacked graphene layers, which have an interlayer spacing of 0.34 nm\cite{273, 274}. Detailed information about the fabrication methods of graphene and its properties have been discussed in Chapter 1.

Key factors to create a good graphene dispersion for membrane separation field;

1. Surface energy and Hansen solubility parameters are the most discussed topics in terms of solvent interaction with graphite. An ideal solvent is necessary to overcome the van der Waals attractions between the adjacent layers of graphite (held in π–π stacking with a distance of 0.34 nm\cite{94}) and make graphite dispersible in relevant solvent to form pure graphene. A suitable solvent helps to minimize interfacial tension which is defined as the force of attraction between molecules at the interface\cite{273} of the solvent and graphite. This is critically discussed in the field of colloid science\cite{276}. In the case of a high interfacial tension, flakes have a tendency to adhere and hinder the dispersion in solvent. This will cause poor dispersibility of the graphite in the relevant solvent\cite{277, 278}. Together with knowing the importance of surface energy, a remarkable amount of research works started to search for possible solvents which have a surface tension close to or matching graphite. It was reported that solvents which have surface tension in the region of ~40 – 50 mJ m\(^{-2}\)\cite{81} are accepted as suitable candidates to disperse graphite (~70 – 80 mJ m\(^{-2}\)). In the current work, three different solvents were used, NMP (~40 mJ m\(^{-2}\))\cite{278}, ethanol (~22.1 mJ
m$^{-2}$) and water-surfactant (~72 mJ m$^{-2}$ pure water$^{[277]}$). NMP like most of organic solvents is a suitable solvent for graphene but has a high boiling point which makes it difficult to work with in terms of removing the solvent from the membrane surface or exfoliated graphene afterwards. In that case, ethanol as a low boiling point solvent might be an alternative due to being easy to remove, eco-friendly and not as toxic as NMP which is preferable. Due to its surface tension and final concentration, the capacity of graphene dispersibility will be so low in the case of using ethanol as a solvent, that it may be insufficient for the mass production of graphene.

Reported concentration of graphene dispersed in pure ethanol or ethanol water mixtures is in the range of 0.002 to 0.014 mg/mL$^{[110, 111]}$. In current work, that is the exact reason salt was used as intercalator to increase the efficiency of ethanol. Furthermore, van der Waals forces can be weakened by this way. For instance, by using an intercalator like an organic salt (KNaC$_4$H$_7$O$_6$) to increase interlayer spacing of graphite up to 5 Å according to reported research$^{[93, 279]}$. Moreover, using water as a dispersant would not be possible due to the hydrophobic nature of graphite and water’s surface tension is too high. In that case, to stabilize the flakes and help to decrease water’s surface tension to match with that of graphene$^{[273]}$, linear chain surfactants i.e. sodium cholate$^{[280]}$ can be used to prevent re-aggregation caused by Coulomb repulsion$^{[278]}$.

2. One should carefully consider controlling internal and external parameters of the fabrication procedure (liquid phase exfoliation technique) i.e., sonication time, centrifuge speed etc. in order to have defect free pure graphene with consists of thin flakes (not more than a few layers, preferably). It has been reported$^{[82]}$ that the final concentration of graphene after centrifugation depends on sonication time, increasing sonication time leads to increased concentration ($C_G$ ∝ $t^{1/2}$) and also decreased the graphene flake sizes ($\propto t^{-1/2}$). However, increased sonication time will create disorder related D peak which is an indication of the quality of graphene$^{[281]}$. Two types of sonication called ultrasonic bath (45kHz, 4-5 h) and ultrasonic probe (60% amplitude, 2-6 h) were used to generate mono or few layer graphene sheets. The graphene structure is broken by the ultrasound waves and resulted in graphitic carbon fragments in different sizes. Sufficient energy is required to exfoliate graphite and allow solvent to intercalate between graphitic layers. Introduced damage can be decreased by the optimizing the sonication time. It has been noted that sonication might also cause damage to graphene. So, it is essential to
adjust sonication time accordingly to conserve graphene’s structural integrity. In order to reduce sonication time, an appropriate solvent should be chosen to achieve graphene dispersion with high efficiency\textsuperscript{282}. Defects can also be found in the form of oxidized carbon atoms at the layer edges\textsuperscript{283}. Centrifugal rotational speed is another important factor that has an effect on dispersion quality. It is feasible to have very thin flakes by carefully adjusting and optimizing the speed at high centrifuge rates \textsuperscript{71}.

In this chapter, exfoliated graphene dispersed in NMP, ethanol and water-surfactant under various experimental conditions were examined and characterized by various characterization techniques like UV-Vis spectroscopy, DLS, Raman spectroscopy, AFM, TEM and XPS in order to study the quality of the obtained graphene flakes which were used later for making graphene based membranes.

\section*{3.2 Results and Discussion}

\subsection*{3.2.1 UV – Vis Spectroscopy}

UV-vis spectroscopy of dispersions were recorded just after completing dispersion preparation process. When a sample is radiated with a light which has an energy that matches electronic transition within the sample, some of the light energy is absorbed by the sample since the electron is excited to a higher energy orbital. Wavelengths are recorded by UV-Vis spectroscopy at which absorption takes place. The resulting spectrum is plotted as a graph of absorbance versus wavelength.

Fig. 3.1 displays the absorption spectra of graphene dispersions exfoliated in three solvents; NMP, ethanol and water-surfactant based aqueous systems. In order to make a reasonable comparison, the spectra were obtained under identical conditions which include waiting time of each dispersion for the UV-vis measurement (all were done just after the dispersion completed), dilution by the same factor etc. The measurement was performed in the between 230 to 800 nm wavelength range for ethanol and water-surfactant mixture. However, in the case of solvent NMP this situation was not valid as the characteristic peak at around $\geq 265$ nm for such aromatic conjugated systems does not appears due to strong NMP interference at such small wavelengths which makes compensation even harder\textsuperscript{284}. It might also be possible that the purity of the solvent was not the same because the spectrometer was not able to distinguish between graphene-NMP and pure NMP.
Figure 3.1. UV-vis absorption spectra of graphene dispersions exfoliated in different solvents (A). As mentioned in experimental work section, N1, N2 and N3 are graphene dispersions in NMP; E1 and E2 are graphene dispersions in ethanol; S1 is graphene dispersion surfactant assisted, sediment and supernatant part of the dispersion. Spectra of graphene dispersion in ethanol (E1, E2) and in aqueous surfactant (sodium cholate) (S1_Se, S1_Su) is enlarged in (B) to identify maximum absorbance peak.

Conjugation is defined\cite{285} as the connection of one pi-orbital (\(\pi\)) with another across a sigma (\(\sigma\)) bond. A region of overlapping p-orbitals can be found in a conjugated system which permits a delocalization of pi electrons across the adjacent pi-orbitals. Graphene and graphite are known as one of the largest conjugated systems. In a UV-Vis absorption spectra, there are two characteristic fingerprints for such aromatic conjugated systems which can be a significant tool to identify material. As graphene is a conjugated aromatic structure we can expect to see a maximum peak at around 267 nm, which is consistent with the literature that suggests maximum peak or such conjugated material in between 260-270 nm\cite{286, 287}, corresponding to the \(\pi\rightarrow\pi^*\) transition of aromatic C-C bonds. The \(\pi\rightarrow\pi^*\) excitation\cite{288} happens from the highest energy bonding pi-orbital (HOMO, the highest occupied molecular orbital) to the lowest energy antibonding pi-orbital (LUMO, the lowest occupied molecular orbital). So, the maximum peak is clearly visible for graphene dispersed in ethanol (E1 and E2) and water-surfactant (S1_Se and S1_Su) as can be seen in Fig. 3.1b. This result, together with the presence of strong absorbance at around 267 nm, is consistent with the dispersions being constituted by graphitic objects. Moreover, this high intensity in that very long range of wavelengths is also a characteristic for extended conjugated systems\cite{289}. 
Another important aspect is to have a featureless spectrum with a decrease in intensity at high wavelengths \(^{290}\) in the visible region. In a typical GO dispersions\(^{291}\), a peak around 300 nm can be found due to the n- \(\pi^*\) transition of C=O bonds. In all dispersion here, this peak is not present which might be an indication that the exfoliated graphene dispersions are not oxidized.

**Table 3.1.** Effects of different factors (i.e. solvent, centrifuge speeds) on the yield of graphene dispersions. Absorption coefficient, \(\alpha\) was taken as 3620 L\(g^{-1}\)m\(^{-1}\) \(^{82, 97}\) for NMP and ethanol-based dispersions and 1390 L\(g^{-1}\)m\(^{-1}\) \(^{127, 292}\) for water-surfactant dispersion. Concentration was calculated from the Lambert-Beer equation.

<table>
<thead>
<tr>
<th>Dispersion Name</th>
<th>Initial Concentration [mg/mL]</th>
<th>Final Concentration [mg/mL]</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>5</td>
<td>0.36</td>
<td>7.2</td>
</tr>
<tr>
<td>N2</td>
<td>5</td>
<td>0.16</td>
<td>3.2</td>
</tr>
<tr>
<td>N3</td>
<td>5</td>
<td>0.101</td>
<td>2</td>
</tr>
<tr>
<td>E1</td>
<td>10</td>
<td>0.08</td>
<td>0.8</td>
</tr>
<tr>
<td>E2</td>
<td>10</td>
<td>0.035</td>
<td>0.35</td>
</tr>
<tr>
<td>S1_Sc</td>
<td>20</td>
<td>0.027</td>
<td>0.14</td>
</tr>
<tr>
<td>S1_Su</td>
<td>20</td>
<td>0.058</td>
<td>0.3</td>
</tr>
</tbody>
</table>

To be able to analyse the dispersion efficiency in various conditions, optical absorption spectroscopy is a commonly used technique. \(^{81, 97, 123, 127}\) Table 3.1 shows the concentration change in mg/mL of each dispersion starting from initial concentration to final concentration after the last step of separation. It is worth mentioning here even though there are three different solvents, classification of dispersion procedures has been also done within itself based on exposure to further centrifugation or applied higher rotation speed. A detailed description was given in Chapter 2 in the preparation of graphene dispersions section. By looking at Table 3.1, it is safe to say that during preparation, quite a lot of material was lost due to the existence of the separation mechanism in the fabrication procedure. The dispersion yield is much higher in solvent NMP cases compared to other conditions. Within these agents, NMP has the best ability to disperse graphene from graphite. Increasing rotation speed from 1500 rpm (N1) to 4500 rpm (N2) caused lower yield due to the loss of carbon content after centrifugation process, yield decreased by almost 45%. So, it means most of the heavier graphitic like structures (unexfoliated) settled down and thinner light graphene flakes were left in the final dispersion. A second further centrifugation at 4500 rpm (N3) resulted in 2% yield with a final concentration 0.101 mg/mL. The dispersion method E1 was adopted from a previous work \(^{110}\) The idea behind this procedure was to use an organic salt (potassium sodium tartrate, KNaC\(_4\)H\(_4\)O\(_6\)) as an intercalator between graphitic
layers to increase the graphene exfoliation in low boiling point solvent ethanol. A few changes were made to the procedure and obtained concentration, 0.08 mg/mL was much higher than in previous work (0.062 mg/mL). This dispersion was centrifuged again at the same rotation speed (procedure E2) to improve the quality by removing possible unexfoliated materials and the final concentration decreased to 0.035 mg/mL.

**Figure 3.2.** Absorption coefficient spectra for graphene flakes dispersed in NMP and ethanol at concentrations from 2 to 35 µg/mL. Optical absorbance ($\lambda = 660$ nm) divided by cell length ($A/l$) as a function of concentration for graphene showing Lambert–Beer behaviour with an average absorption coefficient of 3786 and 3780 Lg$^{-1}$m$^{-1}$ for NMP and 3542 and 3520 Lg$^{-1}$m$^{-1}$ for ethanol. The data was converted from absorbance (660 nm) using the formula $A/l = (\lambda_{660})C$.

Mass transport experiments were conducted in order to compare literature-based extinction coefficient with this work's extinction coefficient. A certain volume of graphene dispersion was filtrated through porous membrane using a dead end filtration cell. Then, the membrane was dried until all the solvent evaporated from the membranes. Afterward, filtered mass was carefully weighed by using a microbalance. So, the final concentration of dispersions (N1,N2,E1,E2) after fabrication procedure were calculated based on measured filtered masses in each case. Then, the dispersions were diluted and the absorbance spectrum was analysed separately. In Fig. 3.2, concentration versus absorbance/cell length was plotted accordingly. As can be seen from the graph, extinction coefficients found in NMP and ethanol cases, approximately 3700 Lg$^{-1}$m$^{-1}$ and 3500 Lg$^{-1}$m$^{-1}$ respectively, are quite close to the literature-based value 3620 Lg$^{-1}$m$^{-1}$. Previous work in literature was estimated as 3780 Lg$^{-1}$m$^{-1}$ which is very similar with this current work$^{(293)}$. 
3.2.2 Dynamic Light Scattering

Dynamic light scattering (DLS) is a simple and fast characterization technique\cite{162} used to analyse the particle size of graphene by calculating the hydrodynamic diameter. Basically, a laser is tracking how fast particles move in a solution. Brownian motion, which means the random movement of particles in the solution, was measured by DLS. The technique is directly related to the diffusion coefficient of the particles in the solution which is converted to particle size by using the Stokes-Einstein equation \cite{294, 295}. Also note that DLS might be a reliable tool for spherical particles than non-spherical particles\cite{296} since the sphere is the only shape which can be described by one number (the diameter of the sphere) \cite{297}. Nonetheless, it is clear that we now have flat, 2D graphene flakes rather than spherical particles. We should take this situation into consideration this situation while making interpretations of particle size from data gathered by DLS. So, for non-spherical particles, DLS gives the diameter of a sphere that moves (diffuses) the same way as relevant sample.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.3.png}
\caption{Hydrodynamic size distribution (number based) of graphene dispersions in NMP (A), in ethanol (B) and in aqueous sodium cholate (C). Measurements were recorded with diluted graphene dispersions (5 \(\mu\)g/mL).}
\end{figure}
Scattered light is recorded by the software to analyse the particle movement in the solution. Scattered light intensity will oscillate over time according to the size of the particles. For instance, the existence of small particles in the solution, since they are moving quickly at high speeds, creates more rapid fluctuations than for larger particles and faster decay of the correlation function which is used to determine translational diffusion coefficient. Particle size distributions can be plotted in several ways such as number, intensity and volume-based distributions. All graphs in Fig. 3.3 were plotted in a number-based particle hydrodynamic size distribution. DLS is a highly sensitive technique in terms of sample preparation which requires adjustment of an optimal concentration for the sample to be analysed in DLS. Otherwise, low concentrations will result in not having enough light scattering and high concentrations might create multiple scattering which affects particle size.

By analysing optical absorbance spectra, we concluded that the separation mechanism by centrifugation in different procedures led to lower concentrations of graphene dispersions due to the loss of carbon content in each step. Furthermore, DLS data now suggests that different preparation methods made a difference with respect to particle size which is a reasonable expectation.

For graphene dispersed in NMP, 25% of flakes in the N1 dispersion have an average particle size around 170 nm. Flake size distribution can be observed mostly in between 144 nm – 243 nm (75%). There are a small number of flakes (12.7%) is in the range of 289 nm – 486 nm. In the case of dispersion N2, the same sonication type and energy was applied to the dispersion but a higher rotational speed (4500 rpm) was applied compared to dispersion N1 (1500 rpm). The results revealed that a remarkable amount of flakes in the dispersion (80%) have a narrow size distribution in the range of 51 nm – 86 nm and showed a peak at around 60 nm with 25%. This result is in line with the expectation that higher speeds separate the large particles out, leaving small sized flakes in the dispersion. Further centrifugation at 4500 rpm of the dispersion N2, which makes dispersion N3, resulted in much smaller flakes with a narrow distribution. Mainly, 76% of the flakes are in the size range of 25 nm – 51 nm and provided a peak at 30 nm (33% flakes). The remaining of 23% can be found in between 60 nm – 120 nm.

Overall, it could be concluded that by increasing rotation speed from 1500 rpm to 4500 rpm (N1-N2), and also exposing the dispersion to a further second centrifugation (N2-N3), resulted in obtaining a graphene dispersion with small flakes and a narrow size distribution.
In ethanol-based dispersions, sonic bath was used in both dispersions instead of a sonic probe. Dispersion E1 was fabricated via 4 hr sonic bath and then centrifuged at 3000 rpm. DLS results showed that 73% of the flake sizes are between 144 nm – 289 nm and the average particle size is peaked at 144 nm (18%). However, it is clear that compared to NMP based dispersions, there is a broader size distribution with 27% of the flakes is in between 344 nm – 818 nm. A further centrifugation, E2, gave a dispersion with the distribution of the flakes mostly in the range of 86 nm – 204 nm (81%) and 243 nm – 409 nm (19%), which is peaked at 121 nm (20%).

In the case of an aqueous graphene dispersion (S1), the supernatant part of the dispersion (Si_Su) has the smallest flake size, around 21 nm (55%), with a very narrow size distribution, 98% of the flakes are in between 18 nm – 30 nm while the sediment part (S1_Se) has a relatively broader size distribution, ranging from 25 nm to 121 nm. This indicated that thin small flakes could be found in the upper part of the dispersion whilst large thick flakes are in the sediment.

It can be noted that using an ultrasonic probe or bath has a significant effect on flake size, higher energy via sonic probe improved the exfoliation efficiency and reduced the size. Same result was observed in NMP based dispersions, further centrifugation provided a better dispersion in terms of a narrow size distribution and flake sizes shifted to small values. By looking at the results of ethanol based graphene dispersions (E1 and E2), it is obvious (referred to UV-Vis spectroscopy and DLS) that the dispersibility of ethanol is not as efficient as that of NMP. This is because NMP is a well suited solvent for the requirement of surface energy based model[81, 298].

From all these, it can be clearly observed from the DLS results that increasing rotational speed and exposing further centrifugation did not only cause narrowing of the size distribution, but also reduced the flake size. This can be seen in the case of N1, N2, N3, E1 and E2. However, it is expected that centrifugation provides better separation with a narrow distribution rather than decreasing the particle size which results mainly from applying ultrasonic energy. The phenomenon can be explained by the Rayleigh Scattering[294] which gives a relationship between the intensity of the scattered light and particle diameter in nm as $I \propto d^6$. It indicates that for instance; a particle with 50 nm size will scatter a factor of $10^{10}$ light while 5 nm particle will scatter a factor of 1 million less than that. Thus, within a wide range of distributions, the contribution of large particles to the total scattered light will be much higher than that of small particles and the scattered light from the smaller flakes can be swamped by the light from larger particles. For example, in our case, the contribution of
small flakes to the scattered light became more pronounced by the increase of rotational speed and cycle of centrifuge exposure since the large particles are removed from the resultant dispersions.

Table 3.2. Average Polydispersity index (PDI) of each graphene dispersion.

<table>
<thead>
<tr>
<th>Dispersion Name</th>
<th>PDI by DLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>0.7 ± 0.02</td>
</tr>
<tr>
<td>N2</td>
<td>0.39 ± 0.01</td>
</tr>
<tr>
<td>N3</td>
<td>0.28 ± 0.08</td>
</tr>
<tr>
<td>E1</td>
<td>0.48 ± 0.34</td>
</tr>
<tr>
<td>E2</td>
<td>0.42 ± 0.2</td>
</tr>
<tr>
<td>S1_Se</td>
<td>0.13 ± 0.15</td>
</tr>
<tr>
<td>S1_Su</td>
<td>0.62 ± 0.41</td>
</tr>
</tbody>
</table>

It is required to minimize the polydispersity index (also known as heterogeneity index) which gives an information that the dispersion is monodisperse or polydisperse\cite{299, 300}. The term ‘polydispersity’ is used to define the non-uniformity degree of particle size distribution in a suspension\cite{301}. It is a dimensionless index and PDI values smaller than 0.05 are generally found in highly monodisperse standards. PDI values bigger than 0.7 show that the suspension has a very broad particle size distribution\cite{301}. These results confirmed that further centrifugation also led to smaller polydispersity index (PDI) and smaller hydrodynamic particle size (from N1 to N3 and from E1 to E2).

3.2.3 Raman Spectroscopy

Raman spectroscopy is a useful technique to study graphitic structures and to determine whether resultant dispersions are single-, bi- and few-layered graphene or bulk graphite.\cite{302} Fig. 3.4 shows Raman spectra of exfoliated graphene in various agents. There are two prominent features in a typical Raman spectrum of dispersed graphene; the G-band at around 1580 cm\(^{-1}\) indicates the existence of C=C sp\(^2\) carbon and the 2D-band at around 2700 cm\(^{-1}\)\cite{303-305}. However, it is possible that there might exist the D-band might exist which lies at around 1350 cm\(^{-1}\), which relates to the first order of zone-boundary phonons. Existence of the D-band in Raman spectra of exfoliated graphene is generally accepted as a measure of disorder which is attributed to edge/basal defects \cite{102, 292, 303, 306}. Furthermore, the 2D band (known also as second order of D peak) is caused by the second order of the two-phonon process and this remarkable peak can be used to estimate the number of layers by studying its position, shape and intensity \cite{307}. 

81
Figure 3.4 Raman spectra of graphene sheets in the dispersion. Disorder related $I_D/I_G$ value is calculated by dividing the intensity of D band to the intensity of G band. Graphene dispersion in NMP via procedure N1 (g), N2 (f) and N3 ©. Graphene dispersion in ethanol via procedure E1 (d) and ©(c). Graphene dispersion in ethanol via procedure E1(d) a©E2 (c). Graphene dispersion in aqueous sodium cholate via procedure S1_Se (b) and S1_Su (a).

The resultant Raman spectra mainly exhibits three major peaks (D, G and 2D peaks) which are clearly visible in all cases from a to g. As can be seen in Table 3.3 and Fig. 3.4, there are slight difference in peak positions, shapes and intensities.

Table 3.3. Raman spectra peaks of three characteristic bands D, G and 2D in each of the graphene dispersions.

<table>
<thead>
<tr>
<th>Dispersion Name</th>
<th>D [cm⁻¹]</th>
<th>G [cm⁻¹]</th>
<th>2D [cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>1349</td>
<td>1582</td>
<td>2701</td>
</tr>
<tr>
<td>N2</td>
<td>1348</td>
<td>1577</td>
<td>2688</td>
</tr>
<tr>
<td>N3</td>
<td>1340</td>
<td>1569</td>
<td>2681</td>
</tr>
<tr>
<td>E1</td>
<td>1344</td>
<td>1569</td>
<td>2688</td>
</tr>
<tr>
<td>E2</td>
<td>1340</td>
<td>1564</td>
<td>2681</td>
</tr>
<tr>
<td>S1_Se</td>
<td>1344</td>
<td>1577</td>
<td>2681</td>
</tr>
<tr>
<td>S1_Su</td>
<td>1344</td>
<td>1581</td>
<td>2681</td>
</tr>
<tr>
<td>Pristine graphite[^306]</td>
<td>1322</td>
<td>1567</td>
<td>2700</td>
</tr>
</tbody>
</table>
Table 3.4. Ratios of intensity and integrated area of D, G and 2D peaks.

<table>
<thead>
<tr>
<th>Dispersion Name</th>
<th>Intensity ratios</th>
<th>Area ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I_D/I_G</td>
<td>I_2D/I_G</td>
</tr>
<tr>
<td>N1</td>
<td>0.21</td>
<td>0.42</td>
</tr>
<tr>
<td>N2</td>
<td>0.43</td>
<td>0.22</td>
</tr>
<tr>
<td>N3</td>
<td>0.37</td>
<td>0.20</td>
</tr>
<tr>
<td>E1</td>
<td>0.50</td>
<td>0.37</td>
</tr>
<tr>
<td>E2</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>Se</td>
<td>0.74</td>
<td>0.40</td>
</tr>
<tr>
<td>Su</td>
<td>1.15</td>
<td>0.44</td>
</tr>
<tr>
<td>Graphite</td>
<td>0.06</td>
<td>0.31</td>
</tr>
</tbody>
</table>

There are various ways to get information about the degree of defects in a relevant sample. Either the relative intensity ratios of the D and G bands (I_D/I_G) or integrated area ratios of the D and G band (this is often labelled as A_D/A_G) can be used to estimate the degree of defects in carbon materials. Of course, the height and areas of the peaks are related so similar information can be obtained from each of these approaches. The one instance in which there would be an appreciable difference is in the case of very defective graphite/graphene where the peaks broaden significantly \[308, 309\]. It has been suggested in literature that the area ratio would be preferable in the case of small disorder while peak intensity and full width at half maximum (FWHM) would be preferable for large disorder\[310-312\].

In Table 3.4, data suggests that the relative intensity and integrated area ratio of the D and G peaks are very similar in both methods, little difference was observed. However, the integrated area ratio of 2D and G peaks are quite different from the intensity ones, specifically in sample N1 (NMP based dispersion). However, this should not be paid much more attention. Because, when the quality of the dispersions from N1 to N3 and E1 to E2, are increased then the value of the ratios decreased in both methods. In general, there was a clear trend of I_2D/I_G from 0.42 to 0.2 and from 0.37 to 0.18, and this trend matched what it has been seen with the ratios of area method (A_2D/A_G). This can be a good additional confirmation for the existence of a systematic change of the layer thickness (number of the layers stacking together).

It is also significant to mention that D and G peaks are not adjacent but well-separated which differs from graphene oxide (GO), in which the peaks are overlap\[130\]. This result indicated that our graphene dispersion was not effected by severe in-plane disruption such as GO \[313\].

Regarding 2D band, there is some ambiguity associated with the 2D/G ratio using either the heights or the areas ratios. Note that 2D band intensity and position can be varied with excitation laser frequency\[307\], doping\[314\] and defects\[315\]. It would also be more informative
to look at the shape of the 2D band to determine the number of graphene layers. The
intensity ratios, \(I_{2D}/I_G\), are expected to be around \(\sim 2\) for a single layer, \(\sim 1\) for a bi-layer
and less than \(1\) for multi-layer graphene \[306\].

From the 2D band intensities and shape (mostly broad except sample N1) there is nothing to
suggest that material thinner than \(\sim 5\) layers is presents, although this is common for liquid
phase exfoliated graphene \[316\]. Additionally, full width at half maximum (FWHM) for each
dispersion is calculated to evaluate the 2D peak. FWHM \(2D_{N1} = 54 \pm 3.7\) cm\(^{-1}\), FWHM
\(2D_{N2} = 75 \pm 1.8\) cm\(^{-1}\), FWHM \(2D_{N3} = 79 \pm 1.7\) cm\(^{-1}\), FWHM \(2D_{E1} = 74 \pm 2.6\) cm\(^{-1}\), FWHM
\(2D_{E2} = 84 \pm 2.4\) cm\(^{-1}\), FWHM \(2D_{Se} = 65 \pm 2.5\) cm\(^{-1}\), FWHM \(2D_{Su} = 67 \pm 2.2\) cm\(^{-1}\).

FWHM of single layer graphene has been reported as \(~26.3\) cm\(^{-1}\)\[317\] and \(30\) cm\(^{-1}\)\[318\] and
this value is almost doubled in the case of bilayer graphene. While few layer and multi
graphene exhibits an FWHM between 39-65 cm\(^{-1}\) and broader than 65 cm\(^{-1}\), respectively\[149,\
150\]. With an increase in the number of layers, the expectation would be to observe further
widening of the 2D peak (increased FWHM) due to being more complex of the splitting of
the electronic bands\[318\]. This data showed that the resultant graphene dispersions, N2, N3,
E1, E2, consist of multilayer graphene structures, while sample S1_Se and S1_Su are
composed of few-layer flakes. N1 has the largest sized flakes and probably the largest degree
of stacking with respect to size plus layer numbers.

There is some spread in the D/G ratio for different samples. Even though the defect related
D-band peak was observed in all cases, indicating the presence of defects, the intensity ratio
of the D to G band \(I(D)/I(G)\) is mostly in between \(\sim 0.2-0.7\), significantly higher that pristine
graphite \(\sim 0.06\)\[303\], and hence some defects are induced during the ultrasonication process.
An exception occurred in the case of the graphene dispersion prepared via S1_Su. This
dispersion has a narrow particle size distribution in between 18 to 30 nm according to DLS
results (section 2.1.3.1.2) and \(I_D/I_G\) is 1.15. Thus, this finding confirmed that samples with
a larger D/G ratio may consist of flakes with smaller dimensions \[313, 319\].
Figure 3.5 Enlarged Raman spectrum of D (a), G (b) and 2D (c) peaks of exfoliated graphene dispersions.

As can be seen in Fig. 3.5a, among all dispersions, the intensity of the D peaks in the case of S1 (water-surfactant based) is higher than the other samples. This might be explained by the sonication time, in which graphite was sonicated via ultrasonic probe for 6 h during the whole dispersion process. So, increasing sonication time would result in decrease in flake size and giving a higher intensity D peak. In addition to this, by looking at FWHM values at D band for ethanol-based dispersions, FWHM_D_E1 = 68 cm\(^{-1}\) and FWHM_D_E2 = 88 cm\(^{-1}\), prepared via 4 hr ultrasonic bath has broader D peak compared to others. Similar behaviour was observed in NMP based dispersions, sample N2 and N3, FWHM_D_N2 = 37 cm\(^{-1}\) and FWHM_D_N3 = 48 cm\(^{-1}\). This situation which referred narrower D band by exposure of further centrifuge would be a result of separating defective graphitic like structures from the dispersion with a further centrifuge which was applied in from E1 to E2 and from N2 to N3. Overall, there is a dependency on the D peak intensity with the type of sonication used to separate graphite layers, whether ultrasonic probe or bath as the sonication energy might cause damage to the graphene sheets and create defects.

3.2.4 Atomic Force Microscopy

It is worth knowing here, that the interlayer distances of graphite and single layer graphene are considered as approximately 3.35 Å\(^{[320]}\) and ~ 8 Å\(^{[134]}\), respectively. However, it is also important to take into consideration some other factors which might affect the measured height of the graphene layer. Van der Waals forces, the substrate-graphene spacing, wetting etc. could increase the thickness of the graphene layer on a substrate\(^{[320, 321]}\). Single layer graphene deposited onto 285 nm SiO\(_2\)/Si revealed a step height between 1.2 – 1.58 nm at various points\(^{[320]}\). Yang et al.\(^{[102]}\) reported that height profile of graphene flakes reduced after removal residuals from the surface. This included washing the graphene deposited on silicon several times followed by inserting it into fresh water for 60. They observed that the
removal of excess molecules had been successfully done with each further wash but was limited to the 3\textsuperscript{rd} wash.

Figure 3.6 Atomic force microscopy (AFM) images together with thickness and lateral flake size histograms of graphene dispersion in NMP via procedure N2 (a) and N3 (b).

The thickness of a single layer of graphene in the current work is assumed to be 0.8 nm\textsuperscript{[114]}. A large number of graphene flakes were analysed (\sim 100 flakes) for each sample (N2 and N3, further centrifuged version of N2). In sample N2, atomic force microscopy images revealed the existence of relatively thick graphene flakes with an average thickness (width, w) of 10-20 nm (\sim 42\%) which corresponds to 12 to 25 layers and lateral size (length, L) of 300-400 nm (37\%). A few large flakes with a lateral size greater than 500 nm (16\%) also exist in the dispersion. As can be seen in Fig. 3.6, graphene flakes were clearly represented by AFM images. The height profiles (inset) showed that the flake was about 6 nm thick and a few hundred nanometres wide.

Further centrifugation was applied in order to improve the quality of the NMP-based graphene dispersion by separating unexfoliated graphitic structures from the well-dispersed
graphene sheets. By doing so, sample N3 was obtained. The obtained AFM results were presented in Fig. 3.6b. From the statistical analysis of graphene sheets, it could be possible to conclude that most of these flakes (80%) have a lateral size in between 100 – 400 nm and a thickness of 10-30 nm (55%) while ~ 6% of these flakes have a thickness less than 5 nm (≤ 7 layers). Both thickness and lateral dimension histograms indicated that thick materials were removed from the dispersion by a further centrifuge at 4500 rpm. However, the resultant AFM histograms of sample N3 also revealed that there is a pronounced change/variation in lateral dimension statistics. This could be explained by sample preparation which was kept the same for each sample. If there was any residual solvent on the silicon substrate this might have caused an overestimation of the graphene layer through thickness. This phenomenon was also observed in AFM results of the E2 ethanol based dispersion mentioned below.

Figure 3.7 Atomic force microscopy (AFM) image together with thickness and lateral flake size histograms of graphene dispersion in ethanol via procedure E1 (a) and E2 (b).
AFM was carried out in order to investigate the exfoliation degree of ethanol-based graphene dispersions (E1 and E2, further centrifuged version of E1). Representative images are shown in Fig. 3.7a and Fig. 3.7b. In both AFM images, graphene flakes can be well-identified in terms of expected shape. In sample E1, flakes are mostly between 10-40 nm thick (~50%) while 12% of flakes are ≤ 10 nm thick and ~63% of the flakes have a lateral dimension ≤450 nm. As can be seen in Fig. 3.7a, the flakes are not flat, instead they are mostly clustered and tend to be folded and restacked. Many flakes are typically in the order of ~20 nm thick (Fig. 3.7a, inset). The thinnest flake size is 4 nm. Further centrifugation was applied to this dispersion (E1) for the same purpose as in N3 in order to remove thick graphitic materials. As expected, flakes greater than 80 nm thick were removed and the final graphene dispersion (E2) has ~80% of flakes are less than 30 nm thick and less than 400 nm lateral size.

### 3.2.5 Transmission Electron Microscopy

Transmission electron microscopy provides high resolution image of graphene flakes and by studying these images it is possible to measure their lateral dimension, analyse morphology and purity. A statistical histogram of flakes can be obtained by analysing a wide range of flakes. Furthermore, the transparency of graphene sheets gives estimated information about the thickness of the graphene samples; transparent layers consist of mostly single or thin layers of flakes while dark spots mainly include more graphene layers stacked on top of each other. More precisely, the number of layers can be counted by looking at the edges[283].

![Transmission electron microscopy image](image)

**Figure 3.8** Transmission electron microscopy (TEM) image of graphene dispersion in NMP via procedure N2 (a), N3 (b) and in ethanol via procedure E1 (c), E2 (d).
Figure 3.8 shows representative TEM images of graphene dispersions via the NMP based procedures N2 (a), N3 (b) and the ethanol-based procedures E1 (c) and E2 (d). The observed graphene flakes have a lateral size mostly in between 100-300 nm for N2, 100-700 nm for N3, 100-500 nm for E1 and 100-300 nm for E2 (70% of ~30 flakes). Furthermore, during TEM measurement it was observed that some flakes were folded and had wrinkled areas (referred to appendices, Fig. 5A.24) which would affect thickness measured by AFM and cause the appearance of the D-peak in Raman spectrum. Note that, TEM results are not in agreement with AFM findings in the case of dispersion N3, AFM results revealed that 80% of flakes have the lateral size in between 100 – 400 nm for N3. However, in TEM images large size flakes are notably prominent. This situation might occur due to the loss of smaller and thinner flakes through the holes in the TEM grid during sample preparation since holey carbon grids were used as substrate material to drop cast graphene onto it. These grids are so tiny and needs extra caution during the solvent evaporation period. Another phenomenon mentioned previously in AFM section would be the residual solvent which was clearly observed in some of flakes in dispersion N3, as shown in Fig.3.9. These images indicated that NMP was not completely removed from the substrate as some solvent residuals can be seen in the images.

Figure 3.9 TEM images of graphene dispersion fabricated via method N3.
3.2.6 **X-ray Photoelectron Spectroscopy**

The kinetic energy and the number of electrons which are ejected from the material are analysed. By this technique, not only elemental composition but also the ratios of elements and identity of the functional group can be obtained\(^{[283]}\).

X-ray photoelectron spectroscopy (XPS) was carried out to characterize the quantitative elemental composition of graphene dispersions. NMP-based (N2) and water-sodium cholate based (S1_Se and S1_Su) graphene dispersions were used to perform XPS analysis. High resolution C 1s spectra for each sample are presented in Fig. 3.10.

In sample N2, graphene nanosheets showed a sharp, relatively narrow peak at 283.59 eV that is related to C-C bonds of carbon atoms in such a conjugated honeycomb lattice. However, an evaluation of the Auger C KLL line in terms of sp\(^2\) hybridization was not possible, because a possible graphite like signal was superimposed by the remaining residual NMP and C contamination auger signal. (C-N is the carbon atom in NMP bonded to a nitrogen; C=O is the carbon atom in NMP ring double bonded to an oxygen atom). On the other hand, in sample S1_Se and S1_Su, they are both aqueous based graphene dispersions assisted by a surfactant (sodium cholate). The C1s peak was fitted with binding energies ~284.96 eV (sp\(^2\) C), ~286.36 eV (C-O), ~287.86 eV (C=O) and ~288.87 eV (COOH) as shown in Fig. 3.11. We can confirm that oxygen groups exist (C-O, C=O and COOH) in the spectra and this further suggests the contribution of sodium cholate which inherited oxygen-containing groups. To conclude, the C 1s peak corresponds to the graphene structure which is mainly sp\(^2\) hybridized while the other peaks are related to sodium cholate’s structure (C\(_{28}\)H\(_{39}\)NaO\(_{5}\)).
Figure 3.10 XPS analysis of graphene dispersion in NMP via procedure N2 (a) and in aqueous sodium cholate via procedure S1_{Se} (b), S1_{Su} (c). Contribution of the components used in fitting of C 1s peak is also listed in each of graph.
3.2.7 Comparison of Results from DLS, AFM and TEM

Dynamic light scattering, atomic force microscopy and transmission electron microscopy were studied in order to examine flake lateral dimension and thickness. Each of those techniques provided some results which were presented in Table 3.5. As discussed in earlier section, all graphene dispersions predominantly consist of multilayer graphene sheets in the range of 5 - 30 nm thick that refers to 6 – 37 layers of graphene by assuming the thickness of single layer graphene in the current work is assumed to be is 0.8 nm\(^{114}\). Based on AFM statistical thickness and lateral size histograms, these dispersions are quite same in size and thickness. When looking at lateral dimensions, which is mostly in between 100 – 400 nm in AFM and this result is consistent with TEM data. However, the graphene sheets obtained from N3 provided lateral dimension up to 700 nm, which is not coherent with the AFM result in the same dispersion, indicating the flake dimensions less than 350 nm. This situation was associated with either residual solvent (NMP) on the substrate (supported by XPS analysis, Fig 3.10) or folded phenomenon of graphene sheets (Fig. A24), which effected the correct dimension measurement.

It is obvious that control fabrication parameters such as solvent-graphite interactions (graphite=NMP/ethanol/water-surfactant), sonication times (4 h in N2 and N3; 5 h in E1 and E2), sonication energy (sonic probe for N2 and N3; sonic bath for E1 and E1) and centrifugation rotational speed (1500 rpm for N2, 4500 rpm for N3; 3000 rpm for E1 and E2) provided graphene flakes in the almost same range of size and thickness. Not much difference was observed in different procedures. Furthermore, N3 and E2 have the thinnest and smallest flakes and besides, they have narrow flake lateral size distribution compared to others.

Table 3.5. Flake lateral dimension (L) and thickness (W) obtained from DLS, TEM and AFM.

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>DLS ( L_{\text{mean}} )</th>
<th>TEM ( 100 \text{ nm} &lt; L &lt; 300 \text{ nm} )</th>
<th>AFM ( 100 \text{ nm} &lt; L &lt; 400 \text{ nm} ) (70%) 10 nm &lt; W &lt; 30 nm (64%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>198 nm</td>
<td>100 nm &lt; L &lt; 300 nm</td>
<td>100 nm &lt; L &lt; 400 nm (70%) 10 nm &lt; W &lt; 30 nm (64%)</td>
</tr>
<tr>
<td>N3</td>
<td>120 nm</td>
<td>100 nm &lt; L &lt; 700 nm</td>
<td>100 nm &lt; L &lt; 350 nm (85%) 5 nm &lt; W &lt; 30 nm (78%)</td>
</tr>
<tr>
<td>E1</td>
<td>560 nm</td>
<td>100 nm &lt; L &lt; 500 nm</td>
<td>150 nm &lt; L &lt; 450 nm (63%) 5 nm &lt; W &lt; 60 nm (76%)</td>
</tr>
<tr>
<td>E2</td>
<td>360 nm</td>
<td>100 nm &lt; L &lt; 300 nm</td>
<td>150 nm &lt; L &lt; 400 nm (81%) 5 nm &lt; W &lt; 30 nm (74%)</td>
</tr>
</tbody>
</table>
In Table 3.5, \(<L>\), flake mean lateral dimension was calculated from the primary peak position from the intensity distribution data provided from DLS by using the fit data suggested by Lotya et al.\(^{[162]}\) (section 1.1.5, (vi) dynamic light scattering). By this method, it is possible to estimate the lateral dimensions of graphene nanosheets. The data clearly suggested that the mean L values outputted by DLS scaled in the range of the data provided by TEM and AFM.

### 3.3 Conclusion

In summary, based on the comprehensive work on graphene dispersion fabricated via liquid phase exfoliation techniques in various solvents (NMP, ethanol and water) using different co-assistance such as surfactant and organic salt at various conditions; various fabrication procedures have been successfully demonstrated in order to directly exfoliate graphite powders into large size, multi-layer graphene nanosheets. The resultant graphene dispersions were compared using different experimental techniques.

From the UV-Vis absorption spectra, it is concluded that the concentration of the final dispersion mainly depends on parameters of the fabrication process such as type of solvent and its dispersibility capacity, applied sonication energy, rotational speed and further centrifugation steps (centrifuge the dispersion several times during fabrication process). It was found that high boiling point solvent NMP based dispersions promoted higher efficiency of exfoliated graphene, with a yield of 7.2% and the highest concentration of 0.36 mg/mL, achieved by 4 h of sonic probe and separated by 1500 rpm rotational speed. However, poor exfoliation efficiency was observed in ethanol cases due to using low-power ultrasonication, and also the mismatch of surface energy between ethanol and graphene, resulting in lower dispersibility. Using potassium sodium tartrate (KNaC\(_4\)H\(_4\)O\(_6\)) in ethanol based dispersions improved the efficiency of exfoliation up to 0.08 mg/mL. It was confirmed by UV-Vis spectroscopy that high rotational speeds like 7.5 krpm and 10 krpm caused to the loss of heavy unexfoliated graphitic structures, which led to a lower carbon content in the final dispersion up to 0.027 mg/mL in S1_Se.

Moreover, the cascade centrifugation method was applied in an aqueous surfactant assisted system and provided a separation mechanism which allows the separation of nanosheets into desired sizes and thicknesses. In addition, the use of an ultrasonic bath or probe affected exfoliation efficiency and flake dimensions, in which higher sonic energy caused an increase in the concentration of the dispersion and decrease in flake size.
DLS data suggested that it is possible to produce flakes with hydrodynamic sizes from 170 nm to 30 nm using NMP based dispersion procedures, from 144 nm to 121 nm in ethanol based dispersions and from 51 nm to 21 nm using the modified aqueous based fabrication method. The results indicated that different fabrication procedures led to different qualities of dispersions in terms of flake size and dispersion efficiency. Lateral sizes of flakes are mainly in the range of 100 to 400 nm in sample N3 and E2 based on AFM results which were consistent with TEM results. Thickness histograms by AFM provided 10 to 20 nm thick flakes which mostly indicated that the obtained dispersions were composed of multilayer graphene flakes. The thinnest flake size of 4 nm indicated that dispersions had flakes greater than 5 layers.

XPS studies showed that the graphene nanosheets fabricated via NMP and aqueous based systems contained some oxygen contents, due to the residual solvent NMP and sodium cholate. This finding, which was also supported by TEM, indicated that NMP was not completely removed from the substrate. These residual solvents might have an effect on accurate result of flake size measurements and the solvent removal process should be optimized before characterization takes place.

Raman analysis showed the disorder related D-band peak in all dispersions which indicated the presence of defects, mainly caused by flake edges since smaller thinner flakes brought more edges. Data from Raman spectroscopy also revealed differences between the different preparations with respect to the stacking which was confirmed based on UV-Vis, AFM and TEM.
CHAPTER 4

GRAPHENE BASED MEMBRANES

(I) GRAPHENE COMPOSITE MEMBRANES

(II) GRAPHENE -POLYMER HYBRID MEMBRANES
4.1 Introduction

Based on the knowledge from membrane separation technology, an ideal membrane should have good mechanical strength, be environmental-friendly, have smooth surface, channel and high selectivity with high flux [322]. With the development of nanotechnology, the idea of using nanomaterials in film industry became so popular [323]. By functionalizing membranes with nanomaterials, one can tune membrane properties via various modification techniques, for instance improving permeability or antifouling performance of pristine membranes [324]. Graphene nanosheets are critical element in this work, as being the main material for the selective layer of composite membranes, which play a significant role in determining the membrane’s selectivity [325, 326] against particles to be removed. Thus, a good graphene composite membrane is only valid with a good graphene dispersion. Graphene has a well-matched characteristic with the required demands mentioned above for an ideal membrane. Only one atom thickness and an almost frictionless surface makes a graphene wonder material to generate membranes with low transport resistance and high flux.

- Feasibility of creating thin membranes by graphene nanosheets

Graphene can be used to form assembled laminates via many fabrication methods i.e., filtration, spin or spray coating, evaporation, layer by layer assembly [182, 322], creating selective 2D nanochannels to transport small/ required molecules. In graphene membranes, mass transport pathways are assembled by the stacking of nanosheets where water molecules transport through the interconnected nanochannels between the adjacent layer [192]. By the pressure assisted method, it is possible to have highly ordered graphene laminates [195]. However, keeping graphene layers stable in aqueous systems is an important factor which will affect membrane performance. In the dry state, graphene oxide (GO) layers are tight and stable with a d-spacing of 10.6 Å [199, 327, 328]

Nonetheless, once they are soaked into aqueous systems (i.e., water) they are not stable and tend to swell, in return enlarging the interlayer distance (d-spacing) up to 13.5 Å [327]. XRD results showed that interlayer spacing of graphene varied in between 8.3 Å to 11.5 Å [182].

- Hydrophobic nature promotes fast transport

Many researchers suggested that graphene is hydrophobic [329-331] even though GO includes oxygen containing functional groups which makes it hydrophilic. This hydrophobic property of graphene might be an advantage in membrane separation because graphene membranes
minimize the frictional force between the membrane and water molecules, thus promoting fast transport. Water molecules can easily transport through nanochannels without nearly frictionless surfaces, in return obtaining high water flux\textsuperscript{322}. Moreover, this might be useful to diminish the formation of contamination\textsuperscript{322} since particles do not easily adhered to the membrane surface. Some of the GO membranes reported in literature had the following mass transport performances: water flux 21.8 L/m\textsuperscript{2}hbar and 99% rejection of red 81\textsuperscript{203}; layer-by-layer fabricated GO membrane has water flux 8.276 L/m\textsuperscript{2}hbar and 93-95% rejection of Rhodamine-WT\textsuperscript{332} The rejection of the dye Rhodamine-WT is commonly used as a hydrologic tracer in surface water systems\textsuperscript{333}.

In the current work, a pressure-assisted filtration technique was used to deposit graphene layers onto porous substrates which are commercially available membranes, as a mechanical support to graphene, including Nylon 0.2 (~150µm), Nylon 0.45 (~150µm), PTFE 0.2 (~50µm) and PES (~150µm). Here, graphene membranes were classified into two main work packages,

(1) The first work package is about graphene composite membranes which includes only stacked graphene laminates onto the support membranes. Here, membranes were fabricated via a dead end filtration cell based on a filtration method by using various graphene loadings under a certain of pressure. The thickness of graphene laminates can be tuned by carefully changing the volume of graphene dispersion to be coated.

(2) The second work package is about graphene-polymer hybrid membranes which is based on a layer-by-layer (LbL) assembly technique, also can be called as ‘sandwich model’. This consists of firstly, a positively charged polymer modified support membrane, secondly, graphene with or without a cross linker, followed by a third layer of the polymer on top. It is fundamental to adjust graphene nanochannels by decreasing d-spacing and improving the stability of membranes in wet phases. For this purpose, in this study, graphene nanosheets were covalently cross-linked with a type of diamine monomer known as ethylenediamine (EDA). This is used for decreasing d-spacing and also contributes to improving the layer stability in wet states\textsuperscript{197, 199}. Graphene nanosheets with and without the cross-linker (EDA) were formed/stacked in between two polyethyleneimine (PEI) layers on support membrane (sandwich model). By placing EDA between nanosheets, channels can be generated, leading to substantially small pores that only water molecules pass through. Besides, different from cross-linked graphene, a positively charged polymer, PEI was used to increase the membrane surface charge and also provide a smoother surface for eliminating the possibility of defect formation. PEI is a polyelectrolyte which consists of charged groups found directly on the
backbone and branch by two ethylene groups. The extension of PEI is dependent on the competition between inter-chain and intra-chain interactions. Repulsion between amines are increased by the small space between charges which is in favour of chair extension whilst the molecule is compressed by the inter-chain interactions\cite{334,335}.

![Figure 4.1 Chemical structure of PEI (a) and EDA (b).](image)

4.2 Graphene Composite Membranes

4.2.1 Introduction

In terms of the fabrication of graphene membranes, previously mentioned procedures 1 and 2 (see Fig. 2.7 in section 2.1.2.2) were used in this section which includes using either graphene dispersions with or without dilution. Nylon with a pore size of 0.2/0.45 µm, polytetrafluoroethylene (PTFE) 0.2 µm, and polyethersulfone (PES) 0.1 µm membranes were used as support membranes. Various characterization techniques were applied to the membranes in order to get information about pore size (PMI), porosity (%), surface hydrophilicity/hydrophobicity (contact angle), surface charge properties (zeta potential), surface morphology (SEM) and mass transport characterization (water permeability (LMH/bar) and rejection %). Dextran with different molecular weights was used to determine selectivity of membranes. Dextran is defined as the complex branched glucan. Chains’ length of dextran can vary from 3 kilodalton (kDa) to 2000 kilodalton (kDa). In this work, dextran 4 kDa and 2000 kDa were used. Their average molecular size was calculated in literature based on various methods as shown in the following table.

<table>
<thead>
<tr>
<th>Dextran (Mw)</th>
<th>Reference</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 kDa</td>
<td>2 nm</td>
<td>3.1 - 3.7 nm</td>
</tr>
<tr>
<td>2000 kDa</td>
<td>68.2 nm</td>
<td>54.6 - 55.3 nm</td>
</tr>
</tbody>
</table>

Membranes used in this part are labelled as shown in the following form:

\( G/\text{Support}_Xmg_{-Y} \)
Where G is the graphene deposited onto a support membrane, support is the name of commercial support membrane which can be Nylon 0.2 µm = N02; Nylon 0.45 µm = N045; PTFE 0.2 µm = P02 or PES. X is the amount of graphene deposited (mg) and Y is the applied pressure (bar) during graphene deposition.

### 4.2.2 Results and Discussion

#### 4.2.2.1 Gas Flow/Pore Dewetting Permporometry

The method of capillary flow porometry is employed in Fig. 4.2. In principle, a liquid which does not react with the membrane and has low surface tension is chosen as the wetting agent. Then, N₂ is used to force the liquid out through pores in membrane[268]. The applied gas pressure increases continuously at a constant rate and the gas flow through wet and dry membrane is measured as a function of differential pressure[268]. Fig. 4.2a provides gas flow (L/min) across membrane pores in dry phase as a function of applied pressure.

![Figure 4.2](image)

**Figure 4.2** Gas flow measurement as a function of applied pressure in bar (a) and pore size distribution of N02 and G/N02_1mg_05 membranes (b). Black and red lines represent support and graphene composite membranes, respectively. Membranes were fabricated via graphene dispersion N2.

An unmodified Nylon 0.2 µm membrane is a commercial membrane which has a narrow pore size distribution in between 0.2 and 0.3 µm and gave a peak at 0.27 µm (Fig. 4.2b). By coating this support membrane with ~1 mg of graphene under 0.5 bar pressure, pore size of the composite membrane decreased to 0.087 µm, in addition to some other pores existing at around 0.05 µm and 0.2 µm. This clearly indicated that graphene coverage is not sufficient as it seems there are some parts on the support membrane with less graphene flakes deposited due to the continual presence of large pores. To test gas flow (L/min), membranes were pressurized with N₂ under various pressure. As indicated in Fig. 4.2a, the graphene composite
the membrane has a lower gas flow (about 3 times) compared to the unmodified membrane. This was expected because the deposited graphene layer promoted a longer diffusional pathway, leading to low gas permeability through the spaces between graphene nanosheets. Furthermore, applied gas pressure is inversely proportional with the pore diameter. High pressure is necessary for smaller pores which offer the high resistance\(^3\). This is confirmed by the results at Fig. 4.2a and Fig. 4.3a, support membranes Nylon and PTFE membranes require lower gas pressure in the range of 1-6 bar compared to graphene composite membranes (red line in the graph) which require higher pressure in the range of 1-18 bar due to the presence of smaller pores in the membranes.

**Figure 4.3** Gas flow measurement as a function of applied pressure in bar (a) and pore size distribution of P02 and G/P02_1mg_08 membranes (b). Blue and red lines represent support and graphene composite membranes, respectively. Membranes were fabricated via graphene dispersion N2.

Commercial PTFE 0.2 µm has a very narrow pore size distribution, it gave one peak at 0.28 µm, while the graphene/P02 membrane (Graphene dispersion and the amount was same here as in Fig. 4.2) has an average pore size of 0.055 µm (Fig. 4.3b). The same amount of graphene (1 mg) used for making the selective layer in both of the support membranes (N02 and P02). However, pores coverage with graphene was better in P02 than N02. This situation could be explained by the morphology of the support membrane by further study of top-cross section SEM images which provide the information about support membranes surface smoothness. PTFE has a smoother surface rather than Nylon membrane. But, the capability of completely blocking big pores completely is still complicated topic (see Fig.
4.16a). Moreover, the gas flow of graphene/P02 was nearly 10 times less than that for unmodified P02 membrane.

### 4.2.2.2 Contact Angle Analysis

Water contact angles of the membranes were analysed and shown in Fig. 4.4. The water contact angle values for the reference supports N02, N045 and P02 were measured to be ~44°, 47° and 60°, respectively. The membranes were prepared using different processing parameters, for instance; two filtration pressures were used as the driving force 0.5 - 0.8 bar and various graphene loadings were used to see the effect on the wettability. There is no significant change due to pressure difference on the wettability of the membranes, however, there is a clear trend in all cases that the water contact angle of the substrate increased up to 100°, when graphene was loaded, demonstrating that modified membranes were more hydrophobic that the unmodified ones. This can be probably attributed to the hydrophobic nature of graphene. In osmotic applications, it is not a preferred characteristic to have a highly hydrophobic membrane, which negatively impacts water permeability by prohibiting the transport of water molecules through the membrane’s pores/channels\[^{190, 340}\]. Contact angle values were higher in membranes fabricated via dispersion N2 than N1. Since the two different dispersions have different flake sizes, this could contribute to different levels of roughness. Higher roughness which is caused by smaller flakes which can be mostly found in dispersion N2.

![Figure 4.4](image)

**Figure 4.4** Contact angle of graphene/N02 membranes (a), graphene/N045 membranes (b) and graphene/P02 membranes (c) with different graphene loadings. Orange colour and black colour represent the graphene membranes prepared via method N1 and N2, respectively. Amount of graphene over deposited area varied 0.06, 0.11 and 0.16 mg/cm\(^2\).
4.2.2.3 Study of Membrane Surface Properties

Surface charge of a membrane has a great influence on its filtration mechanism such as permeability and selectivity. It was determined by one of electro-kinetic methods, streaming potential measurements. In this method, two same membranes are mounted on the sample holders and create a capillary flow channel. An electrolyte solution flows across the channel formed by two membranes. The flow of electrolyte solution causes a streaming current, so create a potential difference\(^{[341]}\) by generating charge separation. The results have been shown, as indicated in Fig. 4.5, zeta potential as a function of pH values. The zeta potential (or electro-kinetic potential) value which is closely associated with charged groups on the membrane surface, also depends on ionic strength and pH value of electrolyte solution \(^{[342, 343]}\). The results in Fig. 4.5 (left) indicated that the support membranes are positively charged at low pH with an isoelectric point at pH 3.9 for P02, 5.9 for N045 and 7 for N02 and negatively charged at high pH values. Obviously, P02 is a more negatively charged base membrane compared to the others. It is noted that G is negatively charged \(^{[286]}\). So, after graphene deposition onto the base membranes, isoelectric points were shifted to the lower pH values due to the negative nature of graphene. The shape of the lines also changed as indicated in Fig. 4.5 (right). Moreover, absolute zeta potential values decreased with the addition of graphene content. Overall, there are two important aspects observed here in this analysis.

There was one case with N045 where the zeta potential did not essentially change as a function of pH values. The second aspect is that IEP, or also known as point of zero charge, which is the pH value at which the material surface charge is zero\(^{[344]}\), (seemed to also depend on pores size) did not change very much in all cases. It seemed to add layers which shielded charges. This might have happened because it was a conductive material which changed electrical properties, the effect of the charges was reduced and all the potentials shrank to smaller values.
4.2.2.4 Filtration Performance

Graphene composite membranes listed in Fig. 4.6, Fig. 4.7 and Fig. 4.8 were prepared via the fabrication method of procedure 1 mentioned in the experimental chapter (see section 2.1.2.2). Various amounts of graphene dispersions (0.06, 0.11 and 0.16 mg/cm²) were filtrated through support membranes (Nylon 0.2, Nylon 0.45 and PTFE 0.2) under 0.5 and 0.8 bar pressure to see the their effects on the stacking quality of graphene flakes. Graphene dispersed in NMP via method N1 and N2 were used as a graphene coating solution in order to see the effect of different size of flakes on membrane performance in terms of water permeability and rejection. During the period of operation time, the water permeability of the membranes declined gradually and started to stabilized after 150 min filtration duration. It is a benchmark to identify at which stage what percentage of flux is being lost. Since it cannot be expected that the final membrane (support membrane modification with graphene) provides a higher flux. Resistance of support membrane limits the flux. So, adding any additional layer on top of support membrane have an influence on flux by changing the resistance.
### Table: Water Permeability of Graphene Membranes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Graphene Layer Thickness (nm)</th>
<th>N1</th>
<th>N2</th>
<th>Initial – Final Permeability (L/m².h.bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N02_0.5mg_05</td>
<td>200</td>
<td>2061 ± 185</td>
<td>1460 ± 165</td>
<td>1963-1815 to 1619-1270</td>
</tr>
<tr>
<td>N02_1mg_05</td>
<td>600</td>
<td>437 ± 60</td>
<td>1678 ± 707</td>
<td>562-385 to 3015-1051</td>
</tr>
<tr>
<td>N02_1.4mg_05</td>
<td>900</td>
<td>290 ± 42</td>
<td>960 ± 208</td>
<td>372-262 to 1030-481</td>
</tr>
<tr>
<td>N02_0.5mg_08</td>
<td>200</td>
<td>852 ± 230</td>
<td>1666 ± 566</td>
<td>1160-819 to 1630-1390</td>
</tr>
<tr>
<td>N02_1mg_08</td>
<td>600</td>
<td>600 ± 135</td>
<td>649 ± 109</td>
<td>831-576 to 834-474</td>
</tr>
<tr>
<td>N02_1.4mg_08</td>
<td>900</td>
<td>696 ± 81</td>
<td>315 ± 81</td>
<td>837-627 to 480-223</td>
</tr>
</tbody>
</table>

**Figure 4.6** Water permeability (L/m².h.bar) of graphene/N02 membranes prepared via dispersion N1 (left) and N2 (right) with various graphene loadings (0.5-1.4mg) prepared as a function of operation time. Average water permeability of unmodified Nylon 0.2 membrane is 7338 ± 168 L/m².h.bar. Membrane active area is 9.07 cm².

As shown in Fig. 4.6, the N02_0.5mg_05 membrane showed the highest average water permeability with 2061 L/m².h.bar via dispersion N1. Graphene selective layer thickness was measured 200 nm, indicated the importance of membrane thinness which is inversely proportional with the permeability. This membrane resulted in an approximately 72% permeability reduction compared to the permeability of unmodified Nylon membrane 7338 L/m².h.bar.
<table>
<thead>
<tr>
<th>Membranes</th>
<th>Graphene Layer Thickness (nm)</th>
<th>N1</th>
<th>N2</th>
<th>N1</th>
<th>N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>N045_0.5mg_05</td>
<td>200</td>
<td>936 ± 267</td>
<td>1276 ± 238</td>
<td>1335-533</td>
<td>1715-996</td>
</tr>
<tr>
<td>N045_1mg_05</td>
<td>600</td>
<td>686 ± 202</td>
<td>358 ± 176</td>
<td>1037-475</td>
<td>774-164</td>
</tr>
<tr>
<td>N045_1.4mg_05</td>
<td>900</td>
<td>614 ± 54</td>
<td>539 ± 137</td>
<td>678-511</td>
<td>756-436</td>
</tr>
<tr>
<td>N045_0.5mg_08</td>
<td>200</td>
<td>1585 ± 219</td>
<td>986 ± 445</td>
<td>1927-1309</td>
<td>1974-554</td>
</tr>
<tr>
<td>N045_1mg_08</td>
<td>600</td>
<td>676 ± 160</td>
<td>1013 ± 91</td>
<td>910-424</td>
<td>1206-875</td>
</tr>
<tr>
<td>N045_1.4mg_08</td>
<td>900</td>
<td>436 ± 87</td>
<td>579 ± 122</td>
<td>590-341</td>
<td>771-362</td>
</tr>
</tbody>
</table>

**Figure 4.7** Water permeability (L/m².h.bar) of graphene/N045 membranes prepared via dispersion N1 (left) and N2 (right) with various graphene loadings (0.5-1.4mg) as a function of filtration time. Average water permeability of unmodified Nylon 0.45 membrane is 7656 ± 636 L/m².h.bar. Membrane active area is 9.07 cm².

As shown in Fig. 4.7, the N045_0.5mg_08 membrane with a 200 nm graphene selective layer thickness showed the highest water permeability with 1585 L/m².h.bar via dispersion N1.
Figure 4.8 Water permeability (L/m².h.bar) of graphene/P02 membranes prepared via dispersion N1 (left) and N2 (right) with various graphene loadings (0.5-1.4mg) as a function of filtration time. Average water permeability of unmodified PTFE 0.2 membrane is 11520 ± 563 L/m².h.bar. Membrane active area is 9.07 cm².

As shown in Fig. 4.8, the P02_1mg_08 membrane with 600 nm of graphene selective layer thickness showed the highest water permeability with 6798 L/m².h.bar via dispersion N2 and around a 41% water permeability reduction compared to the unmodified PTFE membrane.

Overall, it could be possible to conclude that no clear difference was observed in terms of the effect of graphene dispersions from N1, N2 and applied pressure 0.5, 0.8 bar on the membrane’s filtration performance. However, increasing graphene up to 0.16 mg/cm² content led to lower permeability, but still no clear correlation found in membrane fabrication parameters and their filtration performance.
Figure 4.9 Average water permeability (L/m².h.bar) of graphene/N02, graphene/N045 and graphene/P02 membranes fabricated via dispersion N1 (black) and N2 (blue) under 0.5 bar and 0.8 bar pressure with various graphene loadings such as 0.5 mg, 1 mg and 1.4 mg. Membrane active area is 9.07 cm².

Even though it is hard to determine the effects of pressure and flake size on the membrane’s permeability and selectivity performance from these results, it is clear that there is permeability loss in all cases caused by introducing graphene onto the support membrane. Apart from a few exception, increasing graphene loading from 0.06 mg/cm² to 0.16 mg/cm² led to decrease in water permeability. Regarding the membranes selectivity, monovalent and divalent salts were used as test solutes such as NaCl, Na₂SO₄ and MgCl₂. The salt concentration was measured by using a conductivity meter (SI Analytics Lab 865, Germany). Unfortunately, rejection in all cases was very low, NaCl (~5%), Na₂SO₄ (~13%), MgCl₂ (~10%). These rejection values indicated that average pore size of graphene membranes are bigger than the diameter of ions[208] (Na⁺ 0.72 nm, Mg²⁺ 0.86 nm, Cl⁻ 0.66 nm). Overall, based on the separation performance of these membranes, it could be concluded that quite high water permeability up to ~5000 L/m².h.bar but very low salt rejection was obtained. This situation directed the focus of work towards the stacking quality of graphene during the filtration. Since, if graphene stacking was not good enough at the beginning (i.e., loose and not well-ordered) and any macro defects, for instance; cracks or disorder on the , occurred.
under the applied pressure during filtration operation, some defective pathways (short-cuts) for the transport would contribute selectivity performance of the membranes.

### 4.2.2.4.1 Membrane Compaction Analysis

In order to analyse the graphene composite membrane’s compaction mechanism which was mentioned above, two membranes, N02_1mg_05 and P02_1mg_08, were chosen for further analysis since they provided the highest water permeabilities. Dextran 4 kDa and 2000 kDa were used to measure rejection and flux values under various pressures from 0.15 bar to 1 bar. Change in flux values was considered as an indication of macro defects in the membrane rather than that in permeability \( \text{L/m}^2.\text{h.bar} \), because flux \( \text{L/m}^2.\text{h} \) value is not dependent on the applied pressure. The results, as shown in *Table 4.2*, indicated that increased pressure resulted in an increase in flux and decrease in rejection. This behaviour can be explained by the formation of some defects on the membrane’s surface under pressure.

<table>
<thead>
<tr>
<th></th>
<th>Dextran 4 kDa</th>
<th>Dextran 2000 kDa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.15 bar</td>
<td>0.25 bar</td>
</tr>
<tr>
<td><strong>P02_1mg_08</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rejection [%]</td>
<td>19</td>
<td>11</td>
</tr>
<tr>
<td>Flux (L/m².h)</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Permeability (L/m².h.bar)</td>
<td>40</td>
<td>72</td>
</tr>
<tr>
<td><strong>N02_1mg_05 R2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rejection [%]</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>Flux (L/m².h)</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Permeability (L/m².h.bar)</td>
<td>36</td>
<td>50</td>
</tr>
</tbody>
</table>

### 4.2.2.4.2 Effect of Using Diluted Graphene Dispersion on Filtration Performance

Here graphene dispersions, N2, E1, S1_Se and S1_Su, were diluted by a factor of 100 and 1000 times before starting deposition, in order to check the effect of using very diluted dispersions on membrane permeability and rejection performance. In Fig. 4.10, it can be clearly seen that water permeability was dependent on graphene amount, increasing graphene content up to 1.2 mg (The membrane name is SX) led to a decrease in permeability to 80 L/m².h.bar and an increase in rejection of dextran 4 kDa up to 23%. However, nearly the same amount of graphene loading was used in the membrane labelled as M5P fabricated via dispersion S1_Se shown in *Table 4.3*. It revealed a water permeability of nearly 303 L/m².h.bar with a 9% rejection of dextran 4 kDa. Approximately the same amount of graphene from two different dispersions behaved differently in membrane mass.
transport characterization. Recall from the DLS results, in which flakes in N2 have a broad size distribution in the range of 40 – 400 nm (peak at 60 nm) while the flakes in Si-Se have a relatively narrow distribution from 20 – 200 nm (peak at 50 nm). This situation is due to either flakes with small lengths providing short pathways, resulting in high permeability (M5P), or the existence of some macro defects larger than 50 nm which contributed to permeability and rejection.

**Figure 4.10** Comparison of average water permeability (L/m².h.bar) and dextran 4kDa rejection of graphene/N02 membranes prepared via dispersion N2 with various concentrations. (a) 160 μg/mL, (b) 1.6 μg/mL and (c) 0.16 μg/mL. Active area of membranes: 9.07 cm². Filtration pressure: 0.5 bar.
<table>
<thead>
<tr>
<th>Membrane No</th>
<th>Dispersion</th>
<th>Amount of Graphene (mg)</th>
<th>Graphene layer Thickness (nm)</th>
<th>Average Water Permeability (L/m².h.bar)</th>
<th>Rejection (%) Dextran 4 kDa</th>
<th>Rejection (%) Dextran 2000 kDa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon (Reference)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>7338 ± 168</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SX</td>
<td>N2</td>
<td>0.4</td>
<td>122</td>
<td>80 ± 56</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>A6</td>
<td>E1</td>
<td>1.2</td>
<td>744</td>
<td>366 ± 12</td>
<td>12</td>
<td>55</td>
</tr>
<tr>
<td>B2</td>
<td>S1-Se</td>
<td>0.04</td>
<td></td>
<td>303 ± 178</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>-</td>
<td>0.22</td>
<td></td>
<td>2686 ± 958</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>M5P</td>
<td>S1-Su</td>
<td>1.3</td>
<td>822</td>
<td>6647 ± 195</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>S1-Su</td>
<td>0.04</td>
<td></td>
<td>2830 ± 288</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>-</td>
<td>0.22</td>
<td></td>
<td>6657 ± 120</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3 Performance of average water permeability (L/m².h.bar) and dextran 4kDa and 2000kDa rejection of graphene/N02 membranes prepared via dispersion N2, E1, S1-Se and S1_Su with dilution factor of 100 times (B1 and B2), 1000 times (C1 and C2) as a function of various graphene loadings. Active area of membranes: 9.07 cm². Filtration pressure: 0.5 bar.

Dilution of graphene dispersions was proposed as a solution in order to increase the stacking quality of graphene in composite membranes. Here, dextran rejection of the SX membrane was examined under 0.25 and 1 bar. As can be seen in Table 4.4, a very slight change was observed in dextran rejection with increasing pressure up to 1 bar, indicating that the stability of the membrane was enhanced successfully.

Table 4.4 Compaction analysis of SX membrane (Table 4.3) with dextran 4kDa and 2000kDa rejection (%) under 0.25 and 1 bar pressures.

<table>
<thead>
<tr>
<th>SX G/N02_{1.2mg_{N2}}</th>
<th>D4 Pressure (bar)</th>
<th>0.25</th>
<th>1</th>
<th>0.25</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>SX G/N02_{1.2mg_{N2}}</td>
<td>Rejection [%]</td>
<td>25</td>
<td>23</td>
<td>47</td>
<td>46</td>
</tr>
</tbody>
</table>
### Table 4.5 Performance of average water permeability (L/m².h.bar) and dextran 4kDa and 2000kDa rejection of graphene/PES membranes prepared via dispersion E1, S1-Se and S1-Su with dilution factor of 100 times (G1) and 1000 times (B⁴, C³, C⁴) as a function of various graphene loadings. Active area of membranes: 9.07 cm². Filtration pressure: 0.5 bar.

<table>
<thead>
<tr>
<th>Membrane No</th>
<th>Dispersion</th>
<th>Amount of Graphene (mg)</th>
<th>Average Water Permeability (L/m².h.bar)</th>
<th>Rejection (%) Dextran 4 kDa</th>
<th>Rejection (%) Dextran 2000 kDa</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES (Reference)</td>
<td>-</td>
<td>-</td>
<td>1890 ± 43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B⁴</td>
<td>S1-Se</td>
<td>0.22</td>
<td>51± 11</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>C³</td>
<td>S1-Su</td>
<td>0.22</td>
<td>48± 4</td>
<td>19</td>
<td>-</td>
</tr>
<tr>
<td>C⁴</td>
<td>S1-Su</td>
<td>0.04</td>
<td>229± 46</td>
<td>14</td>
<td>-</td>
</tr>
<tr>
<td>G¹</td>
<td>E1</td>
<td>0.3</td>
<td>204± 7</td>
<td>-</td>
<td>48</td>
</tr>
</tbody>
</table>

Here in Table 4.5, another support membrane which is a kind of ultrafiltration membrane, polyether-sulfone (PES) was used as it has an average pore size of around 0.12 µm which is smaller than that of Nylon membrane and also has a smoother surface which might be useful to reduce the defect density of graphene membranes. Since PES membranes are not compatible with the high boiling point solvent NMP, only graphene dispersed in aqueous system and ethanol were used to fabricate composite membranes. Water permeability of membranes varied in between 48 to 229 L/m².h.bar as a function of graphene amount. It should be noted that the delamination phenomenon occurred during work with the PES membranes. The stability of graphene selective layer was not found in good quality in aqueous systems. Some of the layers peeled off from the support membrane. This was observed in two ways, either during filtration or during membrane washing process after oven to remove unbonded residuals. This will be discussed in the next section in detail.

#### 4.2.2.5 Stability Test

Since the delamination phenomenon occurred in the case of graphene/PES composite membranes fabricated via aqueous based dispersion, stability analysis of the graphene layers onto support membranes PES and N02, was carried out in two ways. One way was to apply ultrasonic energy for a certain length of times to the graphene membranes to examine the stability of the stacking quality of graphene laminates after ultrasonic waves exposure. To do this, composite membranes were sonicated for 5 min, at 45kHz frequency. The second way was to visually observe changings visually to the surface morphology of the membranes before and after permeability-rejection experiments.

Additionally, in order to analyse the effect of using other type of surfactants on the graphene stacking quality, the water-sodium cholate-based dispersion method of S1 was repeated here using anionic and non-ionic surfactants. Sodium cholate and CTAB are charged stabilized
surfactants while charge is not involved in Pluronic 123. There are many examples showing that colloids are stabilized by charges there are also other examples where colloids are stabilized by using a neutral polymer (Pluronic 123). As a comparison of sodium cholate, CTAB and Pluronic 123, there are two differences in Pluronic 123. It is a neutral surfactant not charged and also a polymer compared to SC and CTAB which are composed of small molecules. Why can one expect that this surfactant will stick to graphene? Because graphene is a hydrophobic. Pluronic 123 is a block co-polymer, featuring one hydrophobic block, PPO (polypropylene oxide) and hydrophilic block. Polymer sticks the central block to the surface and then the hydrophilic blocks are in water (well-hydrated). This situation is called steric stabilization\textsuperscript{[345]} which is defined as the stabilization of colloidal particles\textsuperscript{[346]} by covering the particles in the polymers that inhibits the particles to aggregate or settle down in the range of attractive forces. In stabilizing colloids, there are two fundamentally different mechanism. One is charge and the other is steric, that one basically forms a liquid shell around it. One could think about that if you have this kind of stabilization, if that liquid part of polymers, which is enabling the colloid, is well-dispersed in the liquid because it forms a packed shell around it.

Since the polyether sulfone (PES) membrane is not compatible with the solvent NMP, N1 and N2 dispersions were only used in case of Nylon support membrane. Membranes fabricated by dispersions in NMP (N1, N2) and ethanol (E1, E2) did not show any observable delamination problem during water permeability and rejection experiments. However, specifically after 5 min of sonic bath exposure, the surface morphology of the membranes can be seen in Fig. 4.12. In the case of using water – sodium cholate-based dispersion, stability was very problematic during water permeability tests under pressure and was also an issue after the first contact (or first touch) with water following the drying process (Fig. 4.11). Graphene layers (dispersed via cationic surfactant CTAB aqueous system) on a Nylon membrane (Fig. 4.12c) showed an improved stability after sonication while graphene onto a PES (Fig. 4.12b) membrane revealed poor stability as layers peeled off significantly.
Figure 4.11 Schematic description of the stability problem. Either the graphene layer completely peels off from the membrane surface after first touch with water or partial delamination occurs in membrane surface.

Due of the surface charge properties of PES membrane which is negatively charged support membrane, the charge of the surfactant has a significant effect on the stability of the graphene layer. Even though the positively charged surfactant, CTAB, showed relatively better performance compared to ionic sodium cholate and Pluronic 123 after sonic energy exposure and water filtration experiments, the stability problem has not been completely solved by changing the type of surfactant, because a small amount of graphene layers have been released from the surface during filtration. Although aqueous dispersions assisted by surfactants have many advantages in terms of the resultant flake size, being environmentally-friendly and the easy removal of water from the substrate after graphene deposition; it has been decided to not to continue any further work with this dispersion further due to stability issues.
4.2.2.6 X-ray Diffraction Analysis

In Fig. 4.13a, two G/P02 composite membranes were fabricated by using dispersions N1 (black) and N2 (blue). XRD was carried out in dry state to determine the interlayer spacing of graphene flakes. PTFE chains are arranged through well-ordered crystalline packing. The membrane has a certain degree of crystallinity which helps to identify the substrate peak. Graphene and graphene-oxide interact differently to X-rays. In literature, the typical spacing for graphite was found around 3.36Å, for GO this is around 8.33Å and for graphene it is around 3.70Å [130].

Characteristic GO diffraction peak was found at around 11° in the case of dispersion N2. This data suggested that the membrane made with N1 looked more like graphene, while the membrane with N2, at least some parts behaved like GO. Most likely, the membrane with N1 contained, to a certain degree, unexfoliated graphene (existence of some graphitic structure). This finding can be correlated with the 2D band of the Raman spectrum (section 3.2.3), in which the shape of 2D band suggested that dispersion N1 is more graphitic like structure. Unexfoliated graphitic structures in N1 gave rise to significant intensities. The membrane with N1 was not well stacked, which might indicate that the preparation of the membranes was not good enough. In the membrane made with N2, the non-exfoliated of graphite was absent or almost absent, due to the higher rotation speed, which resulted in separating the unexfoliated graphite out and providing smaller flakes in the final dispersion. These findings are consistent with DLS results (section 3.2.2) which showed that centrifugation rotational speed of 4500 rpm (N2) compared to 15000 rpm (N1) led to remove larger flakes > 200 nm. A weak and broadened peak at 26° and a relatively strong and narrow peak at 11° was observed in the case of dispersion N2. There was some ordered in the stacking of flakes due to the membrane preparation technique.

XRD patterns of G/N02 composite membranes fabricated via dispersion methods N2 (Fig. 4.13b) and S1-Se (Fig. 4.13c) are shown. The membranes were soaked into water for about 2 h before collecting XRD data from the wet phase. When these two figures are compared, it is clear that there is no significant shift of diffraction signals (2θ) in dry and wet states. The peak around 20° is caused by support membranes PTFE and Nylon. In Fig. 4.13b, 2θ cantered at 24.24° (dry) and 24.15° (wet) which resulted in a broad peak with d-spacing 3.66 Å in dry and 3.68 Å in wet phases. In Fig. 4.13c, 2θ is located at 24.22° (dry) and 24.12° (wet) which resulted in a broad peak with d-spacing 3.67 Å in dry and 3.69 Å in wet phases. There is also another peak for this membrane at about 13.6° which might be associated with some oxygen related components (recall XPS analysis, section 3.2.6) due to residual surfactant
chemical composition on the substrate. This peak is almost gone in the wet state. It might be explained by removal of the residual surfactant from the membrane surface by wetting.

Figure 4.13 XRD analysis of graphene/P02 composite membranes fabricated via dispersion N1 and N2 in dry phase (a), graphene/N02 composite membranes fabricated via dispersion N2 (b) and fabricated via dispersion S1_Sc (c) in both dry and wet phases.
4.2.2.7 Scanning Electron Microscopy

The images in Fig. 4.14 reveals the surface morphology of unmodified Nylon and PTFE membranes. Both support membranes have a quite rough top surface with relatively large pores around 270-280 nm, specifically the Nylon membrane. After introducing a certain amount of G onto the PTFE membrane, the top surface of the composite membranes was coated completely with nanosheets, as shown in Fig. 4.15. However, the surface was still rough and patterns of large holes in the substrate could still be identified after graphene coating. Membranes were examined by SEM just after filtration experiments. As can be seen from Fig. 4.16 and Fig. 4.17, the surface structure had more irregularities and defects such as cracks after filtration experiments, caused by the solute particles depositing on the membrane surface or into the pores, degrading the membrane quality. It was likely that over a long period of time this affected the performance of the membrane. It is also noticeable that the top surface morphology of the SX membrane, shown in Fig. 4.18, was relatively smooth even though the images are after filtration. Besides, the cross section image of the same membrane showed a thin graphene layer which has irregularities due to sample preparation for SEM analysis. These results indicated that dilution of graphene dispersion by a factor of 1000 times which made a dispersion N2 with a concentration of (0.16 μg/mL) has a significant effect on the stacking quality of the layers. Graphene content 0.06 – 0.16 mg/cm² provided a selective layer thickness in the range of 200 – 900 nm (Fig. 4.19)

![Image](image1.png)

**Figure 4.14** Top images of Nylon 0.2 (a) and PTFE 0.2 (b) support membranes without any surface modification.

![Image](image2.png)

**Figure 4.15** Top images of graphene/PTFE_1mg_05 composite membrane fabricated via N1 before (a, b, c) and after (d, e, f) filtration experiment.
Figure 4.16 Top images of graphene/PTFE$_{1mg_05}$ composite membrane fabricated via N2 before (a, b, c) and after (d, e, f) filtration experiment.

Figure 4.17 Top (a, b, c) and cross section (d, e, f) images of graphene/Nylon$_{1.4mg_05}$ composite membrane fabricated via dispersion N2 after filtration experiment.

Figure 4.18 Top (a, b, c) and cross section (d, e, f) images of graphene/Nylon composite membrane (SX) fabricated via dispersion N2 after filtration experiment.

Figure 4.19 Thickness of graphene layer deposited onto PTFE 0.2 support membrane. Amount of graphene used for deposition 0.5 mg (a) and 1.4 mg (b).
4.2.3 Conclusion

In this chapter, the aim was to improve selectivity of PTFE and Nylon membranes by creating a highly selective layer from exfoliated graphene fabricated via the LPE technique mentioned in previous chapter.

PMI analysis revealed that the average pore size of the membranes shifted to lower sizes from 270 nm to 55 nm by introducing graphene flakes. Here, it was important to ensure that the support membrane was completely covered with graphene. Otherwise, uncovered pores might affect membrane filtration performance. Surface morphology of the support membrane formed a basis for a good selective layer deposition. For instance, by looking at SEM surface morphology images, it was concluded that the support membranes showed a trend of having a smooth surface in the following order PES>PTFE>Nylon. A smoother surface has a potential of produce less defect formation by complete coverage of support pores with graphene. Various amounts of graphene loading were used for making composite membranes. Higher amounts of graphene deposition (1.4 mg or 0.16 mg/cm²) made a relatively thick selective layer (∼0.9 μm), causing to decreased permeation flux because of increased mass transfer resistance, while less amounts of graphene (0.5 mg or 0.06 mg/cm²) created a selective layer of 0.2 μm thick. Moreover, contact angles revealed that the relatively hydrophilic (44°, 60°) support membranes, Nylon and PTFE, became less hydrophilic after incorporating graphene. Increasing the amount of graphene loading led to an increase in water contact angles up to ∼100° in some cases. Specifically, membranes fabricated by N2 provided higher contact angles compared to N1, which might be attributed to higher roughness caused by the smaller flake size in N2. Furthermore, zeta potential measurements showed a very slight change in isoelectric points which shifted to lower pH values.

NMP based dispersions N1 and N2 were used in order to fabricate graphene composite membranes onto PTFE (0.2 μm) and Nylon (0.2-0.45 μm). PES membranes were not used with NMP based dispersions due to them not being compatible with NMP. In relation to filtration characterization of those composite membranes, a clear trend could not be observed in between the amount of graphene, from 0.5 mg to 1.4 mg, applied pressure, either 0.5 or 0.8 bar, and water permeability-rejection values. This was later confirmed by the presence of high defect densities in N02_1mg_05 and P02_1mg_08 membranes which had quite high water permeability values of 1678±707 L/m².h.bar and 6798±1217 L/m².h.bar, respectively.

Defect density tests suggested that dextran rejection of composite membranes was strongly dependent on applied pressure which meant that there was higher rejection (76%) in low
pressure (0.15 bar), and lower rejection (9%) in high pressure (1 bar). This behaviour was caused by the contribution of defects to rejection by changing pressure. However, these membranes provided very poor monovalent or divalent salt rejection, mostly lower than 15%. This situation was also in indication that the pore size of resultant membranes was not sufficiently small enough to reject salt molecules. More importantly, dilution of the graphene dispersion before the deposition process was found to be very critical in terms of obtaining ordered graphene laminates, with high quality stacking and also reduced defect formation. So, dispersions like N2, E1, S1_Se and S1_Su were diluted to nearly 5 μg/mL before membrane fabrication. The best composite membranes fabricated by diluted graphene dispersions had the following specifications: Graphene/Support Membrane_Amount of G_Dispersion (membrane name)

- G/N02_1.2 mg_N2 (SX): 80 L/m².h.bar water permeance, 23% dextran 4 rejection.
- G/N02_1.3 mg_S1_Se (M5P): 303 L/m².h.bar water permeance, 9% dextran 4 rejection.
- G/N02_0.4 mg_E1 (A6): 366 L/m².h.bar water permeance, 12% dextran 4 rejection.
- G/PES_0.3 mg_E1 (G1): 204 L/m².h.bar water permeance, 48% dextran 2000 rejection.

It was possible to conclude from the filtration results, that dilution of graphene dispersions and using another support membrane which has a smoother surface, assisted in improving composite membrane performances by reducing defects. It was also noticed that exfoliated graphene in ethanol showed relatively good performance compared to N2, which can be accepted as one of the high quality dispersions achieved in this work. Overall, the PES support membrane demonstrated the benefit of a smooth surface by providing improved selectivity compared to Nylon.

Interlayer spacing of graphene nanosheets was studied by XRD analysis. Membranes fabricated via different dispersions like N1, N2 and S1_Se provided d-spacing in the range of 3.43 Å – 3.68 Å, which was consistent with the data for graphitic like structures. However, there was a very slight change in d-spacing for wet phases. Possible explanations for this situation could be either the stability of membranes was good in aqueous phase, or that not enough wetting proceeded to get accurate results. Data from XRD was more or less dominated by the fact that the interlayer spacing was that of graphite and the resultant dispersions consisted of multilayer graphene. Serious stability problems were observed with the combination of surfactant assisted aqueous dispersions and support membranes (PES and Nylon). Thus further experiments were carried out using the best combination of working conditions, which includes the NMP based dispersion N3 and ethanol based dispersions E1,E2 onto PES and Nylon support membranes.
4.3 Graphene-Polymer Hybrid Membranes

4.3.1 Introduction

For the fabrication of graphene membranes in this chapter, previously mentioned procedure 3 and 4 were used (section 2.1.2.2). Nylon and PES were used as the support membranes and graphene-polymer hybrid membranes will be labelled as shown in the following:

\[
\text{Support}/(\text{PEI}_x/G_y/\text{PEI}_z) \\
\text{Support}/(\text{PEI}_x/G_y+\text{EDA}_k/\text{PEI}_z)
\]

Where;

- \(x\) and \(z\): Concentration of polyethyleneimine (PEI) solution, mg/mL.
- \(y\): Amount of graphene per area, mg/cm².
- \(k\): Weight ratio of ethylenediamine (EDA).

4.3.2 Results and Discussion

4.3.2.1 Study of Membrane Surface Properties

Zeta potentials of the unmodified support membranes PES (Fig. 4.20a) and Nylon (Fig. 4.20b) and their graphene/polymer hybrid membranes at pH values from 3 to 11 were shown as in the figures above.

\[\text{Figure 4.20 Zeta potential of PES membrane (unmodified), 0.5 - 3 mg/mL PEI modified PES membranes, graphene/polymer hybrid membranes (a). Zeta potential of Nylon 0.2 \mu m membrane (unmodified), 0.5 - 3 mg/mL PEI modified Nylon membrane, graphene/polymer hybrid membranes (b) PES (PEI}_3/G/\text{PEI}_3) \text{ and Nylon (PEI}_3/G/\text{PEI}_3).\]

Results revealed that the PES membrane without modification was highly negatively charged in a wide pH range of 3 to 11, had an isoelectric point (IEP) (which is pH value at which zeta potential of membrane is zero) at pH 3, while unmodified Nylon was negatively
charged in the range of pH 7 to 11, with an IEP at pH 7. However, it is apparent that after introducing the first PEI layer onto the support membranes, surface charge properties changed immediately and IEP shifted to higher pH values according to the PEI concentration. A higher PEI concentration led to a bigger change in the IEP. After modification with 3 mg/mL of the 1st PEI layer, the IEP shifted from 3 to 8.6 for PES and from 7 to 9.3 for Nylon. In addition to this, it can be seen from the results that coating with graphene led to a further increase in both the absolute zeta potential values and IEP's (from 9.3 to 10.2 for PES, from 8.6 to for Nylon) for both PES and Nylon support membranes. Based on the electrical double layer theory\[347, 348\], a decrease in absolute zeta potential values can be explained by the compression of the electrical double layer due to an increase in ionic strength. The extension of the electrical double layer causes an increase in absolute zeta potential values.

A further increase of the IEP was occurred after the 2nd layer of PEI, 10.3 for PES and 10.4 for Nylon cases. This happened due to the existence of an abundant amino group in PEI. In conclusion, with introducing PEI, the surface charge of membranes became more positive.

4.3.2.2 Fourier-Transform Infrared Spectroscopy (FTIR)

Fig. 4.21 shows the FTIR spectra of PES membranes after each assembling stage with various concentrations of PEI (0.5-3 mg/mL). The unmodified PES membrane had the following vibration peaks; hydroxyl groups -OH stretching vibration at 3309 cm\(^{-1}\), C-H stretching at 2877 and 2934 cm\(^{-1}\), the peak at 1670 cm\(^{-1}\) can be attributed to the carbonyl group (C=O) of amide groups, the peaks around 1487 cm\(^{-1}\) and 1580 cm\(^{-1}\) are C=C stretching in aromatic ring, the peaks at 1170 cm\(^{-1}\) and 1230 cm\(^{-1}\) are due to S=O stretching of PES aromatic rings[349-352]. OH stretching vibration at 3309 cm\(^{-1}\) and asymmetric and symmetric stretching of C-H at 2934 cm\(^{-1}\) and 2877 cm\(^{-1}\) disappeared when PEI was introduced to the membrane surface. Since these aliphatic peaks do not belong to PES, they might have been caused by the water in the membrane which was probably not completely dry. The peaks could also have been caused by the fact that there might have been PVP which binds to water. So, probably the spectrum has been taken for an unmodified membrane which may not have been completely depleted of the additional substances, they were still in the membrane as received, and later these additional substances have been washed out when composite membranes were prepared.
Fig. 4.2b, illustrates the FTIR spectrum of the composite membranes. C-H vibration stretching can be seen at 2845 cm\(^{-1}\) and 2923 cm\(^{-1}\), the carbonyl group (C=O) peak at 1670 cm\(^{-1}\) was found in all membranes. However, extra peak at 1737 cm\(^{-1}\) and 1300-1330 cm\(^{-1}\) appeared in the case of PEI modified G membranes (M15, M4) case due to C=O stretching. These peaks were not observed in cross-linker modified graphene composite membrane cases (M19,M21,M23)[190,200].
Table:

<table>
<thead>
<tr>
<th>Membrane ID</th>
<th>Modification Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>M15-M14</td>
<td>PES (PEI₃/G₀.₀₆/PEI₃)</td>
</tr>
<tr>
<td>M19-M18</td>
<td>PES (PEI₃/G₀.₀₆+EDA₁₂₀₀₀/PEI₃)</td>
</tr>
<tr>
<td>M21-M20</td>
<td>PES (PEI₃/G₀.₀₆+EDA₁₅₀₀₀₀/PEI₃)</td>
</tr>
<tr>
<td>M23-M22</td>
<td>PES (PEI₃/G₀.₀₆+EDA₁₅₀/PEI₃)</td>
</tr>
<tr>
<td>M4</td>
<td>PES (PEI₃/G₀.₀₆/PEI₃)</td>
</tr>
</tbody>
</table>

Figure 4.22 FTIR spectra of an unmodified PES membrane and various concentration of PEI modified PES membranes and graphene-polymer/PES hybrid membranes (a) and enlarged FTIR spectra of graphene-polymer/PES hybrid membranes (b).
In Fig. 4.23, characteristic peaks for Nylon appeared around 2935, 1371, and 1199 cm$^{-1}$ due to CH$_2$ stretching, C-N stretching + in-plane N-H deformation, an amide III band and an amide III band coupled with the hydrocarbon skeleton, respectively\cite{53}. The peak observed at 1630 cm$^{-1}$ is attributed to the amide I band and a carbonyl stretching vibration in the Nylon unit. The peak at 1541 cm$^{-1}$ appears due to the amide II band and CH$_2$ asymmetric deformation\cite{54} \cite{55}. 

**Figure 4.23** FTIR spectra of an unmodified Nylon 0.2 (N02) membrane and various concentration of PEI modified Nylon membranes.
FTIR spectra of an unmodified Nylon 0.2 membrane and various concentrations of PEI modified Nylon 0.2 membranes and graphene-polymer/N02 hybrid membranes (a) and enlarged FTIR spectra of graphene-polymer/N02 hybrid membranes (b).

**Figure 4.24** FTIR spectra of an unmodified Nylon 0.2 membrane and various concentrations of PEI modified Nylon 0.2 membranes and graphene-polymer/N02 hybrid membranes (a) and enlarged FTIR spectra of graphene-polymer/N02 hybrid membranes (b).

Fig. 4.24b shows the enlarged FTIR spectrum of graphene-polymer/Nylon hybrid membranes. The spectrum contained very weak peaks, centred at almost same wavelength, compared to unmodified Nylon membrane. In graphene-polymer hybrid membranes, absorption peaks were almost disappeared or were diminished due to covalent bonds with PEI, EDA and G.
4.3.2.3 X-Ray Diffraction (XRD)

Two membranes fabricated via E1 and E2, which have the best working conditions in terms of water flux and rejection, were chosen for further analysis to monitor interlayer distance changes in dry and wet phases by using XRD measurements. Variations of d-spacing can be explained by the solution which entered/diffused in between the graphene layers. This resulted in destroying hydrogen bonds and π–π interaction, consequently stretching the d-spacing.[199][336][357].

XRD patterns of graphene-polymer hybrid membranes fabricated via dispersion E1 (Fig. 4.25) and E2 (Fig. 4.26) are shown. The membranes were soaked in water for about 2 h before collecting XRD data from the wet phase. When compared to two figures, characteristic diffraction signal (2θ) of graphene in both phases is located at in between~26° - 27°. In the case of PES (PEI3/G0.06/PEI3) and PES (PEI3/G0.06+EDA1200/PEI3) fabricated via E1, d-spacing was 3.336 Å and 3.343 Å in dry state and shifted to 3.345 Å, 3.343 Å in the wet state. In the case of PES (PEI3/G0.16/PEI3) and PES (PEI3/G0.16+EDA1200/PEI3) fabricated via E2, d-spacing was 3.34 Å and 3.354 Å in the dry state and increased 3.354 Å, 3.361 Å in the wet state. From these results, it can be drawn that introducing EDA to graphene caused a slight increase in interlayer distance; however, it enhanced the stability of the membrane in the wet state, which resulted in very little change in the interlayer distance. The peaks in Fig. 4.25 are sharper and stronger due to the presence of not well-exfoliated graphitic like structures in the dispersion (E1) compared to the peaks in Fig. 4.26. This is consistent with particle size results mentioned in chapter 3. Graphene dispersions fabricated via method E1 have a broad size distribution with includes thicker flakes.

Increasing graphene content from 0.06 mg/cm² to 0.16 mg/cm² did not contribute to the d-spacing substantially. However, the membrane with cross-linker graphene showed relatively stable layer formation because there is almost no change in d-spacing in wet phases as can be seen in Fig. 4.25b and Fig. 4.26b. This is consistent with the fact that adding the intercalating cross-linker (EDA) into graphene layers improved stability by enhancing d-spacing.

Membranes fabricated with E1 showed higher crystalline size (Table 4.6), 22 nm and 35 nm, rather than those fabricated with E2, 13nm in both phases. This is in line with characterization results presented in chapter 3, which suggested that E1 was a dispersion with relatively bigger flakes compared to E2 which was formed by the expulsion of some parts of the dispersion from the E1 via further centrifugation. Introducing the cross-linker EDA,
crystalline size became larger, from 22 nm to 35 nm, due to the expansion of graphene domains. However, this was not observed in the case of the membrane with E2 (Fig. 4.26b), which presented 13 nm size in both with and without cross linked graphene. Furthermore, based on the Debye-Scherrer’s equation (Eq. 1.6), estimation of number of layer for each flake in the dispersions was calculated and stated in Table 4.6. So, the results suggested that E1 and E2 dispersions have multi-layer structure of graphene which is consistent with the previous results obtained from AFM.

Figure 4.25  XRD analysis of PES/(PEI$_3$/G$_{0.06}$/PEI$_3$) fabricated via dispersion E1 in both dry and wet phases (a) and PES/(PEI$_3$/G$_{0.06}$+EDA$_{1200}$/PEI$_3$) fabricated via dispersion E1 in both dry and wet phases (b).

Figure 4.26  XRD analysis of PES/(PEI$_3$/G$_{0.16}$/PEI$_3$) fabricated via dispersion E2 in both dry and wet phases (a) and PES/(PEI$_3$/G$_{0.16}$+EDA$_{1200}$/PEI$_3$) fabricated via dispersion E2 in both dry and wet phases (b).
Table 4.6 Crystallite size (nm) of the hybrid membranes from XRD analysis.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Crystallite Size (nm)</th>
<th>Based on Eq. 1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry Phase</td>
<td>Wet Phase</td>
</tr>
<tr>
<td>PES/PEI$<em>3$/G$</em>{0.06}$/PEI$_3$</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>PES/PEI$<em>3$/G$</em>{0.06}$+EDA$_{1200}$/PEI$_3$</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>PES/PEI$<em>3$/G$</em>{0.16}$/PEI$_3$</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td>PES/PEI$<em>3$/G$</em>{0.16}$+EDA$_{1200}$/PEI$_3$</td>
<td>13</td>
<td>14</td>
</tr>
</tbody>
</table>

4.3.2.4 Contact Angle Analysis

The hydrophilicity/hydrophobicity of the membranes surfaces was determined by measuring their water contact angles. Hydrophilic membranes provide a contact angle of 0°< θ < 90° while hydrophobic membranes possess a contact angle of 90°< θ < 180°. It has been expected that because graphene does not provide any hydrophilic functional group, the overall hydrophilicity of the membrane is reduced when graphene is incorporated into the membrane and hydrophobic parts of polymers cause increasing water contact angle, so improved hydrophobicity which is not favourable for enhanced water permeation.

Nylon and PES support membranes have water contact angles of 44° ± 14.7 and 85° ± 5.2, respectively (Fig. 4.27 and Table 4.7). An unmodified Nylon support membrane exhibited more hydrophilic structure than a PES support membrane. After introducing the 1st PEI layer, both support membranes became more hydrophobic, this situation was more pronounced in the Nylon case.

Graphene-polymer/PES hybrid membranes showed mean contact angles mostly in the range of 70° - 80°, and were still hydrophilic in nature whilst graphene-polymer/Nylon hybrid membranes were in between 80° - 100°. This indicated that the hydrophobicity of the final membranes improved with incorporating graphene-polymer content in the case of Nylon membranes. However, the graphene-polymer did not significantly affect the final membranes’ wetting properties in the case of graphene-polymer/PES hybrid membranes.

Increasing graphene amount from 0.06 mg/cm$^2$ to 0.2 mg/cm$^2$ (M14 to M34) led to a decrease in the water contact angle up to 70° ± 3.8 in graphene/PES membranes. The same phenomenon was observed in graphene/Nylon membranes (M6-M8).
Figure 4.27 Water contact angle measurement of graphene-polymer/PES hybrid membranes fabricated via dispersion E2 (M14 – M37) and E1 (PES 15, PES 17) (a), and graphene-polymer/N02 hybrid membranes fabricated via dispersion N3 (M6, M8, M9, M12, M13) and E2 (M30 and M32) (b). Specifications of membranes were shown in below table.
Table 4.7 Water contact angle (°) values of the membranes shown above figure.

<table>
<thead>
<tr>
<th>Membrane Configuration</th>
<th>Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES</td>
<td>85 ± 5.2</td>
</tr>
<tr>
<td>PES/PEI$_{0.5}$</td>
<td>93 ± 5.6</td>
</tr>
<tr>
<td>PES/PEI$_{3}$</td>
<td>87 ± 3.7</td>
</tr>
<tr>
<td>PES 15 PES (PEI$<em>{0.5}$/G$</em>{0.06}$/EDA$<em>{1200}$/PEI$</em>{0.5}$)</td>
<td>76 ± 1.6</td>
</tr>
<tr>
<td>PES 17 PES (PEI$<em>{0.5}$/G$</em>{0.06}$/PEI$_{0.3}$)</td>
<td>83 ± 1.6</td>
</tr>
<tr>
<td>M14 PES (PEI$<em>{3}$/G$</em>{0.06}$/PEI$_{3}$)</td>
<td>93 ± 8.7</td>
</tr>
<tr>
<td>M29 PES (PEI$<em>{3}$/G$</em>{0.06}$/PEI$_{3}$)</td>
<td>86 ± 2.2</td>
</tr>
<tr>
<td>M16 PES (PEI$<em>{3}$/G$</em>{0.11}$/PEI$_{3}$)</td>
<td>73 ± 1.9</td>
</tr>
<tr>
<td>M27 PES (PEI$<em>{3}$/G$</em>{0.16}$/PEI$_{3}$)</td>
<td>76 ± 2.2</td>
</tr>
<tr>
<td>M36 PES (PEI$<em>{3}$/G$</em>{0.16}$/PEI$_{3}$)</td>
<td>-</td>
</tr>
<tr>
<td>M34 PES (PEI$<em>{3}$/G$</em>{0.2}$/PEI$_{3}$)</td>
<td>70 ± 3.8</td>
</tr>
<tr>
<td>M22-M23 PES (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{15}$/PEI$</em>{3}$)</td>
<td>80 ± 9.0</td>
</tr>
<tr>
<td>M18 PES (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{1200}$/PEI$</em>{3}$)</td>
<td>87 ± 16.4</td>
</tr>
<tr>
<td>M20 PES (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{15000}$/PEI$</em>{3}$)</td>
<td>80 ± 6.4</td>
</tr>
<tr>
<td>M37 PES (PEI$<em>{3}$/G$</em>{0.16}$/EDA$<em>{15}$/PEI$</em>{3}$)</td>
<td>77 ± 1.6</td>
</tr>
<tr>
<td>M28 PES (PEI$<em>{3}$/G$</em>{0.16}$/EDA$<em>{15}$/PEI$</em>{3}$)</td>
<td>66 ± 3.8</td>
</tr>
<tr>
<td>M35 PES (PEI$<em>{3}$/G$</em>{0.2}$/EDA$<em>{15}$/PEI$</em>{3}$)</td>
<td>76 ± 4.9</td>
</tr>
<tr>
<td>N02</td>
<td>44 ± 14.7</td>
</tr>
<tr>
<td>N02/PEI$_{0.5}$</td>
<td>150 ± 20.3</td>
</tr>
<tr>
<td>N02/PEI$_{3}$</td>
<td>144 ± 4.1</td>
</tr>
<tr>
<td>M6 Nylon (PEI$<em>{3}$/G$</em>{0.06}$/PEI$_{3}$)</td>
<td>102 ± 7.1</td>
</tr>
<tr>
<td>M8 Nylon (PEI$<em>{3}$/G$</em>{0.11}$/PEI$_{3}$)</td>
<td>88 ± 4.0</td>
</tr>
<tr>
<td>M9 Nylon (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{1200}$/PEI$</em>{3}$)</td>
<td>83 ± 4.5</td>
</tr>
<tr>
<td>M12 Nylon (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{15000}$/PEI$</em>{3}$)</td>
<td>92 ± 5.6</td>
</tr>
<tr>
<td>M13 Nylon (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{15}$/PEI$</em>{3}$)</td>
<td>84 ± 8.0</td>
</tr>
<tr>
<td>M30 Nylon (PEI$<em>{3}$/G$</em>{0.06}$/PEI$_{3}$)</td>
<td>84 ± 2.3</td>
</tr>
<tr>
<td>M32 Nylon (PEI$<em>{3}$/G$</em>{0.06}$/EDA$<em>{1200}$/PEI$</em>{3}$)</td>
<td>84 ± 4.5</td>
</tr>
</tbody>
</table>
4.3.2.5 Gas Flow/Pore Dewetting Permporometry

In both figures shown below, layer-by-layer graphene-polymer hybrid membranes were shown with pore size distribution (%) and gas permeability as a function of pressure. What has been seen from the results in Fig. 4.28 and Fig. 4.29, gas permeability of these modified membranes was much lower than unmodified support membrane (Nylon 0.2). A possible interpretation would be that, some part of the base membrane was not covered completely with graphene and PEI modification, as large pores still existed on the surface.

**Figure 4.28** Gas (dry) flow measurement as a function of applied pressure (a) and pore size distribution (b) of graphene-polymer/Nylon hybrid membranes fabricated via dispersion N3. Unmodified Nylon 0.2 and 0.5/3 mg/mL of PEI modified Nylon 0.2 membrane were also added to the graphs.

**Figure 4.29** Gas (dry) flow measurement as a function of applied pressure (a) of pore size distribution (b) graphene-polymer/Nylon hybrid membranes fabricated via dispersion E1. Unmodified Nylon 0.2 and 3 mg/mL of PEI modified Nylon 0.2 membrane were also added to the graphs.
Modified membranes had a broad pore size distribution with big and small pores, a combination of pores in the range of $0.06 \mu m \leq x \leq 0.2 \mu m$. This situation confirmed the existence of uncovered pores which caused the unfortunate consequence that the majority of permeability (Fig. 4.33) without gaining selectivity was lost.

Figure 4.30 Gas (dry) flow measurement as a function of applied pressure (a) and pore size distribution (b) of graphene-polymer/PES hybrid membranes fabricated via dispersion E1. Unmodified PES and 0.5/3 mg/mL of PEI modified PES membrane were also added to the graphs. Graphene content: 0.06 mg/cm².

Graphene-polymer/Nylon and graphene-polymer/PES hybrid membranes were prepared via the exfoliated graphene dispersion E1. The average pore size of commercial support membranes and modified composite membranes were measured by capillary flow porometry (PMI) as shown in Fig. 4.30 and Fig. 4.31. It has been observed that unmodified PES membrane had a very narrow size distribution and gave a peak at 0.12 µm (Fig. 4.31a) and Nylon gave a peak at 0.2~0.27 µm as indicated earlier in Fig. 4.2b and Fig. 4.31b.
Figure 4.31 Gas (dry) flow measurement as a function of applied pressure (a) and pore size distribution (b) of graphene-polymer/Nylon hybrid membranes fabricated via dispersion E1. Unmodified Nylon 0.2 and 0.5/3 mg/mL of PEI modified Nylon 0.2 membrane were also added to the graphs. Graphene content: 0.06 mg/cm².

In the case of PES support membrane, after assembling the first PEI layers with concentrations of 0.5 mg/mL and 3 mg/mL, pore size shifted to smaller values 0.1 µm and 0.084 µm, respectively. Increasing PEI concentration led to a decrease in pore size. The same behaviour also was observed in Nylon support membrane cases. Increasing the concentration of the first layer of PEI from 0.5 to 3 mg/mL, caused to a decrease of the support membrane's average pore size up to ~ 0.1 µm. In that case, 0.5 mg/mL of PEI was not enough to cover the majority of pores as it only assisted in a shift to ~ 0.2 µm. A more pronounced improvement came from 3 mg/mL of PEI since Nylon has a bigger pore size compared to the PES membrane.

Interestingly, PES (PEI₀.₅/G) which is plotted as green in Fig. 4.31a, revealed 99% of the pores in to be 64 nm. However, after incorporating the 2nd layer of PEI, the membrane PES (PEI₀.₅/G/PEI₀.₅), which was represented with the purple, exhibited a broad pore size distribution in the range of 64 nm – 100 nm. The appearance of bigger pores after introducing an additional PEI layer can be explained by the delamination of some graphene layers during the PEI modification, which caused to big pores to become visible again. This might be due to the stability issue of the graphene layer on PES membranes as it has not been observed in Nylon membrane cases (Fig. 4.31b). 98% of pores of N02 (PEI₀.₅/G/PEI₀.₅) membranes were exactly 88 nm.
4.3.2.6 Filtration Performance

The effects of PEI (Fig. 4.32b) and graphene deposition (Fig. 4.32c) were analysed based on PES membrane filtration performance in terms of pure water permeability and dextran 2000 kDa rejection.

Figure 4.32 Average water permeability (L/m².h.bar) and rejection for PES membranes without any surface modifications (a), with PEI surface modifications at various concentrations and various operating times on a hot plate at 70°C (b) and PES 9 membrane, PES-graphene and PES_(PEI₀.₅/G₀.₀₄) (c).

Unmodified commercial PES membranes showed a water permeability behaviour in the range of 1400 – 1930 LMH/bar with almost zero rejection of dextran 2000 kDa which was confirmed by pore size analysis of the PES membrane (Fig. 4.30a). The capillary pore size analysis indicated that the average pore size of PES was around 0.12 μm (Fig. 4.30b). So, very low rejection of dextran 2000 kDa matched with the expectation of bigger pore sizes >50 nm (the approximate molecular size of dextran 2000 kDa, Table 4.1) in the support membrane.

Furthermore, it has been questioned whether 2 hours at 60 °C oven drying process after graphene deposition onto PES support membrane caused any chemical deterioration or not. In order to explore this, the membrane after the water permeability test, before moving directly to rejection test, two membranes (PES 2 and PES 5) were dried at 60 °C for 2 hours in between the experiments. Apparently, there is no significant difference with or without drying.

As shown in Fig. 4.32b, after introducing PEI at various concentrations under different time conditions into the membrane, water permeability decreased by nearly 18% to 1592 LMH/bar (PES 6) or even by 53% to 911 L/m².h.bar (PES 3) and rejection was improved up to 25%. This can be explained by surface modification with PEI which led to create a
thin smoother dense layer (SEM image, Fig. 4.43) on the membrane surface and resulted in decreased pore size. However, after graphene deposition on unmodified and PEI (0.5 mg/mL) modified PES membranes, permeability sharply decreased to 204 and 165 L/m².h.bar and rejection increased up to 48% and 60%, respectively. This suggested that graphene had a significant effect on permeability and rejection as a small amount of graphene amount led to an increase in membrane thickness. So, membrane resistance was mainly caused by graphene content rather than PEI modification. It is clear that the PEI layer has an influence on flux (loss in flux) as it increases the membrane’s resistance. That depends on the membrane, structure of PEI and PEI concentration.

**Figure 4.33** Performance of average water permeability (L/m².h.bar) and dextran 4kDa and 2000kDa rejection of graphene-polymer/Nylon hybrid membranes prepared by dispersion N3.

Fig. 4.33 indicates the impacts of unmodified and modified graphene with the cross linker (EDA) on the pure water permeability and rejection of layer-by-layer graphene-polymer hybrid membranes. Increasing graphene amount deposited onto Nylon membrane (Fig. 4.33a) from 0.06 mg/cm² to 0.11 mg/cm² resulted in a decrease in water permeability from 175 L/m².h.bar to 166 L/m².h.bar. Furthermore, it can be observed that the membranes showed lower water permeability with EDA cross-linked graphene (Fig. 4.33b) compared to the membranes fabricated by graphene without cross-linker (Fig. 4.33a). Increasing the
amount of EDA (G-EDA wt/wt 1:15, 1:1200, 1:15000) by keeping graphene content constant (0.06 mg/cm²) caused a decrease in water permeability up to 43 L/m².h.bar as shown in above figure. However, despite this big loss in permeability, from 7338 (Nylon support membrane) up to 43 L/m².h.bar, there was no significant improvement in dextran rejection which might be explained by the presence of a high defect density. Alternatively, in the case of 1-1200 (T), the membrane was dried at 50 °C for 12 h in a vacuum oven after graphene assembly (before the 2nd layer of PEI) in order to see the effect of drying time effect on the chemical cross-linking reaction of graphene and EDA. Comparing filtration result of this membrane with 1-1200, which is identical with 1-1200 (T) except for the drying time (2 h in 1-1200 membrane), water permeability behaviour was very similar. However, dextran 2000 kDa rejection increased up to 46%. This might be explained by exposure of the membrane to long hours of heat treatment, which as a result, reduced some defects with enhanced chemical bonding between EDA and graphene. To conclude from these filtration results, big reduction in water permeability and poor dextran rejection of graphene-polymer/Nylon membranes might be caused by some parameters in fabrication mechanism such as type of graphene dispersion (solvent effect), surface morphology of the support membrane. The membranes in Fig. 4.33 were fabricated by using NMP based dispersion (N3). High boiling point solvent, NMP might be caused some defects on the membrane along with the removal process by changing the pore morphology[358]. So, considering these possible variations, some changes were studied on membrane filtration performance. i.e., ethanol based dispersion, another type of support membrane (PES) which has smaller pores (~0.12 μm) than Nylon (~0.27 μm) and PEI concentration (mg/mL).
Figure 4.34 Performance of average water permeability (L/m²·h·bar) and dextran 4kDa and 2000kDa rejection of graphene-polymer/Nylon and graphene-polymer/PES hybrid membranes prepared by dispersion E1 in two different support materials, Nylon and PES.

Fig. 4.34 shows the water permeability and rejection comparison of layer-by-layer graphene-polymer hybrid membranes fabricated via dispersion E1 onto PES (Fig. 4.34c, Fig. 4.34d) and Nylon (Fig. 4.34a, Fig. 4.34b) support membranes. When comparing the membranes filtration performance, it was apparent that graphene-polymer/PES hybrid membranes showed superior performance with water permeability in the range of 17 - 35 L/m²·h·bar and with over 90% rejection of dextran 2000kDa (Fig. 4.34c, Fig. 4.34d). Specifically in Fig. 4.34c, increasing the PEI concentration from 0.5 mg/mL to 3 mg/mL in graphene-polymer/PES membranes did not affect permeability and rejection significantly, it only led to a small change in both values. However, cross-linked graphene (Fig. 4.34d) led to a bit more decrease in permeability from 28 to 17 L/m²·h·bar.

However, graphene-polymer/Nylon hybrid membranes had much higher permeability compared to graphene-polymer/PES hybrid membranes and still lower dextran rejection below 20% in all cases, which might be explained by the existence of pores which were not completely covered with graphene, or major defects which contributed mostly to the permeability and selectivity of the membranes. These results confirmed that support membrane (PES) with a small pore size provided better filtration performance.
SEM images and capillary flow porometer analysis of Nylon and PES revealed that Nylon has much bigger pores, which also made possible for creating non-ordered graphene laminates with high defect densities possible.

**Figure 4.35** Top (right) and cross section (left) SEM images of membrane graphene-polymer/Nylon hybrid membrane. Nylon/(PEI 0.5/G0.06+EDA1200/PEI 0.5)

An phenomenon was observed during the experiments. The SEM images taken by one of the graphene-polymer/Nylon hybrid membranes in Fig. 4.35 indicated that a bunch of graphene flakes and EDA had agglomerated on top of the membrane surface. This situation directed to consider the following question: Did this occur because of a possible aggregation of the monomer ethylenediamine (EDA) with the graphene mixture during reaction time? To understand this, changes in particle hydrodynamic size have been analysed by using dynamic light scattering (DLS) measurement. Aggregation test for graphene and ethylenediamine (EDA) mixture was conducted in order to study how hydrodynamic size of particles changed within a certain of time.
Figure 4.36 Particle size (nm) change of Graphene + EDA mixture during a certain of time. Graphene dispersion was fabricated via method E1. Particle size of Graphene + EDA mixture peaked at 289 nm (37%), 486 nm (31%), 687 nm (41%) after 5, 7 and 12 h respectively.

A certain amount of ethylenediamine (EDA) was added to the dilute graphene dispersion in order to enhance the stability of graphene nanochannels and improve stacking quality of graphene selective layer during the graphene deposition process. Since the reaction time for the mixture (graphene+EDA) varies in literature, in the first experiments 7 h was given to enhance the strength of the covalent bonds between graphene and EDA.

DLS was used to study the change in particle size of the diamine modified graphene nanosheets during the reaction time. As can be seen in Fig. 4.36, there is an obvious shift to bigger sizes and the particle size of the mixture significantly increased over the time. The obtained results implied that the graphene+EDA mixture started to aggregate after 5 hours and continued to aggregate until 12 hours. This situation also was confirmed by the above SEM image taken of an layer-by-layer graphene-polymer/Nylon hybrid membrane (Fig. 4.35) which showed a ‘hill’ (a cluster of graphene and diamine) on top of the membrane surface. In further analyses, some of improvements was considered and studied in order to increase the quality of the membranes such as using a better dispersion which is E2 compared to E1 in terms of flakes size and thickness, adjusting cross-link reaction time which was set at 1 h to eliminate the aggregation problem and focusing only PES support membrane to enhance the filtration performance of the graphene-polymer hybrid membranes.
In Fig. 4.37, various amounts of graphene from dispersion E2, with and without EDA, were used in order to find the best working conditions of graphene-polymer hybrid membranes onto PES support membrane. As shown in Fig. 4.37a, increasing graphene content caused a decrease in water permeability by a factor of almost 50% from 77 to 33 L/m$^2$.h.bar and increase in the rejection of dextran 4 kDa up to 30% and 2000 kDa up to 94%. It was also observed that the decline in water permeability from 0.16 mg/cm$^2$ to 0.2 mg/cm$^2$ was no more pronounced than in other loadings. This might be attributed to the saturation point of graphene content on water permeability. Once graphene content has reached a certain level any additional effects become negligible. In Fig. 4.37b, the weight ratios of graphene and EDA were analysed to find the best combination, as different ratios were used during this work. While keeping the graphene content constant (0.06 mg/cm$^2$) and increasing the amount of EDA (t ratio) from 1-15 to 1-1500 caused slight change in membrane filtration performance in terms of permeability (reduced water permeability by ~15% (from 53 to 45 L/m$^2$.h.bar) and rejection (increased by ~36% for dextran 4 and ~7% for dextran 2000). However, when keeping the EDA amount constant (1-15), increasing graphene amount from 0.06 mg/cm$^2$ up to 0.2 mg/cm$^2$ led to reduction in permeability by ~43% (from 53 to 30 L/m$^2$.h.bar) and higher rejection (increased by ~75% for dextran 4 and ~28% for dextran 2000).
2000) (Fig. 4.37c). These filtration results revealed that contribution of graphene amount of membrane filtration is more pronounced rather than cross-linker amount.

It is possible to conclude that the best membranes based on the optimum filtration performance (as much as high water permeability with dextran 2000 rejection over 90%) without cross-linker content had the following specifications: PES as support membrane, 3 mg/mL PEI surface modification, 0.2 mg/cm² graphene from dispersion E2 (PES (PEI₃/G₀.2/PEI₃)) and the best membrane with cross-linker content had the following specifications: PES as support membrane, 3 mg/mL PEI surface modification, 0.2 or 0.16 mg/cm² graphene from dispersion E2 and 1-15 or 1-1200 (wt/wt) graphene-cross-linker ratio (PES (PEI₃/G₀.2+EDA₁₅/PEI₃) - PES (PEI₃/G₀.1₆+EDA₁₂₀₀/PEI₃)).

![Figure 4.38](image-url) Relative water flux (L/m².h) decline of graphene-polymer/PES hybrid membranes; M34, M35 and M43 as a function of filtration time. J is the permeate flux (L/m.h) and J₀ is the initial flux (L/m.h).

Another significant factor which has an important impact for determining membrane performance is water flux decline during the filtration process. According to Fig. 4.38, the ratio of the permeate flux (J) at the time (t) to the initial flux (J₀) changed with the filtration period. Water flux of all three graphene-polymer/PES hybrid membranes considerably decreased over testing time before becoming stable. The results showed that membranes modified with a cross linker (M43 and M35) maintained initial fluxes of 33% and 25%, respectively compared to that of membrane without cross-linker (M34), which maintained 19% of its initial flux. During the filtration process in a dead-end filtration cell, membrane
is pressurized and then, starts to compact and became deformed after a period of time. Decrease in water flux mainly associated with either compaction of support membrane [359-361] or increase in selective layer thickness or decrease in porosity [360, 362]. The change in the support membrane thickness was studied by examining cross-section SEM images of support membrane PES and M43, M35 and M34 membranes. In Fig. 4.39, the results showed that thickness of porous support membrane PES decreased from 45.1 µm to 40.6 µm after operation in pressure. Thickness reduction in membranes fabricated by cross-linker (M43 and M35) was much lower than that of membranes fabricated without cross-linker (M34). This finding was also supported by the flux decline. So, it could be concluded that the loss of the flux was caused by compaction.

![Cross section SEM images and thickness of porous support of PES membrane (a), membrane 43 (b), membrane 35 (c) and membrane 34 (d).](image)

**Figure 4.39** Cross section SEM images and thickness of porous support of PES membrane (a), membrane 43 (b), membrane 35 (c) and membrane 34 (d).

In the following study, graphene-polymer hybrid membranes after deposition process were exposed to longer heat treatment in order to study the effect of heat on membrane filtration performance.
Here, in Fig 4.40, the parameter that is different from the other experiments was an increase to the time that membranes stayed in the oven before the 2nd layer of PEI, from 2h to 12 h. So, M29, M30, M31 and M32 membranes after graphene assembly, were dried at 50 °C for 12 h in a vacuum oven in order to see the effect of drying time effect on membrane performance. When compared to the previously mentioned M26 membrane in Fig. 4.33 (Nylon (PEI₃/G₀.06+EDA₁₂₀₀/PEI₃)), these composite membranes showed higher water permeance with poor rejection in all cases. These results indicated that long heat treatments, up to 12 h, did not help to improve the filtration performance of graphene-polymer hybrid membranes. Therefore, the previously achieved filtration performances, of graphene-polymer/PES membranes, have not been improved upon as seen in membrane M29 and M31. These results were also an indication that once a certain level of chemical cross-linking has been achieved, it was not possible to exceed it.
4.3.2.7 Scanning Electron Microscopy

The surface morphology of unmodified and modified support membranes (Nylon and PES) were examined by scanning electron microscopy. Both support membranes have sponge-like structures as can be seen in SEM cross section images. Furthermore, the surface of the PES membrane is smoother (Fig. 4.41b) than the Nylon membrane, as Nylon has bigger pores (Fig. 4.41a). As clearly presented in Fig. 4.42 and Fig. 4.44, a higher PEI concentration led to the formation of a woven mesh-like structure by intertwining PEI chains on the membrane support, which is adequate for absorbing graphene nanosheets and also providing a smooth surface for graphene coating.

![Figure 4.41](image1.png)  
**Figure 4.41** Top images of Nylon (a) and PES (b) membrane without any surface modification.

![Figure 4.42](image2.png)  
**Figure 4.42** Top (a, b, c) and cross section (d, e, f) images of PES/PEI.
Figure 4.43 Top (a, b) and cross section (c, d) images of PES/PEI$_{0.5}$.

Figure 4.44 Top (a, b) and cross section (c, d) images of N02/PEI$_{3}$.

Figure 4.45 Top (a, b) and cross section (c, d) images of N02/PEI$_{0.5}$.
Figure 4.46 Top (a, b, c) and cross section (d, e, f) images of M14 (PES (PEI\textsubscript{3}/G\textsubscript{0.06}/PEI\textsubscript{3})). Membrane is fabricated via dispersion E2.

Figure 4.47 Top (a, b, c) and cross section (d, e, f) images of M16 (PES (PEI\textsubscript{3}/G\textsubscript{0.11}/PEI\textsubscript{3})). Membrane is fabricated via dispersion E2.

Figure 4.48 Top (a, b, c) and cross section (d, e, f) images of M28 (PES (PEI\textsubscript{3}/G\textsubscript{0.16}+EDA\textsubscript{15}/PEI\textsubscript{3})). Membrane is fabricated via dispersion E2.
The thickness of the selective layer, made of graphene-polymer on the membrane surface, is a crucial factor in terms of the membrane’s selectivity. It increases as the amount of graphene deposited increases, resulting in a water permeance decline as shown in Fig. 4.37. The dense selective layer also reduces possible defects gradually. The thickness of the selective layer, of graphene-polymer/PES (Fig. 4.46–Fig. 4.48) and graphene-polymer/Nylon hybrid membranes (Fig. 4.49), were measured by using cross-section SEM images of each sample. It should be noted that thickness does not increase linearly with graphene content for both support membranes. A loosely packed graphene layer was obtained with a G content of 0.06 mg/cm². On the other hand, increasing the graphene content up to 0.16 mg/cm² resulted in a tight graphene layer, as can be seen in Fig. 4.48. The type of support membrane is another significant factor which affects overall membrane performance. 0.06 mg/cm² and 0.11 mg/cm² of graphene, formed layers of 0.7 μm and 0.78 μm onto Nylon (Fig. 4.49) while 1.39 μm and 1.10 μm were formed onto PES support membranes (Fig. 4.46–Fig. 4.48) respectively. This could be attributed to the membrane’s surface smoothness. As the Nylon membrane has a rough surface with some irregularities and relatively big size pores, some thin small graphene flakes might penetrate through these pores in the substrate. This leads to the creation of a thinner deposited layer compared to the layer formed on the PES membrane which has flatter surface, shown in Fig. 4.50.
4.3.3 Conclusion

In this chapter, the aim was to obtain hybrid membranes, by modifying them with or without cross-linker graphene with polymer (PEI), onto PES and Nylon support membranes for the purpose of improving the relation between water permeance and dextran rejection. In order to find the optimum working conditions, screening experiments have been carried out under various experimental conditions, which includes varying PEI solution concentration, graphene and EDA weight ratios and chemical reaction time for cross-linking, different graphene dispersions, type of support membrane etc. The following results were found:

Unmodified highly negative PES support membrane with an isoelectric point at 3 pH and unmodified Nylon support membranes with an isoelectric point at 7 pH became positively charged hybrid membranes with the assistance of graphene-polymer modification, resulting in IEP at 10.3 for PES (PEI$_3$/G/PEI$_3$) and IEP at 10.4 for N02 (PEI$_5$/G/PEI$_3$).

XRD analysis revealed that there was nothing suggesting that the resultant dispersions E1 and E2 were graphene oxide like structures. Therefore, 2θ peaks were quite sharp and narrow at around 26° - 27° which is a characteristic position for graphene and graphite. E2 had at broader and not so sharp peak 2θ peak which meant it consisted of more graphene like structures rather than E1. Additionally, d-spacing is consistent with the literature, which is about 3.3 Å in the dry phase and exhibits very little change in the wet phase. Membranes fabricated with EDA modified G showed higher stability in wet phase. PES (PEI$_5$/G$_{0.2}$/PEI$_3$) which is one of the best membranes that had the best working performance showed a contact angle of 70 ± 3.8 which is still in the hydrophilic region.

PMI analysis revealed that most pores in the N02 (PEI$_{0.5}$/G$_{0.06}$/PEI$_{0.5}$) hybrid membrane were in the region of 96 nm whilst PES (PEI$_{0.5}$/G$_{0.06}$/PEI$_{0.5}$) hybrid membranes had a broad average pore size distributions, the majority were found 64 nm (36%) with some bigger sized pores in the range of 100 nm.

Unmodified support membranes Nylon and PES had a water permeance of 7338 L/m$^2$.h.bar and 1400-1930 L/m$^2$.h.bar, respectively. Graphene-polymer/N02 hybrid
membranes provided low water permeability, reduced up to 166 L/m².h.bar (referred to M8 in Fig. 4.33) with almost zero dextran rejection in some of the hybrid membranes. This was attributed to the presence of a high defect density. However, a big flux reduction was also observed in graphene-polymer/PES hybrid membranes, up to 17 L/m².h.bar but this was accompanied with significant improvements to dextran rejection, over 90% (Fig. 4.34).

After quality improvement the quality of the graphene dispersion (E1) via further centrifugation, in which dispersion E2 was obtained, and the reduction of chemical reaction time for EDA-graphene mixtures allowance from 7 h to 1 h (since aggregation occurred in 7h), filtration performance of graphene-polymer/PES hybrid membranes were examined under dead-end filtration cell. With the dispersion E2, which has thinner graphene flakes (80% of the flakes <30 nm thick) compared to E1 (50% of the flakes 10-50 nm), and reduced reaction time, the hybrid membranes showed better performance. An inverse linear relation was determined between the amount of graphene and water permeance, while a directly proportional relation between graphene amount and dextran rejection was found. Increasing graphene amount up to 0.2 mg/cm² resulted in 33 ± 11 L/m².h.bar water permeability and 96% dextran 2000 kDa, 27% dextran 4 kDa rejection (recalled membrane M34, PES (PEI₃/G₀.₂/PEI₃), Fig. 4.37). Introducing EDA to a diluted graphene dispersion (0.2 mg/cm²) with the ratio of 1:15 resulted in 30 ± 3 L/m².h.bar water permeability and 93% dextran 2000 kDa, 28% dextran 4 kDa rejection (recalled membrane M35, PES (PEI₃/G₀.₂+EDA₁₅/PEI₃), Fig. 4.37). These results confirmed that an ultrafiltration support membrane (PES) can be successfully modified with a graphene-polymer and that the filtration performance of the resultant hybrid membranes can be achieved with almost complete dextran 2000 kDa rejection. This is also an indication that most of the pores were smaller than 50 nm, the molecular size of dextran 2000 kDa (referred to Table 4.1). Increasing graphene content to a certain value helped to improve the membrane’s performance by completely covering the defects of graphene nanosheets and also the defects of the support membrane’s surface. This might have helped to resolve possible short-cuts in the transport pathways, which were formed by graphene nanosheets defects.

SEM images revealed that graphene-polymer/PES hybrid membranes had selective graphene layers between 1.10 μm to 1.44 μm thick from 0.06 mg/cm² to 0.2 mg/cm² while for graphene-polymer/N02 hybrid membranes these ere 0.7 μm to 0.78 μm.
CHAPTER 5

FORWARD OSMOSIS
CHARACTERIZATION
FORWARD OSMOSIS CHARACTERIZATION

5.1 Introduction

Forward osmosis can be defined as the passage of water molecules through a semipermeable membrane, from a low concentration solution (feed solution, FS) to a higher concentration solution (draw solution, DS). There is no pressure applied to the both sides of the solution. The driving force that transports the water is the osmotic pressure difference between the aqueous solutions on either sides of the membrane. The draw solution, which drives/pulls water molecules, is diluted during the FO process. Afterwards, the diluted DS is recycled through a suitable process (i.e., ultrafiltration membrane processes) to reuse in the next cycle of FO experiments as DS[363].

Asymmetric membranes which are composed of a thin, less than 0.1 μm dense layer and a hydrophilic thick support layer < 200 μm were mainly used for forward osmosis applications [364, 365]. The dense layer of these membranes plays an important role on the membrane’s selectivity. Pore size, chemical structure and thickness of the dense layer are responsible for defining the separation performance. The first FO research was started with an asymmetric acetate membrane[366] made from synthetic materials in the 1960s[367]. However, the results of many other reverse osmosis membranes, like cellulose acetate (CA) were not promising and did not warrant any further analysis in this work due to relatively thick support layers, which resulted in an increased of concentration polarization for such osmotically driven membrane processes[368].

Characteristics of desired FO membranes:

An ideal FO membrane should fulfil the following requirements: [369] (1) high salt retention and high water flux, (2) low concentration polarization, and (3) resistance to various pH as well as long-term mechanical and performance stability. A thin membrane with a high density of active layer, minimum porosity of the support layer to reduce ICP, high hydrophilicity and low fouling tendency would be desirable for such systems[214].

Criteria for the ideal draw solute:

The draw solute has a significant effect on the efficiency of the FO performance. Recently, a remarkable amount of studies have been devoted to exploring the ideal draw solution which should meet the following characteristics: f (1) high osmotic pressure which creates
high water flux; (2) low reverse solute transport; (3) easy recovery of the diluted draw solution after FO tests; (4) being nontoxic and cost-friendly\cite{370,371}.

In order to discover the most suitable draw solute, many possible candidates have been discussed by the researchers such as ammonium carbonate\cite{372,373}, fertilizers\cite{223,373,374}, magnetic nanoparticles\cite{375}, organic ionic salt\cite{376} and organic compounds\cite{377}. However, in recent years another draw solute candidate has been discovered, from the commercially available and pH responsive polymers family polyelectrolytes\cite{378-381}, due to many unique properties which make them suitable DSs for such systems. Polyelectrolytes of polyacrylic acid sodium salt (PAA-Na), has been found to be an appropriate option for a DS. They are water-soluble polymers with a selection of high molecular weights, have the capacity to produce high osmotic pressures and induce high water flux with low reverse solute flux, which is minimized due to its expanded chain pendant structure \cite{381}. Furthermore, these polyelectrolytes can be found in various molecular weights and structural sizes, which allow them to be recycled easily from diluted DS by using ultrafiltration processes.

In this work, solutions of sodium salts of polyacrylic acid (PAA-Na) with three different molecular weights, 5.1 kDa, 8 kDa and 30 kDa have been prepared and investigated using FO experimental setups. Their FO performances were analysed to determine possible candidates for draw solutes. Their water flux (\(J_w, \text{L/m}^2\cdot\text{h}\)) and reverse solute flux (\(J_s, \text{g/m}^2\cdot\text{h}\)) were calculated accordingly in the FO test systems.

Molecular weight in terms of polymers, it is known as the molar mass of a polymer chain. This is a critical parameter to determine the length of the polymer chains. The polymer consists of molecules which are not a single chain length but rather a wide range of lengths. So, the molecular weight (\(M_w\)) determines the polymer’s properties. It can be derived by multiplying the mass of each repeating unit by the degree of polymerisation and adding the mass of end groups\cite{382}. For example, a polymer is expected to have a higher viscosity in the case of a high molecular weight, since if the chains are long, then it is hard to make the material flow due to it being more tangled\cite{383}.

Polyacrylic acid (PAA) is a high molecular weight polymer of acrylic acid. It is an anionic polymer. Within an aqueous solution, PAA loses its protons and obtains a negative charge which makes PAAs polyelectrolytes with the ability to easily absorbing water and quickly swelling. PAAs can be found in the forms of alkali metals, such as polyacrylic acid sodium salt (PAA-Na) with the chemical formula [−\(\text{CH}_2\text{−CH(CO}_2\text{Na)}\)]\(_n\), in which the positively charged sodium ions are bound to the polyacrylate. It is an anionic polyelectrolyte with negatively charged carboxylic groups in the main chain\cite{384}.
The test membrane which had the best working performance during this work with an average water permeability 33 ± 11 LMH/bar and dextran rejections for 2000 kDa and 4kDa of 96% and 27%, respectively were chosen for FO experiments with the following name labelled M34 (PES_PEI3/G0.2/PEI3) // Graphene content: 0.2 mg/cm². Experimental work of FO test was explained in detailed in section 2.1.2.3. Water was chosen as the feed solution and polyacrylic acid sodium salt (PAA-Na) solution with various molecular weights (5, 8, 30 kDa) were chosen as the draw solution.

5.2 Results and Discussion

5.2.1 Viscosity Analysis of PAA-Na

Since poly(acrylic acid) is a weak polyacid, its degree of dissociation decreases with the increase of concentration, so that long-range interactions due to electrostatic repulsion lose its importance, resulting in polymer chains with smaller volumes[385]. Viscosity is an important impact on the efficiency of FO performance since it may result a serious concentration polarization and effect the mass transfer during filtration. Draw solution with a high viscosity reduces mass transfer and thereby results in lowering the water flux[228, 386].

Viscosity measurement was carried out by a rheometer (Rheometer Physica MCR301, Anton Paar). The viscosity changes of PAA-Na (5kDa), PAA-Na (8kDa) and PAA-Na (30kDa) as a function of temperature were shown in Fig. 5.1. When the concentration increased from 0.5 mM to 2 mM, the viscosity of PAA-Na (5kDa) and PAA-Na (8kDa) increased significantly. However, there was almost no change in viscosity in the case of PAA-Na (30kDa). In addition to that, the viscosity at a concentration of 0.5mM, showed a decreasing trend at higher temperatures higher than 41 °C, this situation was prominent specifically for PAA-Na (5kDa) and PAA-Na (8kDa). This indicated that the viscosity was greatly affected by temperature at a lower concentration.
Figure 5.1 The viscosity of 0.5 mM and 2 mM of PAA-Na 5kDa, 8kDa and 30kDa as a function of temperature.

Figure 5.2 The average viscosity of 0.5 mM and 2 mM of PAA-Na 5kDa, 8kDa and 30kDa draw solutions in between 33 °C – 45 °C temperature.

As shown in Fig. 5.2, the average viscosities of PAA-Na (5kDa), PAA-Na (8kDa) and PAA-Na (30kDa) at different molar concentrations were recorded. It can be concluded that the viscosity increased with an increase in the polymer concentration. At the same molar concentration, polyelectrolyte with a higher molecular weight exhibited lower viscosity at various temperatures. This finding is not in line with the work done by Ge et al. [381], in which it was found that an increase in polymer molecular weight at the same concentration led to
an increase in viscosity. In this work, the results showed that at the low concentration (0.5 mM), 5kDa of PAA-Na was more viscous with a viscosity of 0.057 Pa.s, followed by 8kDa of PAA-Na with 0.035 Pa.s and then 30 kDa was the least viscous with 0.029 Pa.s. The viscosity of the DS that is directly linked with the DS concentration is an important factor which affects water flux in the forward osmosis process. An increase in the viscosity of the DS results in decrease in water flux due to concentration polarization occurs on the membrane[387]. These results implied that PAA-Na (30kDa) would provide the best osmotic behaviour in FO test as a draw solution since it is less viscous compared to the others.

It is expected to have higher resistance for more viscous solutes[380], a lower diffusion coefficient and CP in the case of transporting through the membrane. So, it causes a decline in water flux accordingly[241]. As can be seen in Fig. 5.5, 2mM of PAA-Na (30 kDa) produced the highest water flux with 2.1 ± 0.9 LMH in PRO mode, while due to the high viscosity of PAA-Na (5 kDa) with 2mM concentration, water flux was the lowest value of 0.8 ± 0.44 LMH in PRO mode.

![Gel permeation chromatography (GPC) analysis of PAA-Na solution prepared by using 5 kDa, 8 kDa and 30 kDa molecular weights.](image)

**Figure 5.3** Gel permeation chromatography (GPC) analysis of PAA-Na solution prepared by using 5 kDa, 8 kDa and 30 kDa molecular weights.
The molecular weight of a polymer should be defined as the average molecular weight which is calculated from the molecular weights of all chains in the polymer. Gel permeation chromatography is also known as GPC which is a widely used size exclusion chromatography technique used for analysis of polymers. In GPC analysis, there are different average values used for different purposes. Mn is the most important average molecular weight, it is the statistical average molecular weight of all the polymer chains in the substrate. The other significant factor is D which shows the polydispersity index and is used for determining the broadness of a molecular weight distribution of a polymer. This can be calculated from \( D = \frac{M_w}{M_n} \). If the value of D is 1 then this is an indication that all the chain lengths are the same and the polymer is monodisperse. Looking at Fig. 5.3, the polydispersity index, D indicated that the current polymers were monodispersed and besides, Mn values suggested that all there substances, PAA-Na (5kDa), PAA-Na (8kDa), PAA-Na (30kDa), were very similar. Most surprisingly, the molecular size distribution of 8 kDa and 30 kDa seemed to be almost identical. Even more strange was that 5kDa seemed to have a higher molecular weight. These results were not in line with the expectations. The average molecular weight should have been found in the following order 30kDa>8kDa>5kDa as indicated on the label of each substance provided from the supplier company.

5.2.2 Forward Osmosis Characterization

The osmosis water flux \( (J_w, \text{L/m}^2\text{.h, LMH}) \) was calculated based on the mass change in the draw solution. Reverse solute flux \( (J_s, \text{g/m}^2\text{.h, gMH}) \) is defined as the amount of solute passed from draw solution to feed solution across the membrane within a certain of time. Three different concentration of draw solutions (0.2 mM, 0.5 mM and 2 mM) were used for each molecular weight of PAA-NA (5, 8 and 30 kDa) to discover the effect of the concentration of the draw solution on the water flux \( (\text{L/m}^2\text{.h, LMH}) \) and reverse solute flux \( (\text{g/m}^2\text{.h, gMH}) \).
According to the results of FO characterization gathered by using a U-tube apparatus in Fig. 5.4, the average water flux (L/m².h) increased with the increase in molar concentration of PAA-Na, as the driving force increased with the draw solution concentration. Meanwhile, reverse solute flux (g/m².h) from the draw side to the feed side increased because a higher solute concentration gradient formed through the active layer of the test membrane.
Average water flux (L/m².h) and reverse solute flux (g/m².h) as a function of 2mM PAA-Na 5kDa, 8kDa and 30kDa as draw solute. Two orientations: active layer faces with feed solution (AL-FS) or active layer faces with draw solution (AL-DS). Test system is the cross cell.

The two orientations, AL-FS and AL-DS, can be called as FO mode and PRO mode, respectively. It can be clearly seen from the results in Fig. 5.5 that the average water flux was higher with 2.1±0.9 LMH in PRO mode compared to that in the FO mode with 1.4±0.5 LMH when 2 mM concentration 30 kDa of PAA-Na was used as the draw solution. This can be attributed to the fact that internal CP occurred in AL-FS mode which has a greater influence on the flux decline than the external CP that occurred in AL-DS mode.\cite{228}

Additionally, at the same mass concentration (2 mM), water flux and reverse solute flux in PRO mode showed an increasing nonlinear trend along with the increasing molecular weight from 5 to 30 kDa. However, the increment was not directly proportional to the Mw of the draw solute. For instance, the water flux increased from 0.8 ± 0.44 LMH to 1.1±0.82 LMH with increasing Mw from 5 kDa to 8 kDa and also increased up to 2.1 ± 0.9 LMH in the case of 30 kDa. Besides, draw solute flux was 0.1 gMH at 5 kDa and this increased up to 0.6 gMH at 30 kDa draw solute. In the case of using water as a feed solution in the PRO mode, water was transported from the feed to draw side due to the osmotic pressure gradient across the membrane. This created external concentration polarization (ECP, dilutive) in the active layer. At the same time, the draw solute was transported from the draw to feed side, resulting in internal concentration polarization (ICP, concentrative) in the porous support layer.\cite{380} In the FO mode, dilutive ICP and concentrative ECP occurred on the porous support layer and active layer, respectively.\cite{260, 388, 389}
The specific reverse solute flux \( \frac{J_s}{J_w} \) which is defined as the ratio of reverse solute flux \( J_s \) to water flux \( J_w \). It is a value which indicates draw solute loss per volume of water permeated. *Table 5.1* revealed that the specific reverse solute flux was independent of membrane orientation. The solute loss to the feed solution was found to be lower and higher in PAA-Na (5kDa) and PAA-Na (30kDa), respectively.

**Table 5.1** Specific reverse solute flux \( \frac{J_s}{J_w} \) in various testing conditions.

<table>
<thead>
<tr>
<th></th>
<th>( \frac{J_s}{J_w} )</th>
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<tbody>
<tr>
<td><strong>AL-FS, 30kDa</strong></td>
<td>0.286</td>
</tr>
<tr>
<td><strong>AL-DS, 30kDa</strong></td>
<td>0.286</td>
</tr>
<tr>
<td><strong>AL-DS, 8kDa</strong></td>
<td>0.182</td>
</tr>
<tr>
<td><strong>AL-DS, 5kDa</strong></td>
<td>0.125</td>
</tr>
</tbody>
</table>

The change in osmosis water flux (L/m\(^2\).h, LMH) and solute flux (g/m\(^2\).h, gMH) as a function of FO operation period (hr) can be seen in *Fig. 5.6 – Fig. 5.18* (graphs at the top). Besides, the fluctuations in the osmotic pressure of feed and draw solutions as a function of time (hr) were plotted in *Fig. 5.6 – Fig. 5.18* (graphs at the bottom). In all cases, it is clear that there is a downward trend in water flux when reverse solute transport started to occur from draw to feed side. Reverse solute transport caused to concentrate the feed solution which led to increased feed osmotic pressure (upward trend) and decreased draw osmotic pressure (downward trend). So, net osmotic pressure difference which is the driving force for such systems is reduced within the time and resulted in low water flux.
Figure 5.6 FO results of 0.2 mM of PAA-Na (Mw 5kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).

Figure 5.7 FO results of 0.5 mM of PAA-Na (Mw 5kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).
Figure 5.8 FO results of 2 mM of PAA-Na (Mw 5kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).

Figure 5.9 FO results of 0.125 mM of PAA-Na (Mw 8kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).
Figure 5.10 FO results of 0.5 mM of PAA-Na (Mw 8kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).

Figure 5.11 FO results of 2 mM of PAA-Na (Mw 8kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).
Figure 5.12 FO results of 0.033 mM of PAA-Na (Mw 30kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).

Figure 5.13 FO results of 0.5 mM of PAA-Na (Mw 30kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).
Figure 5.14 FO results of 2 mM of PAA-Na (Mw 30kDa). Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).
Figure 5.15 Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) // AL-FS. Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).

Figure 5.16 Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) // AL-DS. Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).
Figure 5.17 Forward osmosis experimental results of 2mM of PAA-Na (Mw 8kDa) // AL-DS. Water and reverse solute flux (a), osmotic pressure and net driving force of feed and draw solution (b) as a function of operation period (hr).

Figure 5.18 Forward osmosis experimental results of 2mM of PAA-Na (Mw 5kDa) // AL-DS. Water flux and reverse solute flux (a), net driving force estimated from calculated draw and feed osmotic pressures (b) as a function of operation period (hr).
5.3 Conclusion

In this chapter, the aim was to characterize one of the best graphene-polymer/PES hybrid membranes labelled as M34 (PES_\text{PEI}_3/G_{0.2}/\text{PEI}_3) which provided the best performance under filtration conditions by using forward osmosis test systems. Results of FO characterization are summarized in the following:

(1) The viscosity of PAA-Na, at different Mws was analysed as a function of molar concentration (mol/L), assuming each PAA-Na had an average Mw (5, 8 and 30 kDa) defined by the supplier company. However, GPC analysis revealed that all three polymers had a very similar in molecular size distribution. So, it was later noticed that the effect of the polymer on the viscosity might have been underrepresented because of the use of smaller mass concentrations (g/L). So, viscosity has been shown for different mass fractions of the polymer. As a result of this, the trend was not perfectly clear since molar concentration was used instead of mass concentration. In the end, the three different polymers (PAA-Na-5,8,30kDa) were more similar than that expected, like the GPC results had previously shown. In a pragmatic way, it is possible to conclude that the differences as a function of drawing agent were not as consistent as one would expect. These commercial drawing agents were very similar. So, more important information results were those regarding the variation of mass concentrations.

What can be seen in the characterization results was that the samples were not labelled according to specifications. There was definitely disagreement between the specification which had been used for the selection and the results of the characterization which have been obtained in parallel.

(2) Among PAA-Na (5), PAA-Na (8) and PAA-Na (30) at different molar mass concentrations, 2 mM PAA-Na (30) provided the best FO performance. It showed water flux of 0.258 LMH and reverse solute flux of 1.787 gMH using a U-tube test system as well as 2.1 LMH and 0.6 gMH reverse solute flux (notably that reverse solute flux was much lower than NaCl ,1.9 g/L_{\text{NaCl}}^{390}) in AL-DS mode and 1.4 LMH and 0.4 gMH reverse solute flux in AL-FS using a custom design cross-cell.

(3) The results of the FO experiments suggested that the cross-cell test system was more preferable compared to the U-tube test system due to lowering the concentration polarization and it resulted in achieving a high-water flux with low solute flux.
CHAPTER 6

SUMMARY AND OUTLOOK
SUMMARY AND OUTLOOK

6.1 Summary

As the title of this thesis states, the aim was to study possible preparation methods of producing graphene by using the liquid phase exfoliation technique, for fabrication of graphene-based membranes which have desired characteristics for osmosis applications specifically. The main focus of the work was split into two sections; the first part was to develop reproducible dispersion methods via ultrasonication processes obtaining graphene from graphite, which enables the large-scale production of high-quality graphene with high efficiency. The second part was to fabricate composite or hybrid membranes by modifying symmetric commercial membranes with exfoliated graphene assisted with polymers. Success of the second part was strongly depended on the achievements of the first section since a good membrane was only valid with a good graphene dispersion. Numerous characterization techniques have been used to obtain deeper understanding of exfoliated graphene properties such as UV-Vis, DLS, Raman, AFM, TEM, XPS, SEM and the filtration performance of graphene-based membranes were tested using techniques such as PMI, XRD, FTIR, zeta potential, filtration under dead-end and forward osmosis tests.

Exfoliation Mechanism to Obtain Graphene from Graphite

Sonication is accepted as the key process for graphite exfoliation in a suitable solvent. However, there is no universally-known or agreed protocol for this process which still remains an open task. Because of that, the forefront of research in the first part of this thesis was to examine and understand the mechanism of exfoliation under various parameters. The exfoliation process could be controlled in order to have a reproducible protocol by systematically adjusting sonication parameters like input energy (high or low), time, temperature and centrifugation conditions like rotational speed, time and further centrifuge steps.

In the current work, graphene dispersions were mainly separated into two parts which include organic solvent assisted (NMP and ethanol) and aqueous systems (surfactant assisted). Absorbance spectra from UV-Vis showed the high yield of the dispersing procedure up to 7.2% by revealing the highest concentration of 0.36 mg mL\(^{-1}\) in one of the NMP based dispersions (N1). Additionally, low boiling solvent ethanol was tested as a liquid medium. Unfortunately, it has been shown that the efficiency of ethanol to disperse graphite is so low
owing to the mismatch of surface tension between graphene and ethanol. However, by using potassium sodium tartrate salt as an intercalator, there has been success in improving the efficiency of graphene dispersions up to 0.08 mg mL\(^{-1}\).

UV-Vis spectroscopy revealed that final concentration of the dispersions decreased for samples that were exposed to a further centrifuge step or higher rotational speeds. Moreover, atomic force microscopy (AFM) and transmission electron microscopy (TEM) suggested that the resultant exfoliated graphene dispersions were composed of a large amount of multilayer graphene, with the majority of lateral flake sizes less than 500 nm. Raman spectra was also in agreement with AFM and TEM by confirming multilayer structures of exfoliated graphene. It also presented the characteristic D, G and 2D peaks, for such materials. The defect-related D band was found in each dispersion with a varying I\(_D\)/I\(_G\) varying from 0.21 to 1.15, which was attributed to the reduction of flake size and increased sonication time. Based on the results, even though XPS showed some small amount of oxygen presented in the substrate, which could be explained by the residual NMP and surfactant on the silicon wafer, it could be concluded that the obtained exfoliated graphene dispersions were free of oxygen related functional groups.

Overall, exfoliated graphene, which consists of mostly multi-layer flakes has been successfully prepared in three different liquid agents, which provides a selection of solvents available for use. All the dispersions have been tested, but ethanol-based dispersions are preferred due to ethanol’s volatility, which makes it easy to remove from the membrane surface later.

**Graphene Based Membranes**

The obtained liquid-phase exfoliated graphene was employed as the material for the selective layer of composite membranes in order to examine its feasibility for osmosis applications. Two types of mechanisms for the fabrication of graphene-based membranes were proposed in this research. Graphene composite membranes consisted of stacked graphene nanosheets on top of each other onto a symmetric support membrane. Graphene-polymer hybrid membranes, called the ‘sandwich model’, were made of stacked graphene nanosheets with or without cross-linker, in between two PEI layers on a base membrane.

A pressure assisted filtration technique was used to fabricate graphene membranes since it has unique advantages compared to other techniques. In this method, applied pressure plays a critical role, less than 1 bar (0.8 bar, 0.5 bar and 0.2 bar) was used in the current work since low pressure enables the formation of highly ordered graphene laminates by giving flakes sufficient time to stack.
Graphene Composite Membranes: Firstly, graphene dispersions from N1 and N2 were directly used, without diluting, for deposition. The effect of using two different dispersions with different flake sizes on membrane performance was examined. A certain amount of each dispersion was filtrated through the base membrane using a dead-end cell under a certain pressure. However, no clear trend was not found in relation to the effect of different flake sizes on membrane filtration behaviour. Two composite membranes N02_1mg_05 and P02_1mg_08, were further analysed to get a deeper understanding. These membranes obtained a water permeance of 1678±707 LMH/bar and 6798±1217 LMH/bar with less than 15% salt rejection. The average pore size, of these composite membranes, was found in the region of 87 nm and 55 nm, respectively. However, some bigger sized of pores were also found due to incomplete coverage of those pores with graphene flakes. More importantly, results have revealed that the dextran rejection of the composite membranes tended to increase with decreasing pressure and vice versa, which indicated a high defect density. In order to reduce the defect density, two mechanisms have been proposed and applied in this research: (i) using a very diluted graphene dispersion (~5 μg/mL) and (ii) using a different support membrane (PES) which has a smoother surface and smaller pore sizes (~120 nm) compared to Nylon and PTFE. The best composite membranes showed relatively high-water permeability, varying from 80 – 366 LMH/bar, and improved selectivity with 48% of dextran 2000 kDa rejection. So, it could be safely concluded that the proposed mechanisms have been successfully carried out and have helped to reduce the defect density and improve selectivity. PES support membranes outperformed Nylon base membranes due to their surface morphology. Therefore, XRD data confirmed that the dispersions obtained were composed of multilayer graphene and provided an interlayer spacing in the range of 3.43 Å – 3.68 Å which could be indicated in graphitic like structures. Amongst all these achievements, one problem was observed during the filtration process. With the combination of sodium cholate assisted aqueous dispersions and PES or Nylon membranes, graphene laminates were easily peeled off from the PES and Nylon membrane surfaces due to the surfactant’s anionic property. This phenomenon was only partly solved with another surfactant, cationic CTAB, but not completely. Thus, surfactant assisted aqueous dispersions were not used in further experiments due to this delamination problem.

Graphene-Polymer Hybrid Membranes: In comparison to the graphene composite membranes, the selectivity of the membrane is controlled, not only by the graphene layers, but also together with a positively charged polymer (PEI) and the cross-linker by ethylenediamine (EDA). Firstly, PEI was used to improve the surface charge properties of the support membrane (PES), which is negatively charged, to obtain a strong attachment
between the surface and graphene nanosheets. Secondly, PEI was used to contribute to the selectivity by increasing surface smoothness. Furthermore, the use of cross-linker EDA, was intended to enhance the stability of nanosheets in aqueous systems and to increase rejection. Notable improvements have been achieved for the ultrafiltration support membrane, PES, which has been modified with various amounts of graphene (SEM showed that thickness of graphene layer onto PES and Nylon varied from 1.10 μm to 1.44 μm and 0.7 μm to 0.78 μm, respectively) and assisted with PEI and EDA. This resulted in water permeabilities in the range of 17 – 35 LMH/bar with a rejection of over 90% of dextran 2000 kDa. Incorporating the cross-linker EDA to the system and increasing PEI concentration from 0.5 to 3 mg/mL caused a small decrease in water permeability a bit but significantly enhanced the selectivity of the hybrid membranes. However, despite the fact that the same experimental conditions were applied during the fabrication of graphene-polymer/Nylon hybrid membranes, the resultant Nylon hybrid membranes showed very poor filtration performance with reduced water permeance instead remarkable rejection of dextran. This is probably due to the rough surface of the Nylon support membrane which caused defect formation.

In order to further increase the performance of the obtained hybrid membranes, some improvements have been. This include, increasing the dispersion quality of E1 and N2 by adding an additional separation process (centrifugation) and decreasing the allowed chemical reaction time of EDA and graphene, from 7 h to 1 h, to prevent aggregation. Afterwards, the filtration results from the combination of PES/(PEI3/Gy/PEI3) showed that increasing the amount of graphene from 0.06 mg/cm² to 0.2 mg/cm² led to superior rejection of dextran 2000 kDa from 53% with 77 LMH/bar water permeance up to 96% with 33 LMH/bar water permeance. This meant that the average pore sizes, of the graphene-polymer/PES hybrid membranes with 0.2 mg/cm² graphene, were smaller than 50 nm, which is the average molecular size of dextran 2000 (referred to Table 4.1). Therefore, the filtration results from the combination of PES/(PEI3/G0.16+EDAn/PEI3) proved that the contribution of EDA on the membranes’ performance was not as pronounced compared to the effect of increasing graphene content. The highest dextran 2000 kDa rejection of 94% with 23 LMH/bar water permeability was achieved in the combination of PES/(PEI3/G0.16+EDAn1200/PEI3). Additionally, increasing the heat treatment time from 2 h to 12 h, for the EDA and graphene mixture, was not successful since the maximum level of chemical reaction had been reached.
In conclusion, positively charged, relatively hydrophilic (~70°) graphene-polymer/PES hybrid membranes have been fabricated via a pressure assisted filtration technique and modified systemically to improve their filtration performance. Eventually, a highly compact graphene layer assisted with a polymer provided a selective layer with a thickness of ~1μm.

**Forward Osmosis Tests**

The membrane M34, PES/(PEI₃/G₀.₂/PEI₃), has been tested under forward osmosis testing conditions in order to determine the feasibility of using such hybrid membranes for osmosis applications. FO tests have been demonstrated by using two test systems in two operational modes: U-tube and custom design cross cell systems. The best results achieved were 2.1 LMH water flux with 0.6 gMH reverse solute flux in AL-DS mode while 1.4 LMH water flux with 0.4 gMH in AL-FS mode. PAA-Na could have potential for use in FO systems as a draw solute due to its lower solute diffusion from the draw side to the feed side. Additionally, between the two FO test systems, the custom-design cross cell outperformed the U-tube test system.
Comparison of Membrane Separation Performances

Table 6.1. Comparison with respect to key parameters, including pure water permeability and rejection values between the performance of the graphene composite and graphene-polymer hybrid membranes prepared in this work and GO membranes reported in the literature.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water Permeability (L/m².h.bar)</th>
<th>Rejection Test Material</th>
<th>R%</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO/PES</td>
<td>27.2</td>
<td>Natural organic matter</td>
<td>12.5</td>
<td>[190]</td>
</tr>
<tr>
<td>GO-EDA/PES</td>
<td>10</td>
<td>Natural organic matter</td>
<td>34</td>
<td>[190]</td>
</tr>
<tr>
<td>GO-PDA/PES</td>
<td>&lt;20</td>
<td>Natural organic matter</td>
<td>24.8</td>
<td>[190]</td>
</tr>
<tr>
<td>GO-mPDA/PES</td>
<td>&lt;20</td>
<td>Natural organic matter</td>
<td>25.3</td>
<td>[190]</td>
</tr>
<tr>
<td>GO/PC</td>
<td>5</td>
<td>Mg (2+) Na (1+)</td>
<td>93.9</td>
<td>[192]</td>
</tr>
<tr>
<td>GO-EDA/PC</td>
<td>17</td>
<td>MgCl₂, NaCl, MgSO₄, Na₂SO₄</td>
<td>Na₂SO₄ (72%) &gt;MgSO₄ &gt;NaCl &gt;MgCl₂ (30%)</td>
<td>[200]</td>
</tr>
<tr>
<td>GO-EDA-HPEI/PC</td>
<td>5</td>
<td>MgCl₂, NaCl, MgSO₄, Na₂SO₄</td>
<td>MgCl₂ (97%) &gt;NaCl &gt;MgSO₄ &gt;Na₂SO₄ (36%)</td>
<td>[200]</td>
</tr>
<tr>
<td>GO-TFN-0.25</td>
<td>15.63</td>
<td>MgSO₄, Na₂SO₄</td>
<td>MgSO₄ (90%), Na₂SO₄ (96%)</td>
<td>[391]</td>
</tr>
<tr>
<td>G₀.₁₁/PTFE</td>
<td>6798</td>
<td>NaCl</td>
<td>≤15</td>
<td></td>
</tr>
<tr>
<td>G₀.₁₁/Nylon</td>
<td>1678</td>
<td>NaCl</td>
<td>≤15</td>
<td></td>
</tr>
<tr>
<td>G₀.₁₃/Nylon</td>
<td>80</td>
<td>Dextran (4 kDa)</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>G₀.₀₁/Nylon</td>
<td>366</td>
<td>Dextran (4 kDa)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>G₀.₀₁/PES</td>
<td>204</td>
<td>Dextran (2000 kDa)</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>PES (PEI₃/G₀.₀₂/PEI₃)</td>
<td>33</td>
<td>Dextran (4 kDa)</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>PES (PEI₃/G₀.₁₆+EDA₁₂₀₀/PEI₃)</td>
<td>23</td>
<td>Dextran (4 kDa)</td>
<td>24</td>
<td></td>
</tr>
</tbody>
</table>
Based on the comparison results based on *Table 6.1*, it could be qualitatively stated:

- The target water permeability and dextran rejection values of the graphene-based membranes in the current study was successfully achieved (Permeability: 23 -33 L/m².h.bar, Dextran 2000 kDa rejection: 94% - 96%) and these results are quite compatible with the literature.

If we compare the FO results of two membranes in *Table 6.2* (Ref. [381] and the current work), conclusions would be stated as in the following:

- It is obvious that there is a trend between draw solution concentrations and water fluxes in the current work, where low water fluxes (2.1 L/m².h) causes by lower driving force (40mM) compared to the one in literature (21 L/m².h, 600 mM)
- It is also expected to observe that the lower draw concentration also reduces the reverse solute flux. However, the current work provided higher reverse solute flux with 0.6 g/m².h compared to 0.17 g/m².h in the literature-based work.

*Table 6.2.* Comparison of water flux, reverse solute flux and specific flux (Js/Jv) of forward osmosis membranes reported in the literature under FO test system.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Water Flux, Jv (L/m².h)</th>
<th>Draw Solution</th>
<th>Reverse Solute Flux, Js (g/m².h)</th>
<th>Operation Mode</th>
<th>Js/Jv (g/L)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hollow fiber CA</td>
<td>21</td>
<td>0.72 g/ml; PAA-Na (Mw:1.2kDa); 600mM</td>
<td>0.17</td>
<td>AL-DS</td>
<td>0.008</td>
<td>[381]</td>
</tr>
<tr>
<td>PES (PEI,G0,2/PEI),M34</td>
<td>2.1 ×10</td>
<td>0.06 g/ml; PAA-Na (Mw:1.5kDa); 40mM</td>
<td>0.6</td>
<td>Al-DS</td>
<td>0.286</td>
<td>Current work</td>
</tr>
</tbody>
</table>

The FO water permeability of the membrane in the current study can compete with the commercial one, however the reverse solute leakage was much higher, and this even for slightly higher molecular weight (bigger molecule size) and -more important- much lower driving force for solute diffusion (because of lower draw concentration).
6.2 Outlook

Based on the results obtained, the incorporation of graphene, polymer PEI and EDA led to an improvement of the overall filtration performance of the PES membranes; however, there is still potential for further improvements. Various scalable approaches to exfoliate graphite into multi-layer graphene by the LPE technique have been demonstrated. However, further optimization of this technique to obtain graphene dispersions (single, double, triple < few layers structures) can be explored in order to study the transport of water across the membrane as well as to tuning the selectivity of the membrane.

Membrane stability in the long terms is another significant factor for industrial based applications. Thus, experiments including longer running periods can be conducted to study the stability of the resultant membranes under various conditions.

In the current work, PAA-Na was used as the draw solute with three different molecular weights; 5 kDa, 8 kDa and 30 kDa. However, based on the viscosity and size exclusion results revealed that there was an error regarding the specifications and all three substances were similar in terms of average molecular weight. So, as a next step, different than those Mw’s could be tested to obtain a better understanding.
Appendices

Graphene/PES membranes fabricated via E2

Figure A.1 Top (a, b, c) and cross section (d, e, f) images of M18 (PES_1(PEI3/G0.06+EDA1200/PEI3)).

Figure A.2 Top (a, b, c) and cross section (d, e, f) images of M20 (PES_1(PEI3/G0.06+EDA15000/PEI3)).
Figure A.3 Top (a, b, c) and cross section (d, e, f) images of M22 (PES_{(PEI_3/G_{0.06}+EDA_{15}/PEI_3)}).

**Graphene/Nylon membranes fabricated via N3**

Figure A.4 Top (a, b, c) and cross section (d, e, f) images of M9 (Nylon_{(PEI_3/G_{0.06}+EDA_{1200}/PEI_3)}).
Figure A.5 Top (a, b) and cross section (c, d) images of M12 (Nylon_(PEI3/G0.06+EDA15000/PEI3)).

Surface Morphology of Membranes Before and After Filtration

Figure A.6 Top images of M16 before (a, b, c) and after (d, e, f) filtration (PES_(PEI3/G0.11/PEI3)).
Figure A.7 Top images of M18 before (a, b, c) and after (d, e, f) filtration (PES\_\text{PEI}_3/\text{G}_{0.06}+\text{EDA}_{1200}/\text{PEI}_3).

Figure A.8 Top images of M20 before (a, b, c) and after (d, e, f) filtration (PES\_\text{PEI}_3/\text{G}_{0.06}+\text{EDA}_{15000}/\text{PEI}_3).
**Figure A.9** Top images of M22 before (a, b, c) and after (d, e, f) filtration (PES_{PEI_3/G_{0.06}+EDA_{15}/PEI_3}).

**Figure A.10** Top images of M6 before (a, b) and after (c, d) filtration. (Nylon_{PEI_3/G_{0.06}/PEI_3}).
Figure A.11 Top images of M8 before (a, b, c) and after (d, e, f) filtration. (Nylon_{(PEI_3/G_{0.11}/PEI_3)}).

Figure A.12 Top images of M9 before (a, b, c) and after (d, e, f) filtration. (Nylon_{(PEI_3/G_{0.06}+EDA_{1200}/PEI_3)})
Figure A.13 Top images of M12 before (a, b, c) and after (d, e, f) filtration. (Nylon_{(PEI_3/G_0.06+EDA_{15000}/PEI_3)}).

**Graphene/PES and Graphene/Nylon membranes fabricated via E1**

Figure A.14 Top (a, b, c) and cross section (d, e, f) images of PES_{(PEI_0.5/G)}.

Figure A.15 Top and cross section images of M4_PES_{(PEI_3/G/PEI_3)}. 
Figure A.16 Top (a, b, c) and cross section (d, e, f) images of PES_\(_{(\text{PEI}_{0.5}/G/\text{PEI}_{0.5})}\).

Figure A.17 Top (a, b, c) and cross section (d, e, f) images of PES_\(_{(\text{PEI}_{0.5}/G+\text{EDA})}\).

Figure A.18 Top (a, b, c) and cross section (d, e, f) images of PES_\(_{(\text{PEI}_{0.5}/G+\text{EDA}/\text{PEI}_{0.5})}\).
Figure A.19  Top (a, b, c) and cross section (d, e, f) images of Nylon_(PEI_{0.5}).

Figure A.20  Top (a, b, c) and cross section (d, e, f) images of Nylon_(PEI_{0.5}/G).

Figure A.21  Top (a, b, c) and cross section (d, e, f) images of Nylon_(PEI_{0.5}/G/ PEI_{0.5}).
Figure A.22 Top (a, b, c) and cross section (d, e, f) images of Nylon (PEI 0.5/G+EDA).

Figure A.23 Top (a, b, c) and cross section (d, e, f) images of Nylon (PEI 0.5/G+EDA/PEI 0.5).
Figure A.24 TEM images of dispersion of N2, E1 and E2.
Figure A.25 Water flux decline of graphene composite membranes during filtration.
Figure A.26 FO results of 0.2mM of PAA-Na (Mw 5kDa). Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

Figure A.27 Forward osmosis experimental results of 0.5mM of PAA-Na (Mw 5kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).
Figure A.28 Forward osmosis experimental results of 2mM of PAA-Na (Mw 5kDa Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

Figure A.29 Forward osmosis experimental results of 0.125mM of PAA-Na (Mw 8kDa Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).
Figure A.30 Forward osmosis experimental results of 0.5mM of PAA-Na (Mw 8kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

Figure A.31 Forward osmosis experimental results of 2mM of PAA-Na (Mw 8kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).
Figure A.32 Forward osmosis experimental results of 0.033mM of PAA-Na (Mw 30kDa)
Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

Figure A.33 Forward osmosis experimental results of 0.5mM of PAA-Na (Mw 30kDa)
Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).
**Figure A.34** Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

**Figure A.35** Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) // AL-FS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).
Figure A.36 Forward osmosis experimental results of 2mM of PAA-Na (Mw 30kDa) // AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).

Figure A.37 Forward osmosis experimental results of 2mM of PAA-Na (Mw 8kDa) // AL-DS Water and reverse salt flux (a), osmotic pressure and net driving force of feed and draw solution (b), experimental fluctuation (c), volume change in both compartments (d) and measured TOC value in feed side and reverse solute transport (e).
Figure A.38 Forward osmosis experimental results of 2mM of PAA-Na (Mw 5kDa)// AL-DS Water flux and reverse salt flux (a), net driving force estimated from calculated draw and feed osmotic pressures (b), experimental fluctuation (water flux/Net driving force and reverse solute flux/Net driving force) (c), volume change in feed and draw compartments (d) and TOC value in feed side and reverse solute transport (e).
Re-calculation of Viscosity Based on Mass Concentration

Here, molar mass concentration was converted to the mass concentration of the polymer, PAA-Na (5,8,30 kDa). Below table was shown accordingly:

<table>
<thead>
<tr>
<th>PAA-Na</th>
<th>g/mL</th>
<th>Average Viscosity (g/mL)</th>
<th>Average Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 kDa</td>
<td>0.01</td>
<td>0.095</td>
<td>0.0025</td>
</tr>
<tr>
<td>8 kDa</td>
<td>0.016</td>
<td>0.148</td>
<td>0.004</td>
</tr>
<tr>
<td>30 kDa</td>
<td>0.06</td>
<td>0.032</td>
<td>0.015</td>
</tr>
</tbody>
</table>

If we assume a linear relationship between mass concentration and viscosity at same Mw of polymer. Increasing mass concentration by a certain factor will then lead to increase by the same factor in viscosity for the polymer to be studied. So, It has been taken the highest mass concentration as reference, 0.06 g/mL and 0.015 g/mL and re-consider viscosity values for each cases accordingly:

<table>
<thead>
<tr>
<th>PAA-Na</th>
<th>g/mL</th>
<th>Average Viscosity (g/mL)</th>
<th>Average Viscosity (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 kDa</td>
<td>0.06</td>
<td>0.57</td>
<td>0.015</td>
</tr>
<tr>
<td>8 kDa</td>
<td>0.06</td>
<td>0.56</td>
<td>0.015</td>
</tr>
<tr>
<td>30 kDa</td>
<td>0.06</td>
<td>0.032</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Here, data suggested that the trend of more viscous to less viscous draw solute was found as 5>8>30 which also meant PAA-Na (5) had the highest Mw, then followed by 8 kDa and 30 kDa.
Unmodified support membranes and graphene composite membranes fabricated with dispersion N1 and N2 were analysed by using gravimetric analysis to characterize porosity. Porosity (%) of support membranes N02, N045 and P02 were found as 77%, 79% and 66%, respectively. Effect of using two different NMP based graphene dispersions on membrane’s porosity was analysed. Results indicated that there is no meaningful trend in between graphene composite membranes fabricated via N1 (black) and N2 (blue). In addition to this, Increase in graphene amount from 0.5 mg to 1.4 mg at same condition did not cause any significant change in porosity (%).

Moreover, it is expected that increasing graphene content causes to form a dense layer which results in decreasing porosity. Therefore, this situation was confirmed by the results indicated in Fig. 4.3, unmodified support membranes N02 and N045 showed higher porosity compared to graphene deposited composite membranes. However, a slight different behaviour was observed in P02 case as porosity (%) unmodified P02 membrane is lower than modified membranes with N1, resulted in 67% for the $P02_{0.5mg}$ and 68% for the $P02_{1.4 mg}$. 

![Figure A.39 Porosity (%) measurement G/P02, G/N02 and G/N045 membranes with various graphene loadings. Black colour represents the graphene dispersion N1 and blue colour represents the graphene dispersion N2.](image)
List of Presentations and Publications

Presentations

➢ NanoteC16 Conference, Carbon Nanoscience and Technology, 31 August-3 Sep 2016, Dublin, Ireland, Poster Presentation.
➢ Nanotube (NT) NT16 Conference, 7-13 August 2016, Vienna, Austria, Poster Presentation.
➢ European Membrane Society Summer School on "Membranes and Membrane Processes Design", Jun 26–1 July 2016, Bologna, Italy, Poster Presentation.
➢ Graphene Week, 13–17 June 2016, Warsaw, Poland, Poster Presentation.

Publications

➢ Sevilay Akca et al., “Multi-layer graphene in various solvents by liquid phase exfoliation technique” (Manuscript in preparation).
➢ Sevilay Akca et al., “Graphene based membranes for osmosis applications” (Manuscript in preparation)
“Everything is theoretically impossible, until it is done.”

Robert A. Heinlein
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