



ICCSE 2018

Molecular Recognition and Interaction of Polyamide Thin Film Composite on the Hydrophobic and Hydrophilic Polymeric Substrate

Wan Zulaisa Amira Wan Jusoh^a, Sunarti Abdul Rahman^{b*}, Abdul Latif Ahmad^c and Nadzirah Mohd Mokhtar^d

^{a,b}Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Kuantan Pahang Malaysia

^cSchool of Chemical Engineering, Engineering Campus, 14300 Nibong Tebal, Universiti Sains Malaysia, Pulau Pinang, Malaysia

^dFaculty of Engineering Technology, Block A3, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300, Gambang, Kuantan, Pahang, Malaysia

Abstract

Thin Film Composite Membranes (TFC) has drawn the researchers and industries due to the superior performance and long-lasting performance compare to pristine pervaporation membrane. TFC is a less than 0.2 μm active layer which layered on the substrate membrane mainly use in pervaporation. In order to obtain high mechanical strength in the support membrane, researchers prefer to apply for hydrophobic supports over to hydrophilic which often neglect the interaction between those membrane supports with the TFC. The success of the TFC membrane is, however, depending on how well TFC attached on support membrane as it is also related to the permeate penetration pathway. As the depositing of the TFC on the support layer however very crucial to be highlighted, this paper focus to examine the interaction molecules between TFC layer and different properties of the support membrane Nylon 6,6 (N66) and Polyvinylidene fluoride (PVDF) by using Molecular Dynamic (MD) simulation. The Condensed-Phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) force field was used with the total simulation runs were set 1000 picoseconds run production ensembles. The temperature and pressure set for both ensembles were 298 K and 1 atm respectively. The validity of our model densities was check and calculated show a good agreement with available experimental where the deviation less than 6%. The comparison between hydrophobic and hydrophilic of the support membrane was found as the larger contribution toward the distance and intensity of Radial Distribution Function (RDF's) trends. The first interaction atom was at the distance 2.25 Å in the N66 system, meanwhile, 3.25 Å inside the PVDF system with the intensity of 2.97 and 1.04 Å respectively. This study purposed that the TFC deposition was better on the N66 membrane than on the PVDF membrane due to similar properties. The solubility in the tertiary system (when exposing monomers to polymeric substrates) were not significant compared with the binary system in the provided simulation time. However, the balance of aqueous and organic monomers is necessary to avoid the swelling effect on the substrate membrane.

© 2019 Elsevier Ltd. All rights reserved.

Selection and peer-review under responsibility of the scientific committee of the International Conference on Chemical Sciences and Engineering: Advance and New Materials, ICCSE 2018.

Keywords: COMPASS force field; Polyamide Thin Film Composite, Molecular Dynamic; Molecular; Interaction.

* Corresponding author. Tel.: +609-5492822

E-mail address: sunarti@ump.edu.my

1. Introduction

Pervaporation (PV) is a membrane-based separation process especially for removing organic compounds from water, for example, separation of isopropanol-water [1–3]. Application of dense, symmetric structure and hydrophilic polymeric membranes in the PV system in the laboratory is widely exploited. However, the limitation of these membranes such as relatively low trans-membrane flux and low mechanical strength make it unfavourable to be applied in PV processes. To encounter these limitations, the asymmetric membrane structure is introduced by depositing the Thin Film Composite (TFC) on the symmetric membrane [4]. TFC is created by a technique called Interfacial Polymerization (IP) by the reaction of the aqueous and organic monomers [5,6].

The compatibility study between the polymers was intensively studied by molecular dynamic (MD). Molecular dynamic (MD) is a device to compute the various parameters such as diffusivity, compatibility of the materials blended and the polymers density [7]. The Condensed-Phase Optimized Molecular Potential for Atomistic Simulation Studies (COMPASS) is one of the force field in the device used to examine the relationship between distance and the magnitude of the forces existing among the molecules involving organic and inorganic material. Thus, the MD is the right tool to recognize the compatible monomers selection and to explicate the behaviour of interfacial diffusion and bonding between the TFC membranes with the support prior experimenting work [8].

It is very important to ensure the good interfacial bonding between TFC and support membrane so that the mass transfer is not being obstructed during PV process [9]. However, when coating the TFC on the polymeric membrane, the challenge is to warrant the stability of the thin film layer coated on the support membrane. This is due to the relatively strong repulsive force while weak interfacial interaction presented between these TFC membranes with the support membrane. To our best of knowledge, this is the first time molecular dynamics simulation was used to examine the intermolecular forces molecular interaction and to find the binding strength between TFC with the Nylon 66 (N66) and Polyvinylidene fluoride (PVDF) using MD.

2. Simulation Method

All simulations were performed on Universiti Malaysia Pahang workstation using Material Studio (version 7.0) software from Accelrys, Inc. For each polymer, the repeating unit as shown in Fig. 1 was first built and its geometry optimized by energy minimization using the COMPASS force field.

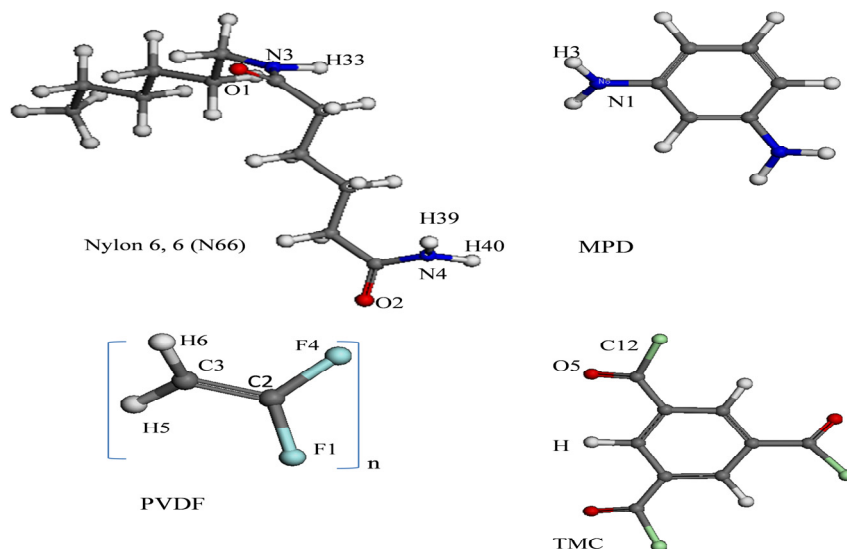


Fig. 1. The repeat unit of monomers chain molecules

M-phenylene diamine (MPD) and trimesoyl chloride (TMC) were main reactive monomers of aqueous and organic phases for the polyamide layer formation represented as a binary system in the simulation. Meanwhile, in the tertiary systems involve of nylon 66 (N66)/ MPD/ TMC and PVDF/ MPD/TMC. Models were firstly undergoing the geometry optimization and then the energy started to be minimized. This process repeated until convergence of charge and energy was completed. Minimizations stages were accomplished operating the Smart Minimization mode that switches from steepest-descent to conjugated gradient and then to the Newton–Raphson method as the energy derivatives decrease in order to speed the computation.

Then, the amorphous cell module was employed to fold one aromatic polyamide chain with repeating units into a periodic unit cell at ambient temperature to generate 10 configurations presented in Fig 2. Then, the configurations were employed an energy minimization process using the followed by NVE (number molecules, volumes, and total energy) and NPT (number molecules, pressure, and temperature) ensemble at 1 atm according to the protocol described by in order to obtain an optimized polymer cell. Each NVE and NPT ensembles have performed a total of 1000 picosecond (ps) simulation time step. The final simulation trajectory analyzed by radial distribution function analysis (RDF).

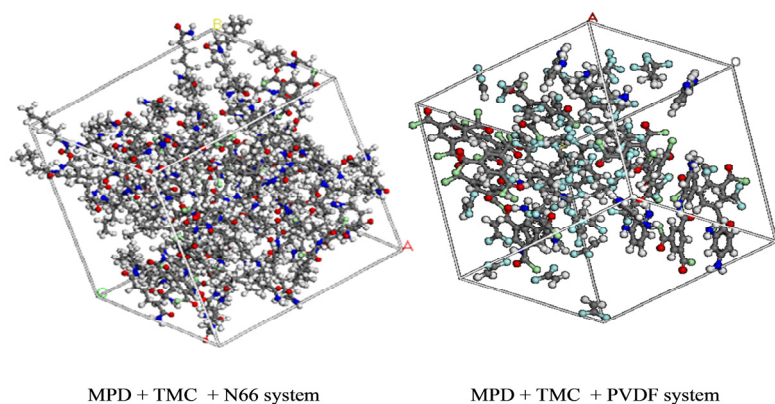


Fig. 2. 3D boxes representing the simulations

3. Result and Discussion

3.1. Density

In laboratory work, PA TFC is produced by exposing the N66 substrates introduce the amine solution first before contacting with organic monomers. Thus, in the simulation, the monomers were introduced separately rather than as TFC membrane to mimic real experimental method. In this case, N66 and PVFF were simulated along with TMC, MPD in a ternary system. In order to make sure the simulation parameters are acceptable, the density initial setting must be less than 6% error than the final density obtained in the simulations. In this simulation, the error percentage calculated was less than 5% displays in Table 1.

Table 1. The deviation of the average simulated densities and temperature.

System	Average Density (g/cm^3)			Temperature (K)		
	Simulated values ^a	Setting values ^b	Deviation (%) ^c	Simulated values ^a	Setting values ^b	Deviation (%) ^c
MPD/TMC	1.050	1.000	4.760	299.100	298.000	0.368
N66/MPD/TMC	1.060	1.050	0.943	297.928	298.000	0.024
PVDF/MPD/TMC	1.160	1.175	1.290	298.025	298.000	0.008

^a Experimental value in reference[10].

^b Predicted by simulation.

^c Deviation = [(simulated value – setting value)/ setting value] x 100.

3.2. RDF's Analysis

RDF plot shows the relationship between r which is the distance between atom pairs in each of the trajectory distance of atom with other neighbouring atom and $g(r)$ is the tendency of the atom to interaction/probability to have interaction between atoms. Binary system consists of N66 and TMC monomer. The atoms were represented as:

- H39 – N4 / H40 – N4 (N66): Intra-molecular interaction between hydrogen no. 39 with nitrogen no.4 /hydrogen no.40 with the nitrogen no.4 in the N66 molecule.
- F1 – C2 (PVDF)/C3 – C2 (PVDF): Intra-molecular interaction between fluoride no.1 with the carbon no.2/ carbon no.3 with the carbon no.2 in PVDF molecule chain.
- N (MPD) / H (MPD): Nitrogen/ Hydrogen in the MPD.
- H (N66) / O (N66)/ N (N66): Hydrogen/Oxygen/Nitrogen atom in the N66 molecules respectively.
- F (PVDF) / H (PVDF): Fluoride/Hydrogen in PVDF group respectively.
- O (TMC)/ Cl (TMC)/ C (TMC): Oxygen/Chlorine/Carbon atom in TMC molecule respectively.

3.2.1 Intra-molecular of the polymers.

Intra-molecular typically considered in this study due to the large molecules of N66 was applied to the simulation system. According to Jensen, it is the best to analyse for intra-molecular interaction the atoms which separated by three or higher covalent bond [11]. In Fig.3 (a), the highest interaction started at the 0.75\AA radii, mainly by the Hydrogen (H) and the Nitrogen (N) at the end of the molecules. There were also repulsive forces detect between adjacent H with H at the end in the distance of 1.75\AA , followed by the intra-molecular interaction between Oxygen (O) and its adjacent, N. The intra-molecular interactions is also known as the non-bonded interaction which mainly driven by the electrostatic potential or Van der Waals forces [12]. This type of interaction can contribute to the total intra-molecular potential energy of the molecule. The number of cross-links influences the distance between polymers indicating that N66 presenting more flexible and polymer backbone atoms are much more compact. Therefore, when new cross-links are formed, the distance between cross-linkers and polymers backbone carbons becomes shorter.

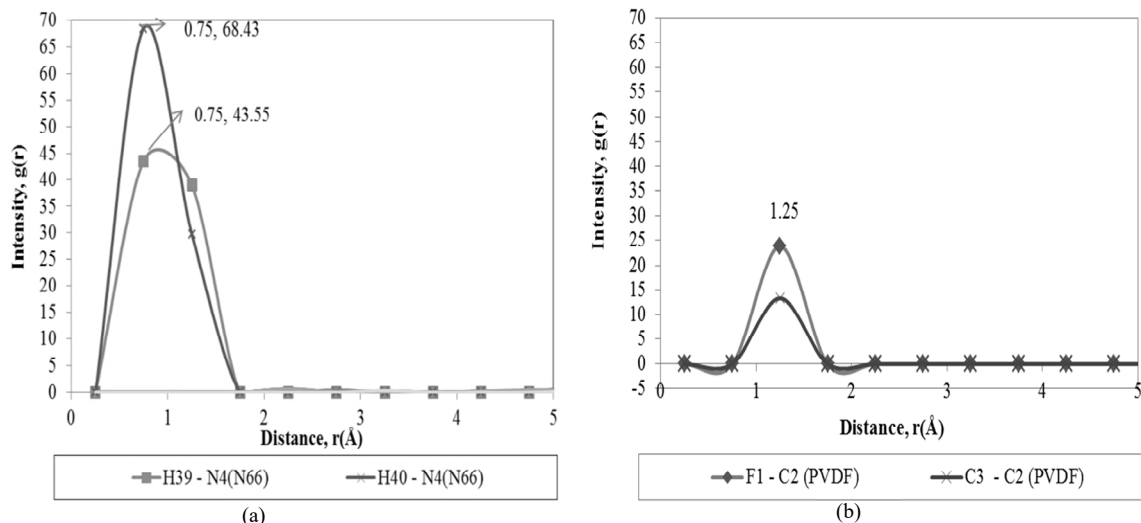


Fig. 3. Intra-molecular interaction in the (a) Nylon 6, 6 and (b) PVDF molecules

From Fig.3 (b) it is clear that the general shapes of the RDF for all the trends under consideration are very similar distance. There are two peaks at a higher intensity followed by two lower intensities at the 1.25\AA° . The highest two peaks correspond to the interactions among the PVDF backbone carbons. It is worthy to realize that the first peak appears at longer distances compared in the N66 backbone. The number of cross-links influences the distance between polymers indicating that N66 presenting more flexible and polymer backbone atoms are much more compact. Therefore, when new cross-links are formed, the distance between cross-linkers and polymers backbone carbons becomes shorter.

3.3. Intermolecular interaction

In a basic procedure, the polymer substrate is contacted with MPD for few minutes before introduced with the TMC. Then, MPD which attached into substrate surface will interact with TMC to complete interfacial polymerization reaction to form a polyamide thin film layer. Thus, the interaction comprises of 1) between MPD - TMC and then 2) between N66/PVDF with TFC.

3.3.1 The RDF's analysis of the TMC-MPD in binary and tertiary system

The interfacial polymerization reaction between TMC and MPD will form polyamide TFC. The cross-linking in the binary and tertiary system was presented in Fig.4. The main interaction was between N from amine group with the C from the main chain of the polymeric polymer and form a covalent bond at 4.25\AA . Shen et al found the interaction between N - C at 3.5\AA [13]. The higher interaction distance obtained from this simulation compared with the previous reference may be contributed by the lower amount of molecules in the simulation system. However, the interaction distance still considers as strong as it was below than 5.0\AA [14].

The system was compared to determine any peak shifting which explains the solubility. The tertiary systems were exposed to lower intensity compared with the binary systems. Suggesting that there was not solubility for both systems detected which we can assume both membranes are stable when exposing to the aqueous solution for a period of time. The probability to find the first neighbouring atom for N1amine - C13 acyl group in N66 and PVDF was at similar radii.

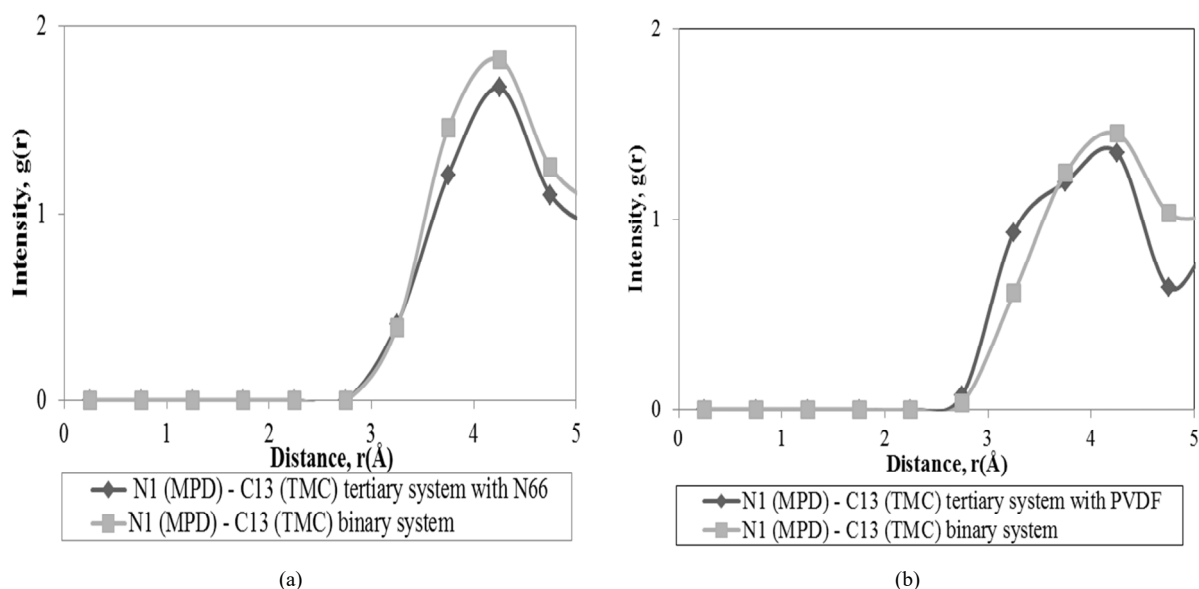


Fig. 4. The interaction between the TMC group with the MPD group in the binary and tertiary

3.3.2 The RDF's analysis on the Polymers – TFC

The interaction of polymers with the MPD starts at 2.75 – 3.0 Å shown in Fig. 5. The calculations of the intermolecular interaction of different N66 molecules to the aqueous monomer molecules showed that there is a large difference in the intensity of interaction even both polymers start the interaction at the similar space. The interaction of N66-MPD system was between N atom from N66 with the H and O within the MPD molecules. Groups of PVDF polymer molecules seem to have a very great repulsive force which extended away from the entire atom toward MPD which show some rejection exist in both sides of the group. In this regard, this situation explains that overall TFC deposition on the top of the hydrophilic membrane is relatively weak and unstable [15]. The loose TFC membrane could be formed and lead to washing away during operation by the aqueous solution.

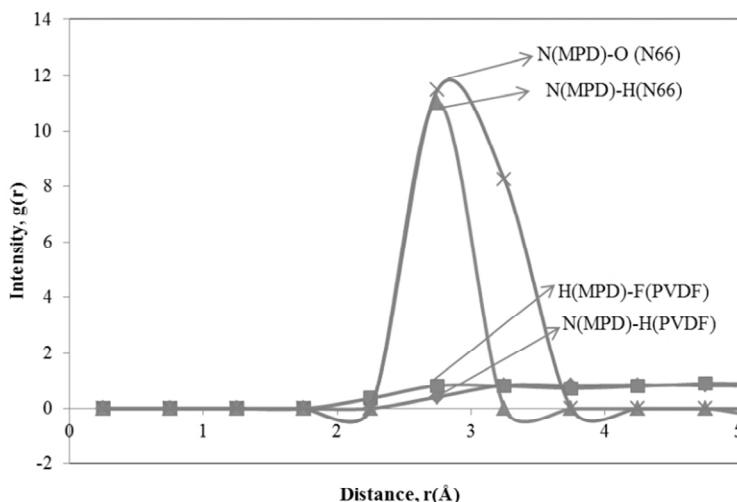


Fig. 5. Intermolecular interaction between polymer chains with MPD

There was also interaction detected between the polymeric substrate with the TMC. The main intermolecular interaction demonstrated in Fig. 6 between N66 with the TMC was by the Cl (TMC) with the O (N66) and O (TMC) with H (N66). The first interaction of Cl (TMC) with O (N66) and O (TMC) with H (N66) was observed by non-polar covalent bond and the hydrogen bonding followed by the covalent bond between respectively. According to Bermejo & Ugarte, as the O - H bonds will keep reducing as the cross-linking degree grows. Inter-molecular hydrogen bonding is most likely contributed to the polymer rigidity [16,17]. Meanwhile, the main bonding is between the carbon atom of PVDF with the Cl atoms of acyl chloride (TMC) which mainly reflected the non-polar covalent bond between F and Cl in the PVDF chain. Refer to the trend of RDF plotted; the probability to find the first neighbouring atom for N66 - TMC was higher compared to PVDF-TMC system at the same timesteps of 1000 ps. The first interaction atom was at the distance 2.25 Å in the N66 system, meanwhile, 3.25 Å inside the PVDF system with the intensity of 2.97 and 1.04 Å respectively. This is shown that the interaction of N66 with TMC was better than PVDF polymer. The weak atomic intermolecular interaction between PVDF and TMC can be explained by the different properties between these two components. N66 is more favourable for TFC as similar hydrophilic characterize. Material with the same hydrophobicity, have lower repulsive force toward each other.

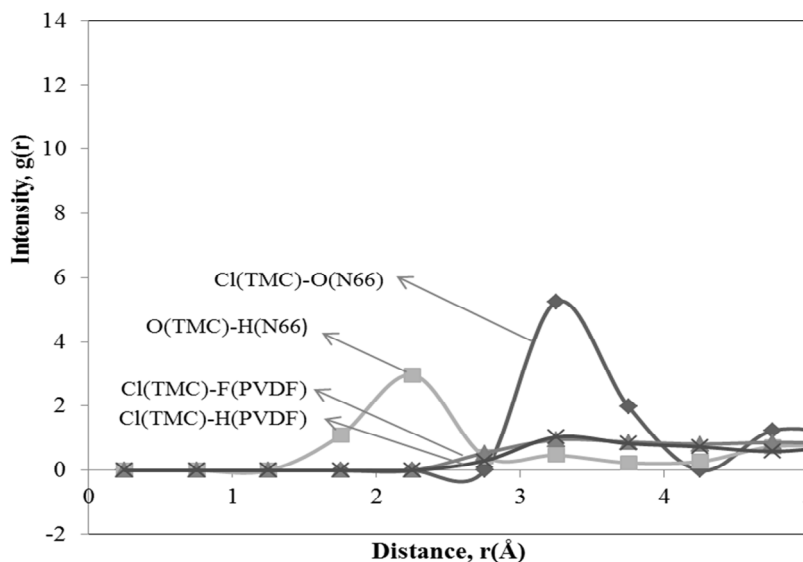


Fig. 6. Intermolecular interaction between polymer chains with TMC

4. Conclusion

Understanding the fundamental of the interaction between two layers at the atomic state by performing the molecular dynamic simulations is much more relevance. The current study, cross-linked networks by means of fully atomistic molecular dynamics simulations, investigate the effects of cross-linking density on chain packing and the interaction bonding between monomers and polymers. The validity of our model densities was check and calculated show a good agreement with available experimental. The comparison between hydrophobic and hydrophilic of the support membrane was found as the larger contribution toward the distance and intensity of RDF's trends. This study purposed that the TFC deposition was better on the N66 membrane with the same properties than on the PVDF membrane.

Acknowledgements

The authors would like to thank the sponsors for the financial support for this research through grants PGRS 180323 and RDU 1803113.

References

- [1] J.R. Khan, S. Muhammad, W. Ahmed, Dehydration of Isopropanol and Ethanol by Pervaporation Technique, *J. Engg. Appl. Sci.* 16 (2015) 67–72.
- [2] G.M. Shi, T.S. Chung, Thin film composite membranes on ceramic for pervaporation dehydration of isopropanol, *J. Memb. Sci.* 448 (2013) 34–43. doi:10.1016/j.memsci.2013.07.049.
- [3] J. Zuo, Y. Wang, S.P. Sun, T.S. Chung, Molecular design of thin film composite (TFC) hollow fiber membranes for isopropanol dehydration via pervaporation, *J. Memb. Sci.* 405–406 (2012) 123–133. doi:10.1016/j.memsci.2012.02.058.
- [4] Y. Huang, J. Ly, D. Nguyen, R.W. Baker, Ethanol dehydration using hydrophobic and hydrophilic polymer membranes, *Ind. Eng. Chem. Res.* 49 (2010) 12067–12073. doi:10.1021/ie100608s.
- [5] Y.T. Ong, S.H. Tan, Pervaporation separation of a ternary azeotrope containing ethyl acetate, ethanol and water using a buckypaper supported ionic liquid membrane, *Chem. Eng. Res. Des.* 109 (2016) 116–126. doi:http://dx.doi.org/10.1016/j.cherd.2015.10.051.

- [6] G.M. Shi, T.S. Chung, Thin film composite membranes on ceramic for pervaporation dehydration of isopropanol, *J. Memb. Sci.* (2013). doi:10.1016/j.memsci.2013.07.049.
- [7] K. Kholmurodov, E. Dushanov, K. Yasuoka, H. Khalil, A. Galal, S. Ahmed, N. Sweilam, H. Moharram, Molecular dynamics simulation of the interaction of ethanol-water mixture with a Pt surface, *Nat. Sci.* 3 (2011) 1011–1021. doi:10.4236/ns.2011.312126.
- [8] M. Yang, V. Koutsos, M. Zaiser, Interactions between polymers and carbon nanotubes: A molecular dynamics study, *J. Phys. Chem. B.* 109 (2005) 10009–10014. doi:10.1021/jp0442403.
- [9] M. Yang, Simulation of mechanical properties of carbon nanotubes and their interaction with polymers, (2005).
- [10] T. Wei, L. Zhang, H. Zhao, H. Ma, M.S.J. Sajib, H. Jiang, S. Murad, Aromatic Polyamide Reverse-Osmosis Membrane: An Atomistic Molecular Dynamics Simulation, *J. Phys. Chem. B.* 120 (2016) 10311–10318. doi:10.1021/acs.jpcc.6b06560.
- [11] K.P. Jensen, W.L. Jorgensen, Halide, ammonium, and alkali metal ion parameters for modeling aqueous solutions, *J. Chem. Theory Comput.* 2 (2006) 1499–1509. doi:10.1021/ct600252r.
- [12] A. Ahmadi, J.J. Freire, Molecular dynamics simulation study of compatibility for the polyvinylmethylether/polystyrene mixture, *Mol. Simul.* 34 (2008) 1253–1258. doi:10.1080/08927020802175233.
- [13] M. Shen, S. Keten, R.M. Lueptow, Dynamics of water and solute transport in polymeric reverse osmosis membranes via molecular dynamics simulations, *J. Memb. Sci.* 506 (2016) 95–108. doi:10.1016/j.memsci.2016.01.051.
- [14] M. Ding, A. Ghoufi, A. Szymczyk, Molecular simulations of polyamide reverse osmosis membranes, *Desalination.* 343 (2014) 48–53. doi:10.1016/j.desal.2013.09.024.
- [15] M.F. Jimenez-Solomon, P. Gorgojo, M. Munoz-Ibanez, A.G. Livingston, Beneath the surface: Influence of supports on thin film composite membranes by interfacial polymerization for organic solvent nanofiltration, *J. Memb. Sci.* 448 (2013) 102–113. doi:10.1016/j.memsci.2013.06.030.
- [16] J.S. Bermejo, C.M. Ugarte, Influence of cross-linking density on the glass transition and structure of chemically cross-linked PVA: A molecular dynamics study, *Macromol. Theory Simulations.* 18 (2009) 317–327. doi:10.1002/mats.200900032.
- [17] J.S. Bermejo, C.M. Ugarte, Influence of Cross-Linking Density on the Glass Transition and Structure of Chemically Cross- Linked PVA: A Molecular Dynamics Study, *J. Memb. Sci.* 5 (2016) 8411–8419. doi:10.1038/nmat4638.