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Interaction study between M-Phenylenediamine, Trimesoyl Chloride and Nylon 66 using Molecular Dynamic Simulation

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Abstract. The thin film composite (TFC) membrane is a porous membrane layered by a polyamide active layer. In the experimental work, the polyamide active layer prepared by the interaction between monomers, m-phenylenediamine (MPD) and trimesoyl chloride (TMC) which deposited on a membrane support. Considering the possibility of producing a loose TFC membrane and affect the separation performance, this study enlightens the interaction between monomers with Nylon 66 (N66) support membrane using simulation - molecular dynamic (MD). Different simulation system has been investigated with varying the ratio molecule of MPD to TMC where, TFC1 (1:1), TFC2 (3:1) and TFC3 (3:2) to the tertiary system of N66/MPD/TMC. The simulation was set for a COMPASS force field, where the equilibrium phases in a micro-canonical (constant volumes and total energy) (NVE) followed by run-production stage (constant pressure and temperature ensembles) (NPT) ensembles. The temperature and pressure were set at 323.15 K and 1atm respectively. The polyamide TFC was found to be formed by the main interactions between nitrogen (N) from MPD group to the carbon, (C) from TMC main chain at ranges of 4.25Å. Overall interaction can be observed between N from TFC layer with O atom from the substrate layer. All of the intermolecular interactions take place at 3.25Å distance. The best interaction in N66 to MPD and TMC system to the weakest is in the arrangement of TFC2 > TFC3 > TFC1. The highest intensity was obtained by the TFC2, indicating the best ratio of 3:1 of MPD molecules to TMC molecule with support polymer when fully polymerized occurred. This study suggests that ratio N66 to MPD and TMC in TFC2 is the best to interaction between TFC layer and substrate for fabrication of the TFC membrane.

1. Introduction

Molecular Dynamic (MD) simulation is employed to simulate the interfacial binding in relation to the molecular structures at the atomic level. It is widely used in the chemical process, especially for polymers. MD is a device to compute the various parameters such as diffusivity, compatibility of the materials blended, and the density of the polymers [1-2]. In MD, the force field represents the interaction between the molecular forces established within the system studied. The common force fields used in the MD are the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS), Assisted Model Building with Energy Refinement (AMBER99), Consistent Valence Force Field (CVFF), etc. [2-3]. COMPASS was created based on the empirical parameterization



techniques and state-of-the-art ab outlined the relationship between distance and the magnitude of the forces existing.

The COMPASS force field utilized to compute the structural, chemical, and physical characteristics of various series of molecules of organic and inorganic material [4-5]. It is very common to determine the interatomic interactions of organic as well as inorganic materials [6]. Compared with the other force fields, the COMPASS is more relevance to study the compatibility between aqueous and organic monomers to form the TFC membrane [7-8]. Sukitpaneenit and Chung used COMPASS force field in MD to study the compatibility of the polymer and mixed solvent systems [9]. Zhang et al. [10] on the other hand, calculate the binding energies between hydroxyapatite (HA) various polymers of polyethylene (PE), polyamide (PA) and polylactic acid (PLA) using the similar force field.

It is feasible to modify the pristine polymer to the thin film composite (TFC) membrane to enhance the separation performances [11-12]. Study the interaction between the two layers of membrane or two materials in the membrane by implementing the MD simulations have been done by Cho and Sung, Zhang et al. and Fereidoon et al. [5,13-14]. Polyamide (PA) TFC is easily prepared by interfacial polymerization (IP) flash reaction. It has both mechanical and performance strength which ideal for both commercial and laboratory study. The IP processes were manipulated in many MD studies to assist them recognize the materials properties before carried out in the real work [15–18]. Many researchers have demonstrated TFC films performance formulated by m-phenylenediamine (MPD) and trimesoyl chloride (TMC) on a various hydrophilic substrate [19–21]. Unfortunately, the hydrophilic lead to the weak mechanical strength of produced TFC membrane [22]. According to Shi et al., the stability between layers are strongly depending on the well interfacial interactions between the thin layer and the polymers [23]. Huang and McCutcheon applied the combination of MPD and TMC on the nylon 6, 6 (N66) as the support membrane and produced hydrophilic - high mechanical strength balance of TFC membrane [24-25]. In this study, MD is utilized to simulate the molecular interaction and to find the binding strength between monomers and the substrate membrane.

2. Methodology

The pairs of organic and aqueous monomers were analysed using RDF in MD for the shortest distance for the interaction to happen as well as the magnitude of the attraction forces. The strongest bonding between organic and aqueous monomers is associated with the stability of the thin film when deposited on the substrate membrane. The substrate chooses for the reasons which hydrophilic and mechanical strength owned by N66 membrane. N66 with the molecule formula $C_{12}H_{20}N_2O_2$ was used as platform for the aqueous and organic monomers, MPD and TMC respectively to react and form polyamide active layer. MPD is aromatic structure with two amine groups while TMC consist of three acyl chloride groups attach to a benzene ring. The molecular structures of the monomers with different number of functional groups and chain length were presented in figure 1.

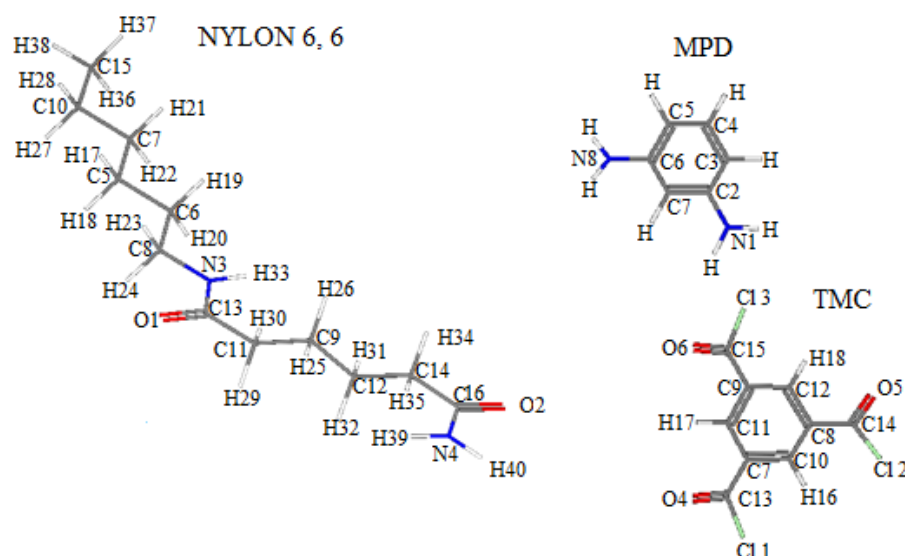


Figure 1. The repeat unit of monomers chain molecules for N66, MPD and TMC.

There is various composition suggested for the organic and aqueous monomers for the IP reactions to form the TFC membrane. MD simulations provide discernment about the process at a molecular state and to evaluate the intermolecular interface between various monomers composition with the substrate membrane. The number of molecules for each monomer was set as shown in table 1. The systems involved of the various composition of molecules namely for N66, 50 molecules, MPD molecules set from 10, and 30 while for TMC was at 10 and 20.

Table 1. Ratio of monomers molecules for the interaction study with support membrane in molecular dynamic simulation.

No.	Name	Number of molecules, N66:MPD:TMC	Equilibrated cell size : A x B x C [Å]
1.	N66	50	26.66 × 26.66 × 26.66
2.	TFC1	50: 10:10	28.83 × 28.83 × 28.83
3.	TFC2	50: 30:10	30.63 × 30.63 × 30.63
4.	TFC3	50: 30:20	31.41 × 31.41 × 31.41

The simulation setting was described according to the Ewald summation, COMPASS force field and velocity verlet algorithm for the function of equilibrium and production phase function, energy interatomic potential calculation and time integrator algorithm calculation respectively. The force field of the bulk phase represented as 3D box as shown in figure 2. The equilibrium phase was performed in micro-canonical, NVE of constant number molecules, volumes, and total energy ensembles, subsequently by constant number molecules, pressure, and temperature (NPT) ensembles for 1000ps each ensemble. NVE was choosing in the annealing step to keep the total energy in the system constant. Meanwhile, NPT ensemble in the production step is applied for the temperature coupling which maintains a fixed pressure rather than a steady volume. The same condition implies for both NVE and NPT ensembles where T and P were set at 323.15 K and 1atm respectively. Then, the final simulation trajectories were evaluated.

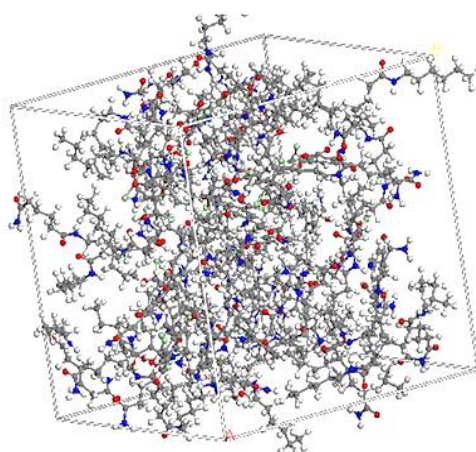


Figure 2. 3D boxes representing the simulation of the N66: MPD: TMC (50:10:10) system.

The simulation started by insert the molecular structures for the geometry optimization, followed by create the box to represent the system where the reaction take place and then minimizing the box. The equilibrium phase was performed in microcanonical, NVE ensembles followed by run-production stage by ensembles NPT. The electrostatics forces were calculation by Ewald summation (convergence parameter of 10^{-6}) in the periodic system. The simulation was run for a 1000 picoseconds (ps) with the time step set 1 femtosecond (fs) for each run and the simulation was periodic in three dimensions (Li et al., 2009). The total simulation time must be 1000ps or exceed than that in order to ensure a complete interaction (Yang et al., 2005). The simulation run-production stage then continues by NPT with the same condition for total 2000 ps with the time step of 1 fs each run. The final simulation trajectory was analyzed by RDFs.

3. Results and discussion

3.1. Interaction within the N66.

There are two main interaction forces can be identified using RDF analysis from the MD simulations which are intra- and intermolecular interactions. Basically, intra-molecular interaction is the repulsive forces between adjacent atoms in a molecule. Meanwhile, intermolecular interaction is the attractive forces among the atoms from different nearby molecules to form larger molecular structure. As for N66, the discussion only involved the intra-molecular interaction as illustrated in Figure 3. The main repulsive forces are within N66 polymer is between the hydrogen (H) and nitrogen atoms (N). These atoms potentially are the active atoms in a N66 functional group to act and react with the other compound introduced.

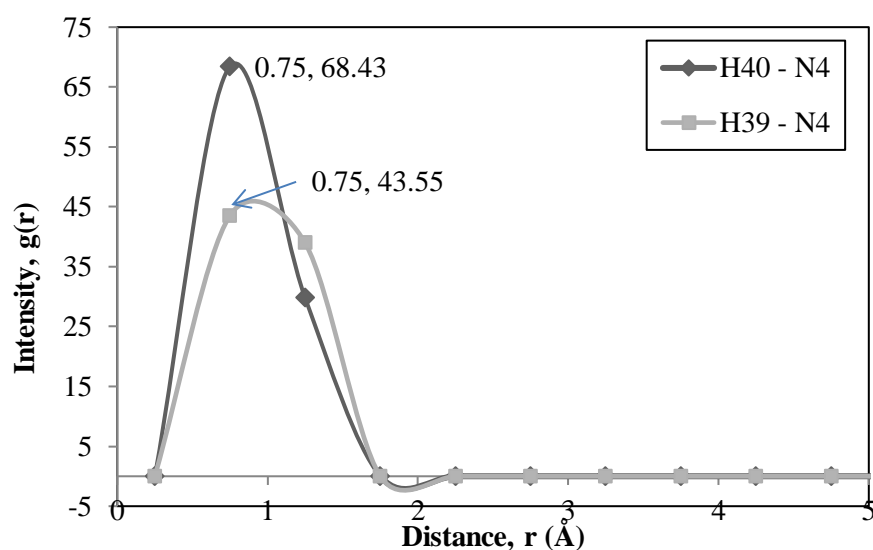


Figure 3. The intra-molecular interaction within N66 chain.

3.2. General interaction of amine group and organic group.

The molecular interaction is important to determine the efficiency of the active thin sheet on the support membrane by avoiding for a loose TFC membrane formation. The COMPASS force field successfully demonstrated the magnitude of binding forces with the contribution to a firm TFC membrane. TFC membrane is produced by the reaction between amine groups (MPD) with the organic group (TMC) on the polymeric support surfaces. The cross-linking interaction can be detected between nitrogen (N) from the aqueous monomer group with the carbon (C) from the acyl group to form the TFC membranes [26]. Figure 4 illustrates the main interaction existing within the N66 support with the TFC membrane. The TFC membrane then interacted with the support membrane for completing the deposition process where the main interaction by the hydrogen bond of oxygen (O) from N66 membrane support with the chloride (CL) from acyl main chain and with the N from amine molecule.

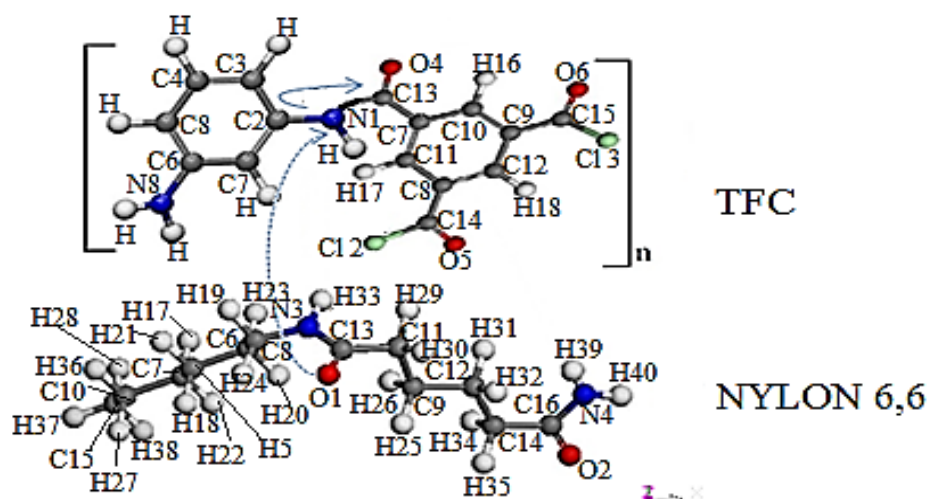


Figure 4. The main interaction between TFC membranes with the N66 support.

3.3. The interaction between amine and acyl group for formation of active layer.

Different simulation system have been investigated with varying the ratio molecule of MPD to TMC where, TFC1 (1:1), TFC2 (3:1) and TFC3 (3:2) to the tertiary system of N66/MPD/TMC in Figure 5.

All the main interactions to form TFC membranes were functioned by N atom from MPD to the C from TMC during IP process at radii of 4.25\AA . The best interaction system to the weakest is in the arrangement of TFC3 > TFC1 > TFC2. The highest intensity was obtained by the TFC3 which indicated the best ratio of 3:2 of MPD molecules to TMC molecule. This finding is in agreement with Shen et al., which showed ratio 3:2 of MPD to TMC was the best composition [27]. The ratio is referred as fully polymerized its monomer composition where the polymerization reaction was completed. Two TMC group would attracted with three amide group generated less monomers excess on the membrane surface. Low amount of TMC (TFC1 and TFC2) reduces the IP rate on the membrane surface as the limited reactants. The ratio 1 to 1 of MPD to TMC system found to form a reaction-aggregation Muscatello et al., [26]. If the system has more reactants, there will be more unreacted amine and acyl chloride groups respectively. This condition would lead to thicker membrane formation as amine and carboxyl groups [28].

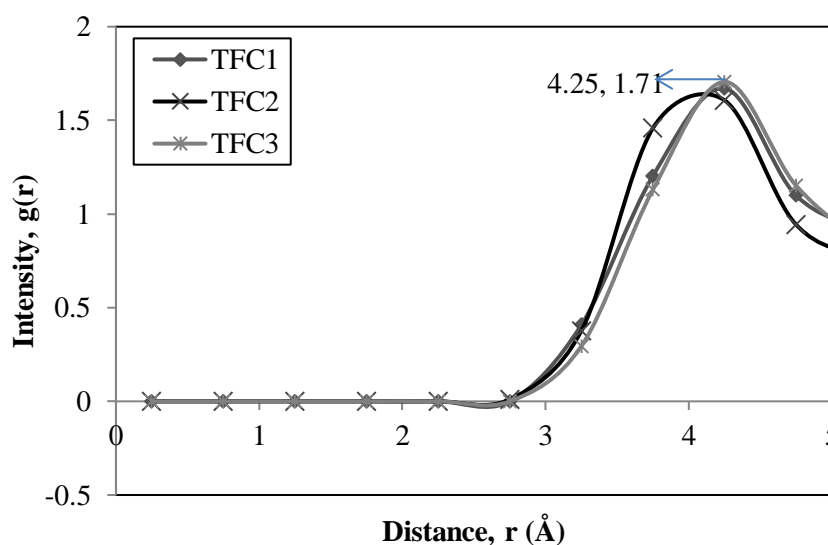


Figure 5. The interaction of nitrogen (N1) from the MPD group with the carbon (C13) from TMC group.

3.4. The interaction between active layer with support membrane, N66.

The significant interaction occurred between TFC layers and the N66 membrane can be observed attributed by the N from TFC layer with O atom from the substrate layer as shown in Figure 6. All of the intermolecular interactions take place at 3.25\AA distance. The intensity of interaction forces was discovered in the range from 1.35\AA to 1.93\AA which indicate strong interaction. Huang & McCutcheon claimed that TFC formed inside the core of the N66 support [25]. Small pores membrane support consist of the high surface area of substrate which draws the TMC solution to diffuse inside the membrane. This is because of the low diffusion rate of MPD solution from the pore attributed by good hydrogen - bonding interactions between MPD and the N66 membrane pore walls. The TFC in the pores provides a longer effective film thickness for water permeation [29].

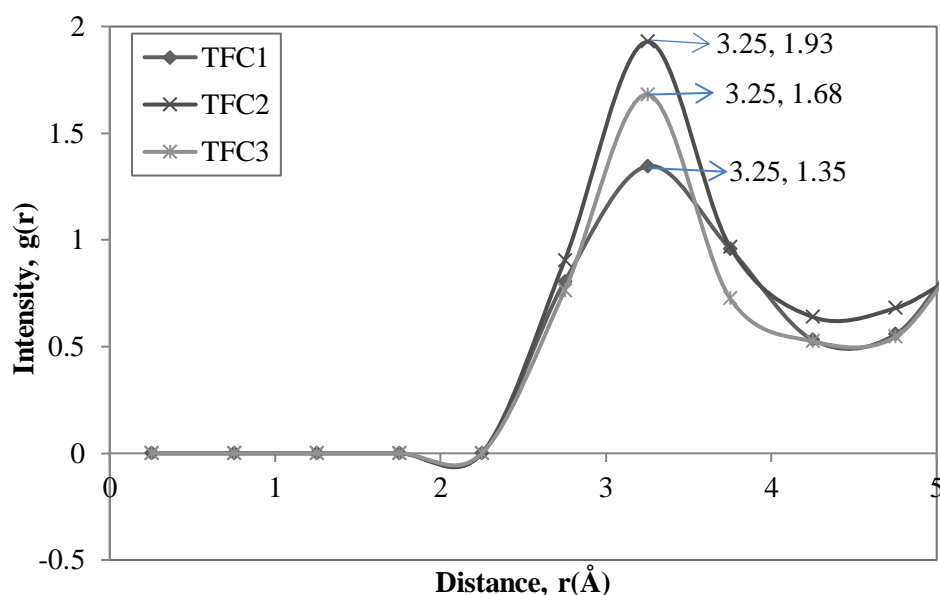


Figure 6. The interaction of atom N1 from TFC (amine group) with the O1 from N66 group.

The ratio of MPD to TMC observed to have affected on the interaction forces from 3:1 (TFC2) > 3:2 (TFC3) > 1:1 (TFC1). More amount of MPD in the system would increase the interaction between TFC layers with the support. Increasing the MPD in real experimental work can be carried out by increasing the MPD concentration or MPD immersion time. This is believed to occur due to higher MPD in the TFC layer and therefore increase the interaction with the carbonyl group of N66 membrane [30]. Result agree to corroborate with the study by Huang et al. [31]. Compare the similar ratio of N66 to MPD to TMC but at larger cell size (between TFC1 to TFC3), the interaction between N66 to TFC observed to be stronger in the smaller cluster size than the bigger size. The higher interaction distance obtained from this simulation may be contributed by the lower amount of molecules in the simulation system [32]. However, the interaction distance still below than 5.0Å [33].

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, complete atomistic molecular dynamics simulations, explore the effects of cross-linking degree on TFC membrane and the interaction bonding between monomers and polymers. The main interactions to form TFC membrane were by N from amine to the C from TMC at radii of 4.25Å where shown the best by TFC3 followed by TFC1 and TFC2. The highest intensity indicated the best ratio of 3:2 of MPD molecules to TMC molecule when fully polymerized occurred. However, for deposition of MPD and TMC on N66, the result shows 3:1 of amount of MPD to TMC possess higher interaction. The interaction between the N from TFC layer at 3.25Å with the O atoms from the support membrane molecule. In the meantime, simulation study suggests that the larger cell size of TFC3 yield weaker interaction compared smaller cluster size TFC1.

Acknowledgements

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