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Enhancing Understanding of Siloxane Surface Properties and Functional Group Effects on Water Deoxygenation

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Abstract: The de-oxygenation process in water used in well injection operations is an important matter to eliminate corrosion in petroleum industry. This study used molecular dynamics simulations to understand the behavior of siloxane surface through studding the surface properties with two functional groups attached to the end of siloxane and their effect on de-oxygenation process. The simulations were performed using LAMMPS to characterize of surface properties. Jmol software was used to generate siloxane chains with (8, 20, and 35) repeat units. Firstly, we evaluated properties such as total energy, surface tension and viscosity. Then, we used siloxane as a membrane to compare the efficiency of de-oxygenation for the both types of functional groups. The results indicated that longer chains length increased total energy, viscosity while decreased surface tension. Replacing methyl groups with trifluoromethyl (CF3) groups increased all the above mentioned properties in varying proportions. Trifluoromethyl (CF3) groups showed better removal efficiency than methyl (CH3) groups but allowed more water to pass. Furthermore, the simulations were run using the class II potential developed by Sun, Rigby, and others within an explicit-atom (EA) model.

Keywords: molecular dynamic; membrane; siloxane; functional group; deoxygenation

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1. Introduction

Polyargansiloxanes are a type of silicone-based polymer known as siloxane. The properties of polyarganosiloxanes can be affected by attaching different organic groups to silicon atoms. Some common organic groups include methyl, phenyl, fluorine containing alkyl groups. These changes in chemical structure vary the properties of polyarganosiloxanes such as flexibility, heat stability, and chemical resistance [1].

Many industries use silicon in their fields due to its unique properties. It is used in coatings, oil and gas separation processes, adhesives, lubricants, and many other products because of its resistance to heat, cold, moisture, and chemicals [3].

The most common methods to prepare polyarganosiloxanes are condensation polymerization and addition polymerization. The properties of the synthesized siloxane can be affected by the choice of synthesis method [4].The main type polymer in the group of polyorganosiloxanes is polydimethylsiloxane (PDMS). PDMS consists of repeating units of dimethylsiloxane, which is represented as shown in Figure 1 [5].

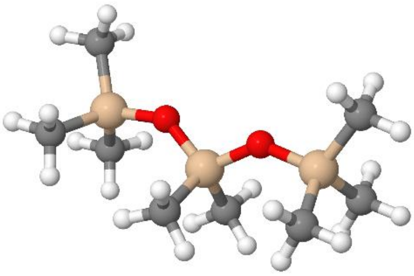


Figure 1. Structure of the PDMS (methyl end group).

In PDMS, each silicon atom is bonded to two oxygen atoms and two methyl groups (CH3), resulting in a flexible and relatively inert polymer chain. The methyl groups in PDMS have low polarity and contribute to a low surface tension, meaning that PDMS tends not to wet surfaces easily. This property makes PDMS suitable for applications where low adhesion to surfaces is desired, such as in mold release agents or coatings for water-repellent surfaces. Another property of PDMS is that it is permeable to gases due to its flexible polymeric chains and large space between methyl groups, this high permeability to gases makes PDMS a valuable membrane in applications such as oil/gas separation [5].

The methyl group in PDMS can be replaced by other functional groups to synthesize polymers for a wide range of other exciting applications, for example fluorine-containing alkyl groups Figure 2 lead to high resistance to hydrocarbon solubility while maintaining low surface tension. This property is important for its application in gas/oil separation and is of direct importance for applications in the oil industry [5,6].

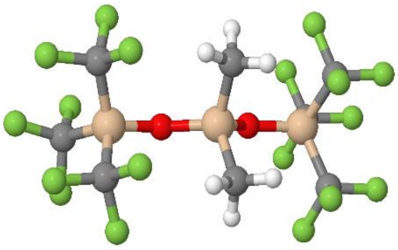


Figure 2. Structure of the PDMS (fluorine alkyl end group).

Many fundamental questions related the relationship between the backbone structure and the functional groups attached to the backbones can be addressed using molecular simulations, with carefully chosen interaction potentials and target boundary conditions with correct sampling procedures.

These good advantages and qualities of PDMS, motivated us to study and improve understanding of the surface behavior of siloxane to enhance the process of removing oxygen from water used in many applications in the petroleum industry to reduce corrosion.

In this study MD simulation by LAMMPS were performed to evaluate the surface properties of siloxane with two different of functional group attached to the end of the chain which are methyl group and fluorinated alkyl represented by Trifluoromethyl. Three types of chains were chosen (8, 20, 35) monomers per chain. Firstly, surface tension, viscosity, and total energy were examined for both cases. Subsequently we replicated the 20 monomer per chain for both end functional groups and used to evaluate efficiency the de-oxygenation of water.

2. Results and Discussion

2.1. Surface Tension

The study of surface tension is a great importance in understanding the behavior of fluids for petroleum gas/oil separation processes [7]. We mentioned in the introduction that the presence of trifluoromethyl groups (CF3) has the unique property of providing high resistance to the solubility of hydrocarbons while maintaining low surface tension. This property makes it valuable in improving the efficiency of separation processes. Table 1 and Figure 3 showed that the surface tension increased slightly by changing end functional group from methyl group to Trifluoromethyl as well as it is decreased when the chain became longer for both type. These results can be used to check the accuracy for the results as the surface tension maintaining in low value.

The strong electronegativity and space barriers in trifluoromethyl groups on siloxane molecules leads to increase surface tension compared to siloxane molecules with methyl (CH3) groups [8]. On the other hand, the surface tension decrease with increasing chain length, conforms with the hypothesis that the interactions of longer chains increases with van der Waals and surface area, which lead to decrease the surface tension [9–11]. This result is observed for both types of end groups, indicating that chain length is a critical factor in determining surface tension. The results show that although the surface tension of siloxane is slightly increased in the presence of a trifluoromethyl group compared to a methyl group, it still maintains a relatively low value, making it suitable for applications in gas/oil separation processes. The observed results confirm the accuracy of the simulation results and provide insights into the molecular interactions.

Table 1. Chain Length and Surface Tension for methyl and Fluorinated alkyl Function Group.

Type of chain	Chain Length	Surface Tension (m N/m)
CH3	8	21.44
CH3	20	19.97
CH3	35	17.8
Average		19.74
CF3	8	24.76
CF3	20	20.183
CF3	35	19.81
Average		21.58

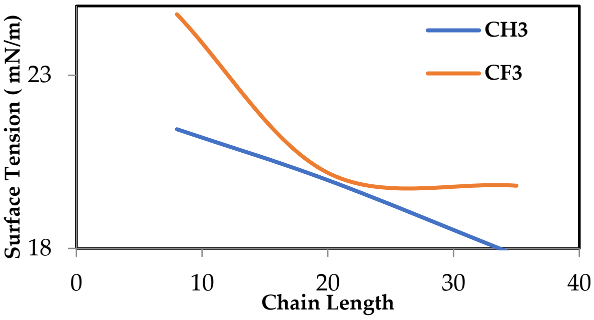


Figure 3 Relation of Surface tension with chain Length and Functional group.

2.2. Viscosity

This section showing simulation results of viscosity at different chains length with two functional end groups. The results in Table 2 and Figure 4 indicate that as the chain length increase, viscosity increased. As well as, the results showed the viscosity for Trifluoromethyl functional group is higher than methyl group. Longer chain lengths and higher viscous decrease the water permeability through membrane [12]. Increasing viscosity with increasing the chains length is due to increased molecular interactions and crosslinking, which impedes the flow of molecules [12]. The observation in results of viscosity has significant effects for membrane technology. Higher viscosity leads to decreased water permeability through the membrane [13]. This understanding can be essential in designing of membranes for various applications.

Table 2. Chain Length and viscosity for methyl and Fluorinated alkyl Function Group.

Type of chain	Chain Length	Viscosity (cp)
CH3	8	8.83
CH3	20	18.4
CH3	35	20
Average		15.74
CF3	8	11.9
CF3	20	17.8
CF3	35	29.9
Average		19.86

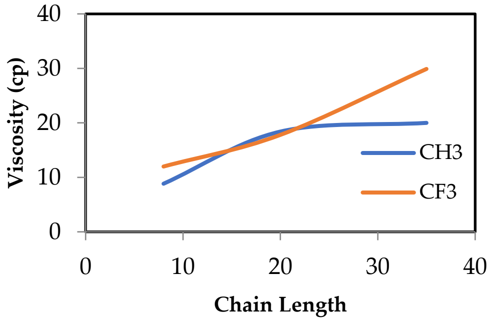


Figure 4. Relation of Viscosity with chain Length and Functional group.

2.3. Total Energy

Evaluation the total energy of molecular interaction of siloxane is essential to understanding its behavior in various applications [13]. This section shows the simulated results of total energy of siloxane chains with (CF3) and (CH3) functional end groups. We observe from Table 3 and Figure 5, the total energy is increased as the chain became longer. The other important noticed is that the total energy for both functional groups approximately is equal. Increasing chain length meaning increasing number of bonds between atoms and then increase interaction between the siloxane chains and this led to increase the total energy.

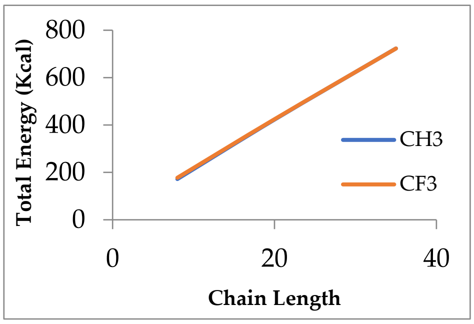


Figure 5. Relation of Total Energy with chain Length and Functional group.

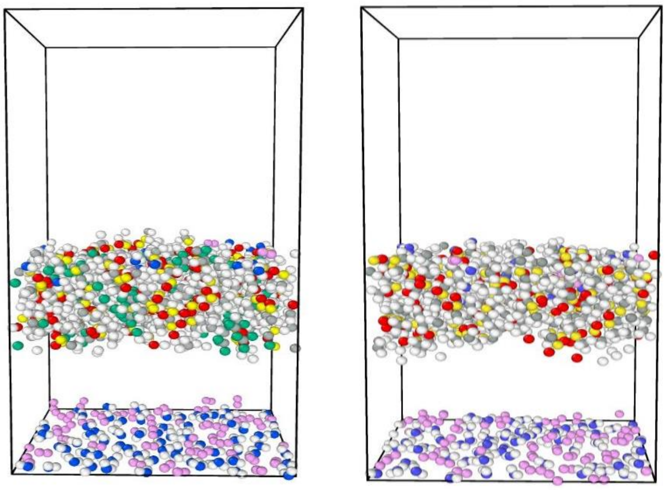
Table 3. Total Energy for Siloxane as a Function of Chain Length and Types.

Type of chain	Chain Length	Total Energy (Kcal)
CH3	8	171.83
CH3	20	422.95
CH3	35	723.16
Average		439.32
CF3	8	177.44
CF3	20	424.47
CF3	35	722.9
Average		441.6

2.4. Evaluation Dissolved Oxygen Removal

This section highlights understanding the effect of functional end groups on the removal of dissolved oxygen by preparing different concentrations of dissolved oxygen in water. Table 4 represented summary of all results that are gain from second part of investigation. We studied 4 oxygen concentrations, represented by (20, 50, 80, 100) % of dissolved oxygen in water. The system for these concentrations consists of for the three types of chain length of PDMS; (8, 20, 35) monomers per chain and each thus contain (87, 207, 357) atoms respectively. To this we then add 100 molecules of water and (20, 50, 80, 100) molecules of oxygen to represent the four concentrations mentioned. To provide a driving force for both water and oxygen molecules we also applied a force of (0.5, 1, 2, 4) (Kcal/mol.°A) to enable the proposed separation within the timescale limitations.

We calculated the percentage of water molecules permeating through membrane then the ratio of dissolved oxygen to water flux or water passage through membrane. Figure 6 represented simulation snapshot of water and dissolved oxygen on siloxane surface during period time of simulation.



(**a**) (**b**)

Figure 6. snapshot of water and dissolved oxygen on siloxane surface during Simulation. Siloxane with CF3 (b) Siloxane with CH3. Color code: dissolved O, pink; Water O, blue; Siloxane O, red; C, grey; H, white; Si, yellow; F, green.

Table 4. Dissolved Oxygen Removal at 300K.

Chains Type	Driving Force (kcal/mol)/ Angstrom	Od Concentration with water	Od Reomoval %	Water pass %	(Od removal %) / (water moleules pass %)
CH3	0.25	20%	0.00	0.00	0.00
		50%	1.98	40.11	4.95
		80%	3.93	62.87	6.25
		100%	157.56	95.68	164.67
		average	40.87	49.67	82.29
CF3	0.25	20%	1.99	43.69	4.56
		50%	63.70	91.62	69.53
		80%	139.73	85.90	162.66
		100%	185.15	82.36	224.80
		average	97.65	75.89	128.66
CH3	1	20%	2.29	37.60	6.09
		50%	94.66	67.51	140.21
		80%	141.68	65.67	215.73
		100%	188.82	69.53	271.55
		average	106.86	60.08	177.86
CF3	1	20%	15.96	58.32	27.37
		50%	91.90	72.52	126.72
		80%	139.73	85.90	162.66
		100%	185.15	82.36	224.80
		average	108.19	74.78	144.68
CH3	2	20%	11.95	38.92	30.70
		50%	75.62	38.28	197.55
		80%	119.92	58.79	203.98
		100%	172.35	52.41	328.86
		average	94.96	47.10	201.62
CF3	2	20%	26.90	64.72	41.57
		50%	63.70	91.62	69.53
		80%	78.84	65.55	120.28
		100%	170.20	71.53	237.95
		average	84.91	73.35	115.76
CH3	4	20%	13.93	50.56	27.55
		50%	53.72	35.75	150.24
		80%	117.24	53.66	218.49
		100%	133.07	47.50	280.13
		average	79.49	46.87	169.60
CF3	4	20%	25.92	73.48	35.27
		50%	69.80	60.19	115.96
		80%	137.03	65.34	209.71
		100%	157.75	62.91	250.75
		average	97.62	65.48	149.09

We showed in Figure 7 that siloxane with CF3 functional group is more active than in methyl group in the removal of dissolved Oxygen at all concentrations. This is because CF3 groups are more polar and electronegative than CH3 groups and this could make stronger interactions with oxygen molecules and increasing the removal efficiency [15].

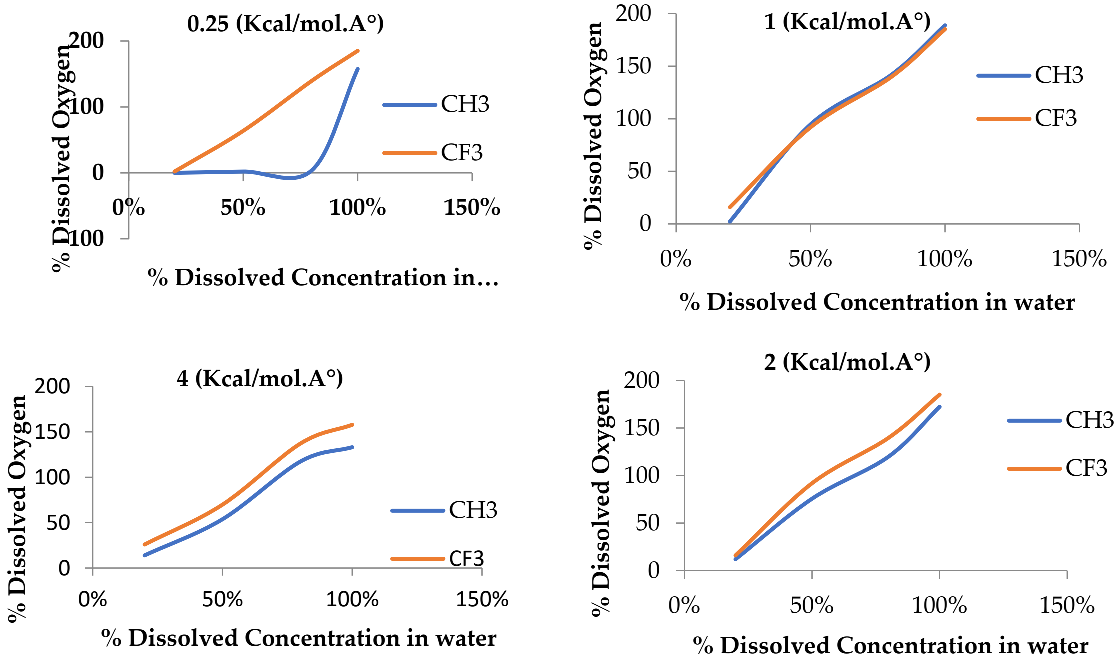


Figure 7. Percentage Dissolved Oxygen Removal with respect to driving Force.

On the other hand, although that CF3 functional group have more efficiency than CH3 functional group however the water percentage pass through membrane are more than in CH3 functional group and this noticed can be seen in Figure 8.

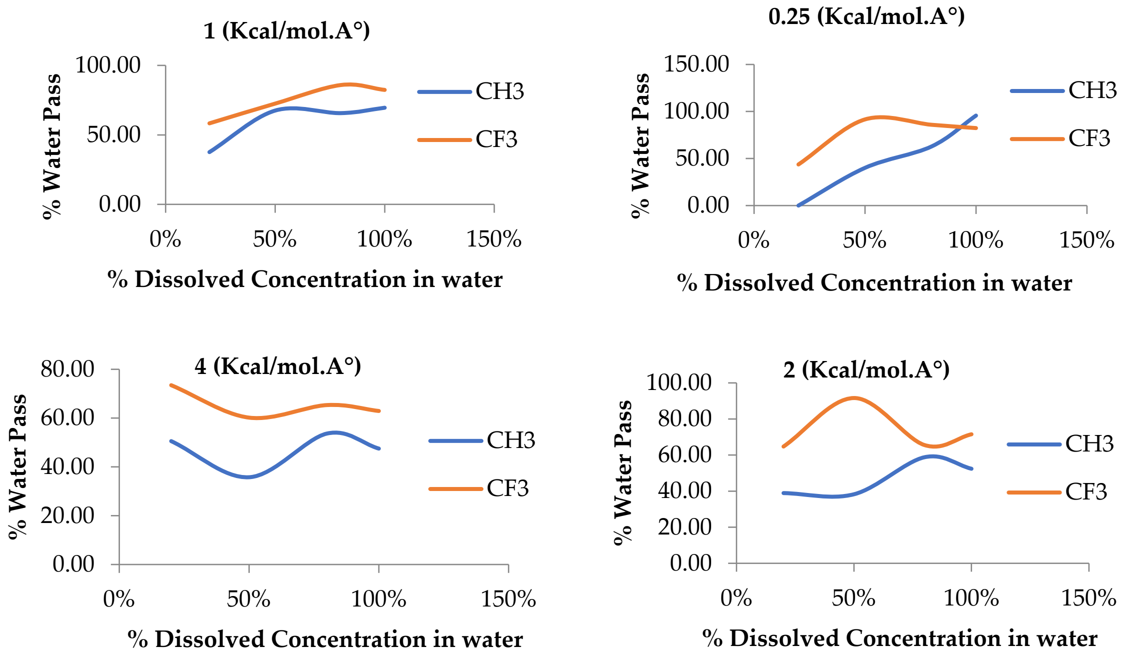


Figure 8. Percentage Water Pass through membrane with respect to driving Force.

In both types of membrane, we evaluate the ratio of percentage of oxygen removal to percentage water passage as shown in Table 4 and Figure 9. We can conclude in over all that ratio of removing oxygen to water passage in CH3 is better than CF3.

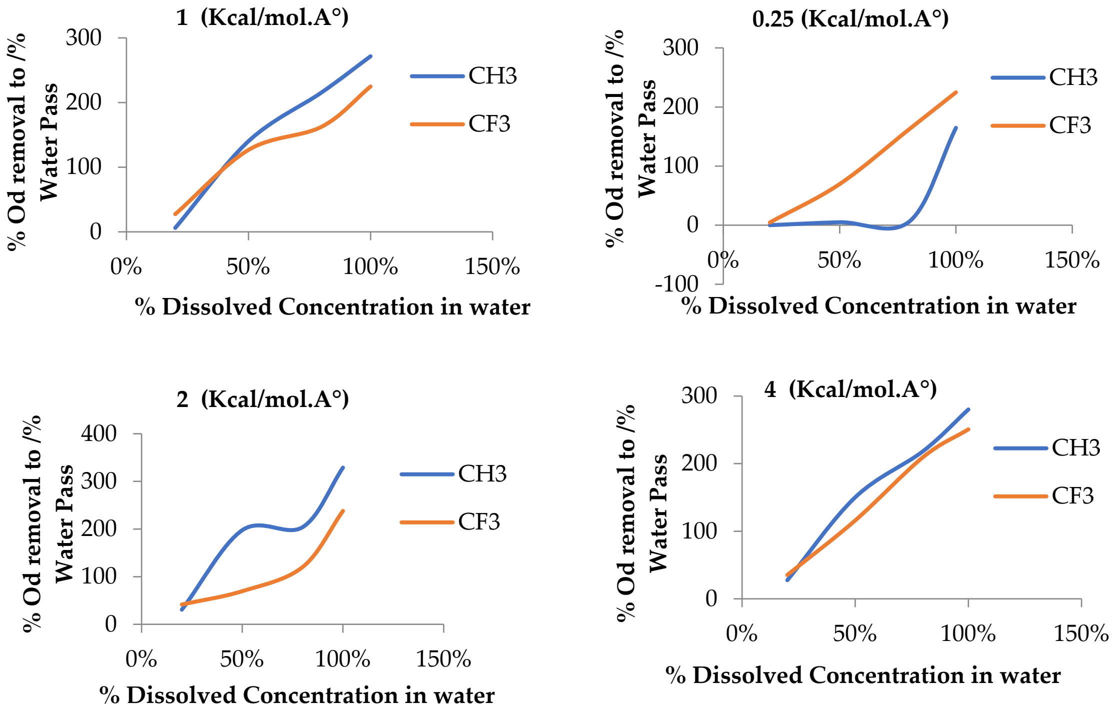


Figure 9. Ratio of percentage removal dissolved oxygen to water pass through membrane with respect to driving Force.

3. Materials and Methods

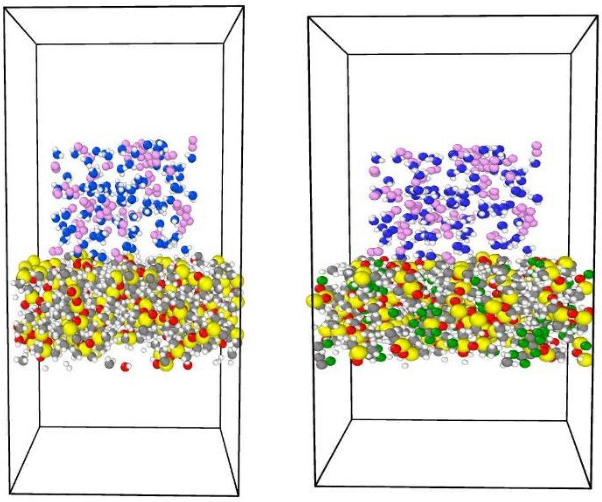
Molecular dynamics simulation through LAMMPS was performed for this study [16]. Jmol software was used to generate chains of siloxane structures with lengths (8, 20, and 35) repeat units, as illustrated in the Table 5 [17]. Methyl (CH3) and trifluoromethyl (CF3) functional groups were independently incorporated into each sample. The simulations were run using the class II potential developed by Sun, Rigby, and others, Table 6 [18,19]. This class II potential is applied within an explicit-atom (EA) model, treating Si, O, C, and H atoms separately. A time step of 0.01 fs and rc = 11 Å was used for all of the simulations. The temperature T was controlled with a Nose-Hoover thermostat at 300 K

Table 5. Number and Molecular Weight of PDMS Structures.

End Functional Group	PDMS structure per Monomer	Total atoms of pdms in Simulation box	Molecular weight (g/mol)
CH3	8	87	607.310
	20	207	1497.169
	35	357	2609.493
CF3	8	87	607.310
	20	207	1497.169
	35	357	2609.493

The methodology consist of two parts, firstly using both the NVT ensemble and NPT ensemble with constant density 0.95 g/cm^3 to evaluate the surface properties of siloxane with both of functional group such as total energy, surface tension and viscosity

In the second part of investigation we chose a chain length (20) repeat unit and replicated four times for both types of functional groups. The main aim of this part is to study efficiency of removing dissolved oxygen in water. In this part, pdms was equilibrated using NVT ensemble with density 0.98 g/cm^3 for methyl functional group and 1.2 g/cm^3 for trifluoromethyl functional groups, then Packmol [20] was used to configure simulation box containing equilibrated pdms in both functional group as a membrane then water with TIP3P force fields and dissolved oxygen randomly placed above the membrane as shown in Figure 10. We choose four different concentrations (20, 50, 80, 100) % of dissolved oxygen with four driving force (0.25, 1, 2, 4). The configured simulation box was run with NVE ensemble and Langevin to control the temperature.



(**a**) (**b**)

Figure 10. Configuration of water and dissolved oxygen slab in contact with siloxane. (a) Siloxane with CF3 (b) Siloxane with CH3. Color code: dissolved O, pink;. Water O, blue; Siloxane O, red; C, grey; H, white; Si, yellow; F, green.

We used the common form of class I intermolecular potentials for bonds, angles, and torsional bonds. Bond lengths, bond angles, and torsional bond angles are preferred in Potential Harmony as mentioned in the equations below respectively [18,19];

$$E = k_b\,(r - r_0)^2 \tag{1}$$

$$E = k_\theta\,(\theta - \theta_0)^2 \tag{2}$$

$$E = k_t\,[1 + \cos(n\varnothing)] \tag{3}$$

Where r_0 is the equilibrium bond distance, k_b is (energy/distance^2), θ_0 is the equilibrium value of the angle, k_θ and k_t is energy, n integer > = 3 and Ø = 180 degrees.

All potential parameters for bond interaction and non-bond interaction used in the simulations are summarized in Table 6 and Table 7 respectively.

Table 6. Potential Parameters for bond interaction.

bond	K_t	r_0	Angle	K_θ	θ_0	dehidral	$K_ø$	n
C-F	496	1.363	C-Si-C	44.4	113.5	F-C-Si-C	0.9006	3
C-H	340.6175	1.105	C-Si-O	42.3	113.1	F-C-Si-O	0.9006	3
C-Si	238	1.809	F-C-F	60	109.5	H-C-Si-C	0.9006	3
O-Si	392.8	1.665	F-C-Si	95	107.8	H-C-Si-O	0.9006	3
			H-C-H	60	109.5	Si-O-Si-C	0.9006	3
			H-C-Si	34.6	112.3	Si-O-Si-O	0.9006	3
			O-Si-O	44.4	113.5			
			Si-O-Si	60	109.5			

Table 7. Potential Parameters for non-bond interaction.

Nonbonded	ϵ[kcal/mol]	σ [Å]	q	mass
C	0.054	4.01	-0.294000	12.0115

F	0.0598	3.2	-0.344300	18.9984
H	0.02	2.995	0.053000	1.0079
O	0.24	3.535	-0.445000	15.9994
Si	0.07	4.284	0.715000	28.085501

The van der Waals and Coulomb potential interactions occurs through electrical interactions between two or more atoms or molecules that are very close together, these interaction parameters are listed in Table 8. Non- bonded potential is defined as follows [18,19]:

$$U_{\alpha\gamma}^{\mathrm{nonbond}}(r)=\begin{cases} U_{\alpha\gamma}^{\mathrm{vW}}(r)+k_q\dfrac{q_\alpha q_\gamma}{r} & r<r_c \\ k_q\dfrac{q_\alpha q_\gamma}{r} & r>r_c \end{cases} \tag{4}$$

Where $U_{\alpha\gamma}^{\mathrm{vW}}(r)$ are the van der Waals interactions, r is the distance between two atoms of type α and γ, q is the electric charge, and r_c is the cutoff distance for the van der Waals interactions.

To determine interaction parameters for non-bonded interaction we used sixthpower mixing rule as below [17];

$$\epsilon_{\alpha\gamma}=\frac{2\sigma_\alpha^3\ \sigma_\gamma^3\sqrt{\epsilon_\alpha\epsilon_\gamma}}{\sigma_\alpha^6+\sigma_\gamma^6} \tag{6}$$

$$\sigma_{\alpha\gamma}=\left(\frac{\sigma_\alpha^6+\sigma_\gamma^6}{2}\right)^{\frac{1}{6}} \tag{7}$$

Table 8. Van der Waals Interaction Parameters for the class II force field.

Bonds	∈ [kcal/mol]	σ [Å]
C-C	4.0100	0.0540
C-F	3.7119	0.0459
C-H	3.6691	0.0233
C-O	3.8091	0.1062
C-Si	4.1583	0.0603
F-F	3.2000	0.0598
F-H	3.1059	0.0339
F-O	3.3881	0.1146
F-Si	3.9199	0.0459
H-H	2.9950	0.0200
H-O	3.3189	0.0615
H-Si	3.8875	0.0229
O-O	3.5350	0.2400
O-Si	3.9952	0.1107
Si-Si	4.2840	0.0700

4. Conclusions

In this research, the effect of functional groups on the behaviors of siloxane surface and deoxygenation efficiency was studied. It has been observed that trifluoromethyl functional groups (CF3) are more resistant to dissolution in hydrocarbons compared to methyl groups (CH3) and slightly increased the surface tension. Furthermore, longer chains length, mainly in both types of functional group led to increased viscosity requiring while the total energy approximately was equal. We concluded in deoxygenation processes, membranes with CF3 functional groups gives more efficiency than methyl group due to stronger interactions with oxygen molecules. Despite this, the percentage of water passing through it is also greater compared to siloxane membrane with CH3 functional group. So the evaluation of deoxygenation ratio to water passage showed that membrane with CH3 functional group performed better in this part. These results enhanced the understanding the nuanced balance between functional group properties and membrane performance, offering valuable insights for optimizing siloxane membranes in various applications such as gas/oil separation.

Supplementary Materials: The following supporting information can be downloaded at:.

Author Contributions: F.S.: investigation, data curation, methodology, and writing—original draft; S.M.: Supervision, conceptualization, investigation, writing—review and editing; S.M: Supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

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