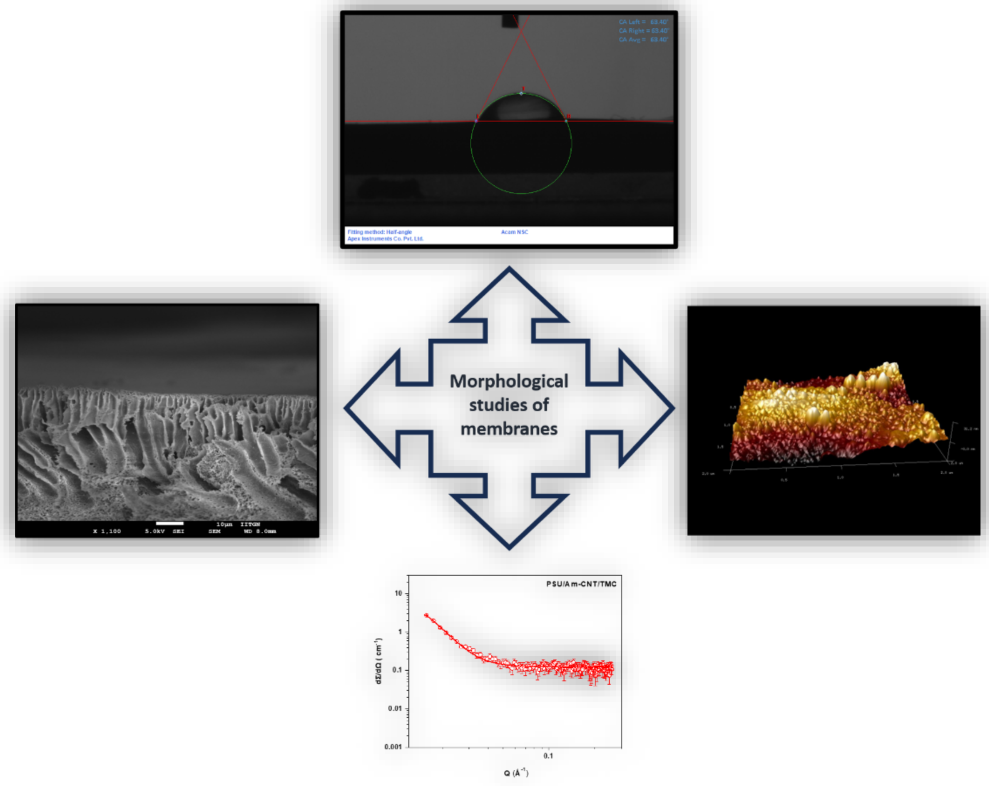
Chapter 5

Results and Discussion



5.1 Morphological Characterization of unmodified and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

5.1.1 FE-SEM

The FE-SEM images in Figure 5.1 shows the cross-sectional images of pristine polysulphone, polysulphone/azide-MWCNTs, and click reaction modified polysulphone/azide-MWCNTs membranes. The cross-section of the membrane shows a sponge-like structure, which suggests a uniform distribution of azide MWCNTs in to polysulphone matrix. The cross-section of the modified membrane exhibits a more asymmetric structure with increased voids. The cross-section of the membrane shows both sponge-like pores and macro voids with irregularities, resulting in increased porosity. Based on the observed surface morphology changes, it can be inferred that no significant changes occurred in the bulk morphology of the modified membrane. Bulk morphology refers to the cross-sectional view of the membrane that remains unaffected by the click reaction[146,147].

5.1.2 AFM

The AFM images in Fig. 5.2 provide information on the surface roughness (Sa) and root mean square (Sq) of the membranes, those are important parameters for studying the membrane surface interactions. The modified membrane via click reaction exhibits higher average surface roughness compared to the unmodified membrane, as depicted in Fig. 5.2. The polysulfone membrane incorporated with azide-MWCNTs showed a decrease in surface roughness compared to the pristine membrane, as expected (Table 5.1), indicating that the incorporation of azide-functionalized CNT smoothens the membrane surface[82,86]. However, after the membrane was modified via click reaction, the surface roughness increased because of the formation of triazole moieties on the membrane surface, indicating that the membrane had undergone surface modification.

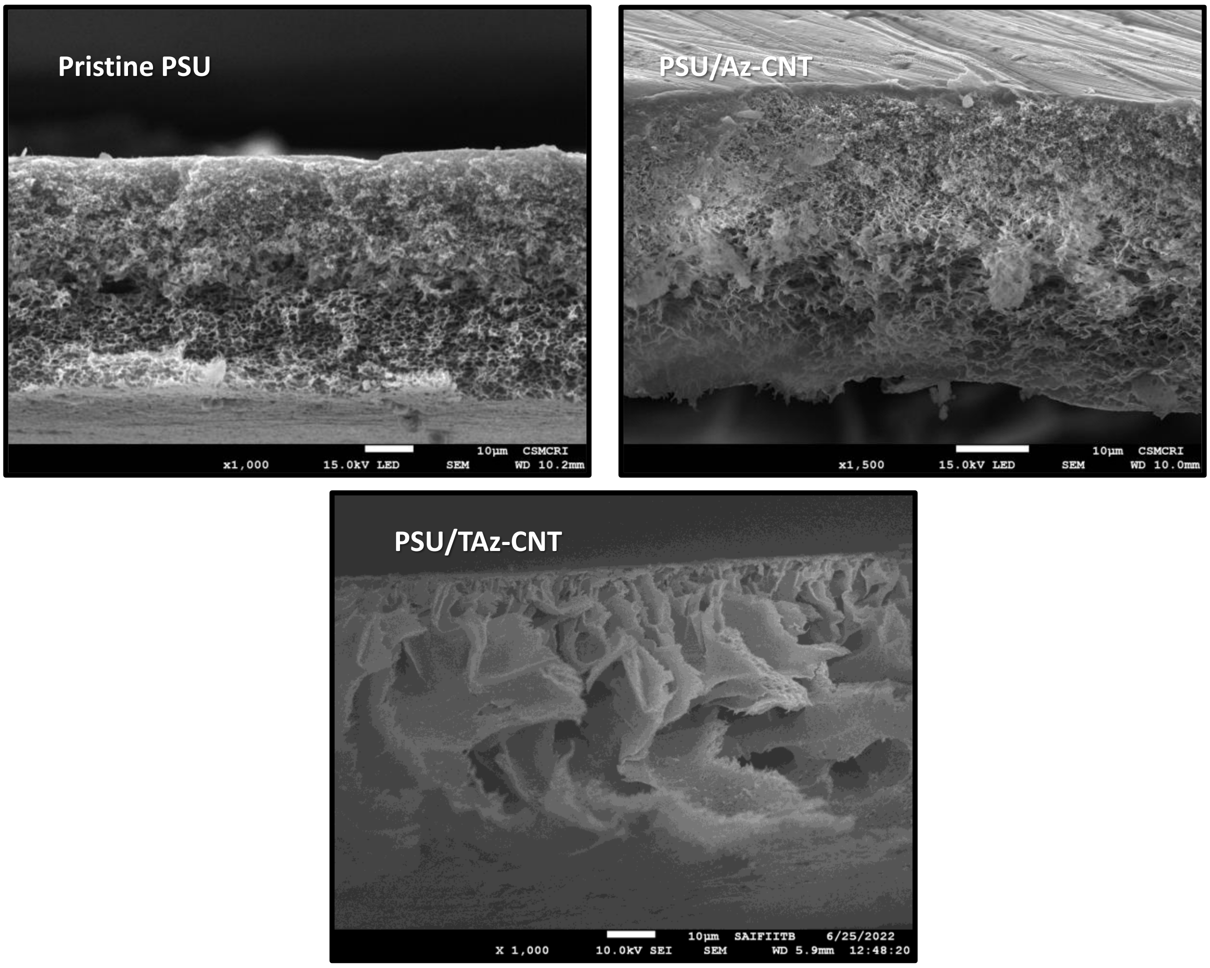


Figure 5.1. Cross-section SEM images of pristine polysulphone, polysulphone/azide-MWCNTs, and click reaction modified polysulphone/azide-MWCNTs mixed matrix membranes

Table 5.1. Surface roughness parameter of pristine polysulphone, polysulphone/azide-MWCNTs, and click reaction modified polysulphone/azide-MWCNTs mixed matrix membranes

MEMBRANES	Average roughness, Sa (nm)	Root mean square, Sq (nm)
Pristine PSU	18.56	23.10
PSU/Az-CNT	6.43	8.18
PSU/TAz-CNT	17.15	21.76

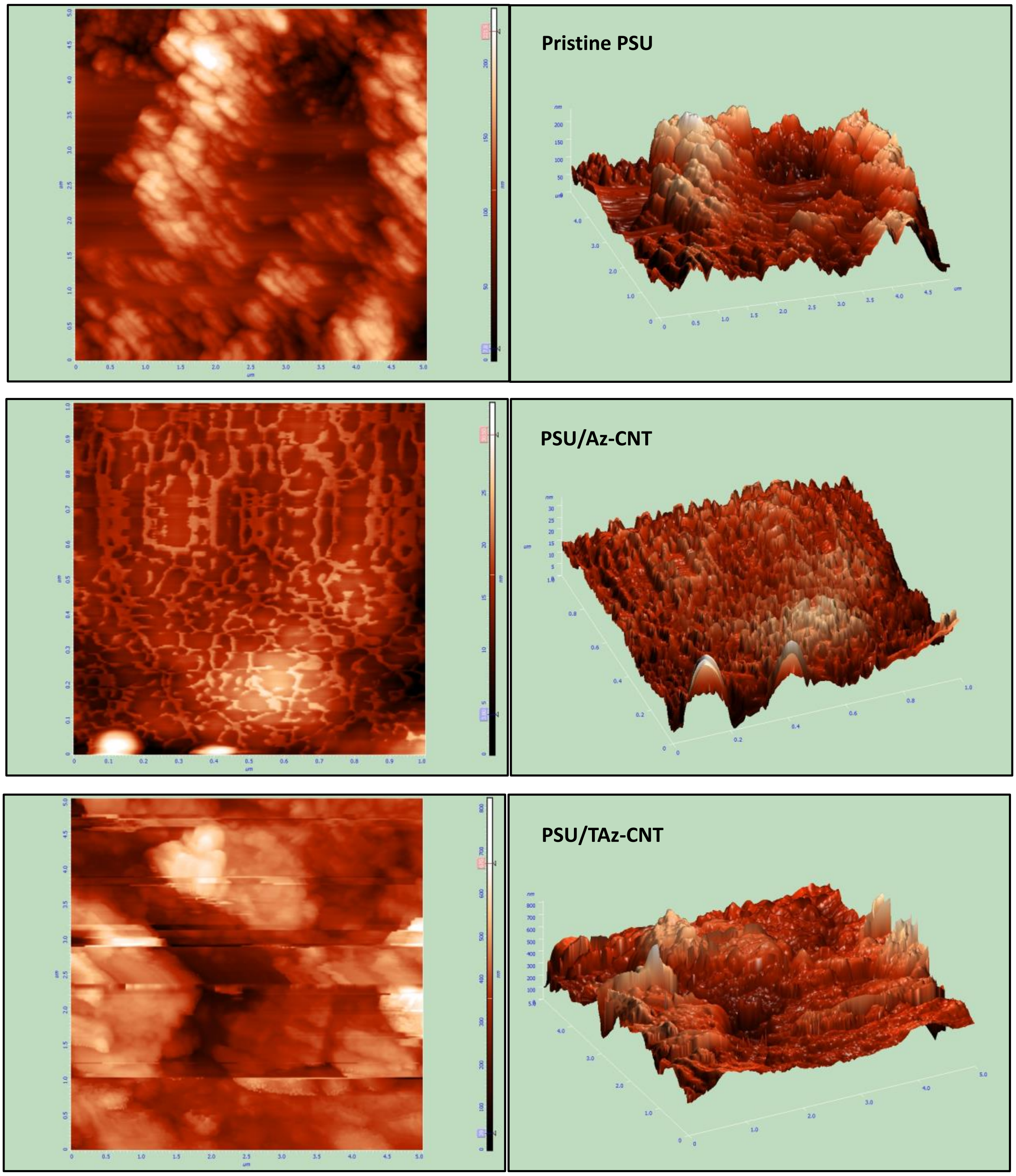


Figure 5.2. AFM images of pristine polysulphone, polysulphone/azide-MWCNTs, and click reaction modified polysulphone/azide-MWCNTs mixed matrix membranes

5.1.3 Contact angle measurement

The contact angle of the pristine PSU membrane is 66.12°, which decreases after the incorporation of azide-MWCNTs into the polysulphone matrix. This is because of the increase in the porosity of the membranes, which makes them more hydrophilic. The modification of the membrane with click reaction enhances its hydrophilicity, The contact angle of the modified membrane via click reaction was found to be 34.48°, which is lower than that of the unmodified membrane polysulphone/azide-MWCNTs membrane (54.30°). This shows that the modified membrane has become more hydrophilic, as depicted in Figure 5.3.

Figure 5.3. Contact angle measurement of pristine polysulphone, polysulphone/azide-MWCNTs, and click reaction modified polysulphone/azide-MWCNTs mixed matrix membranes

5.1.4 SANS

SANS is a new technique for analyzing membrane characteristics, such as pore size, the distribution of pore sizes on the membrane surface, polydispersity. The scattering intensities of different membrane samples are depicted in the Figure 5.4 in arbitrary units, with the data shifted vertically for clarity. Two models are used to interpret the data: the first assumes that the pores are surrounded by a matrix material, while the second model assumes that the pores and matrix material are two distinct phases. The membrane data shown in the figure follows the second model[84,213]. The SANS profiles of PSU/azide-MWCNTs and modified PSU/azide-MWCNTs via click reaction are presented in Fig. 5.4. As seen in Table 5.2, the polysulphone incorporated with azide-functionalized MWCNT has a pore radius of 8.5 nm. However, the pore radius slightly decreases to 8.1 nm after the click reaction on the membranes containing azide functional groups on the surface. This can be attributed to the parallel alignment and uniform distribution of the nanotubes within the polysulphone matrix, which is consistent with previous studies. The modified membrane with the click reaction displays a higher rejection of metal ions, which may be attributed to the presence of the triazole group. This decrease in pore size after modification supports the higher rejection of metal ions for the modified membrane compared to the unmodified membrane. The polydispersity parameter, which is dimensionless and related to the size and distribution of pores on the membrane surface, is found to be the same for both the unmodified and modified membranes. This implies that the distribution of pores with uniform pore size within the membrane is non-uniform or polydisperse[147].

Table 5.2. Pore radius and Polydispersity of polysulphone/azide-MWCNTs, and click reaction modified polysulphone/azide-MWCNTs mixed matrix membranes

MEMBRANES	Pore radius (nm)	Polydispersity (σ)
PSU/Az-CNT	8.5	0.45
PSU/TAz-CNT	8.1	0.45

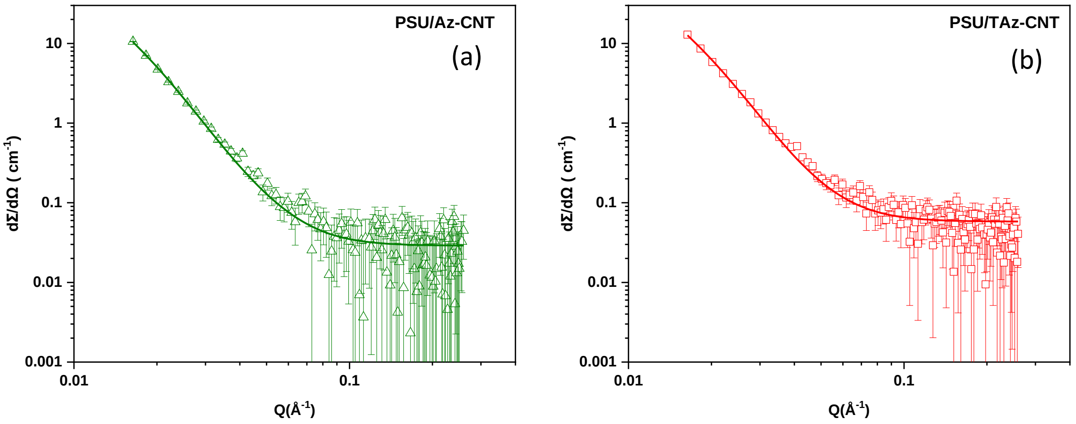


Figure 5.4. SANS profile of (a) polysulphone/azide-MWCNTs mixed matrix membrane and (b) modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

5.2 Morphological Characterization of unmodified and modified polyether sulphone and polysulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

5.2.1 FE-SEM

In scanning electron microscopy (SEM) images (Figure 5.5 and 5.6), polyether sulphone membranes exhibit a finger-like structure, whereas polysulphone membranes exhibits a sponge-like structure. These structures remain unaltered after adding amine-functionalized multi-walled carbon nanotubes (MWCNTs) and even after subjecting the membranes to surface modification using trimesoyl chloride and cyanuric chloride. This indicates that the bulk morphology of the membrane remains the same after adding MWCNTs and surface modification. The term "Bulk morphology" refers to the cross-sectional structure of the membranes, which remains intact even after surface modification[146,147]. The two polymers used in membrane formation exhibit different structures due to a complex phase separation process, with both structures possessing unique properties. Finger-like structures provide higher surface area and better selectivity, while sponge-like structures offer good mechanical stability and allow for fluid flow through interconnected pores. The selection between these two structures depends on the specific requirements of the application, with sponge-like structures preferred for applications where mechanical stability and support are essential, and finger-like structures preferred for applications where high flux and selectivity are required. However, finger-like structures may be more prone to fouling and have lower mechanical stability compared to sponge-like structures[214,215].

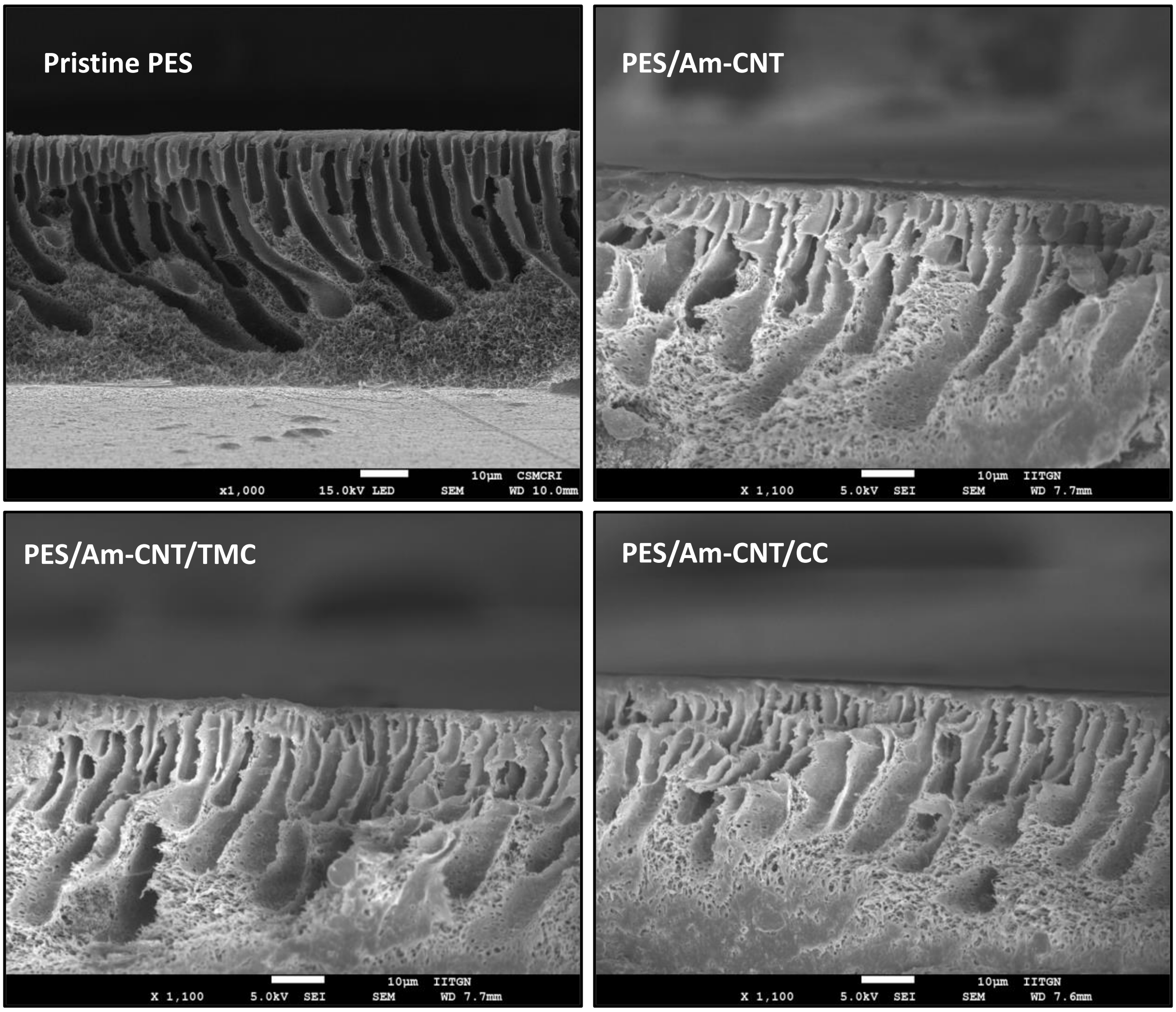


Figure 5.5. Cross-section SEM images of pristine polyether sulphone, polyether sulphone/amine-MWCNTs, and modified polyether sulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

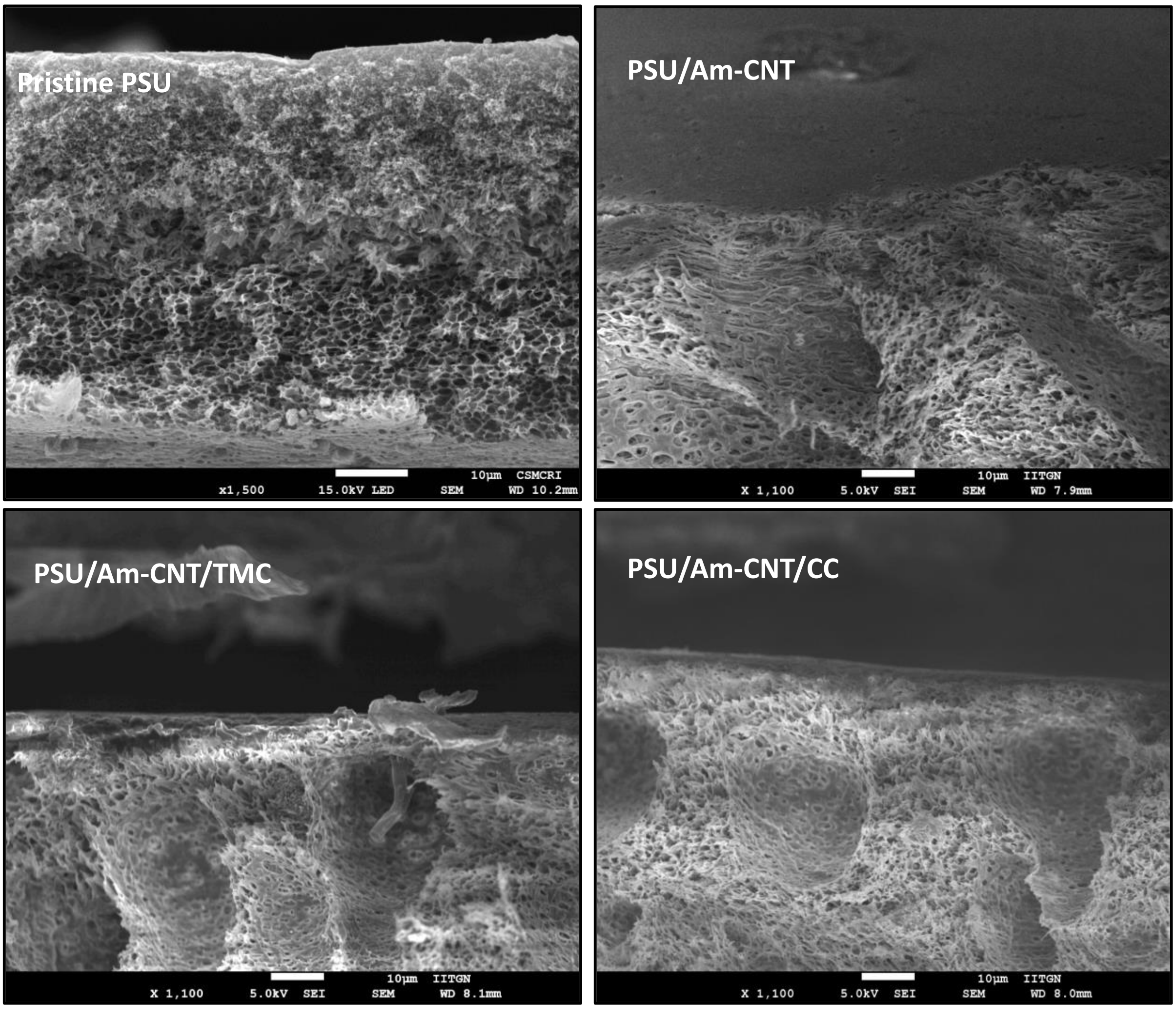


Figure 5.6. Cross-section SEM images of pristine polysulphone, polysulphone/amine-MWCNTs, and modified polysulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

5.2.2 AFM

The surface roughness of the unmodified and modified membranes was investigated by atomic force microscopy. The analysis revealed that the membrane became smoother after the incorporation of amine-functionalized MWCNTs. However, the roughness slightly increased after undergoing treatment with trimesoyl chloride and cyanuric chloride. On the other hand, the addition of amine-functionalized MWCNTs improved the smoothness of the membrane, while treatment using trimesoyl chloride and cyanuric chloride caused a minor rise in roughness. The amine-functionalized MWCNTs result in smoother membranes due to uniform surface coverage. However, the treatment with trimesoyl chloride and cyanuric chloride may cause minor roughness increment due to structural modifications or irregularities. These differences can be associated with the distinct chemical interactions and morphological changes induced by the respective modifications, illustrating the complex relationship between functionalization methods and membrane surface properties[216,217]. The addition of amine-functionalized multiwalled carbon nanotubes (MWCNTs) to a membrane can result in a smoother surface, with the aim of improving the hydrophilicity, antifouling properties, and permeability of the membrane. Enhancing the separation efficiency of the membrane was expected due to the smoother surface, which was a consequence of the functionalization of the MWCNTs, altering the surface properties of the membrane[104,218–220]. Although the modification of the membrane surface with trimesoyl chloride and cyanuric chloride may have caused a minor increase in roughness, this change is unlikely to have a significant impact on the membrane performance. The improved rejection of heavy metals and antifouling properties can be attributed to the increased surface area resulting from the modification[147,221].

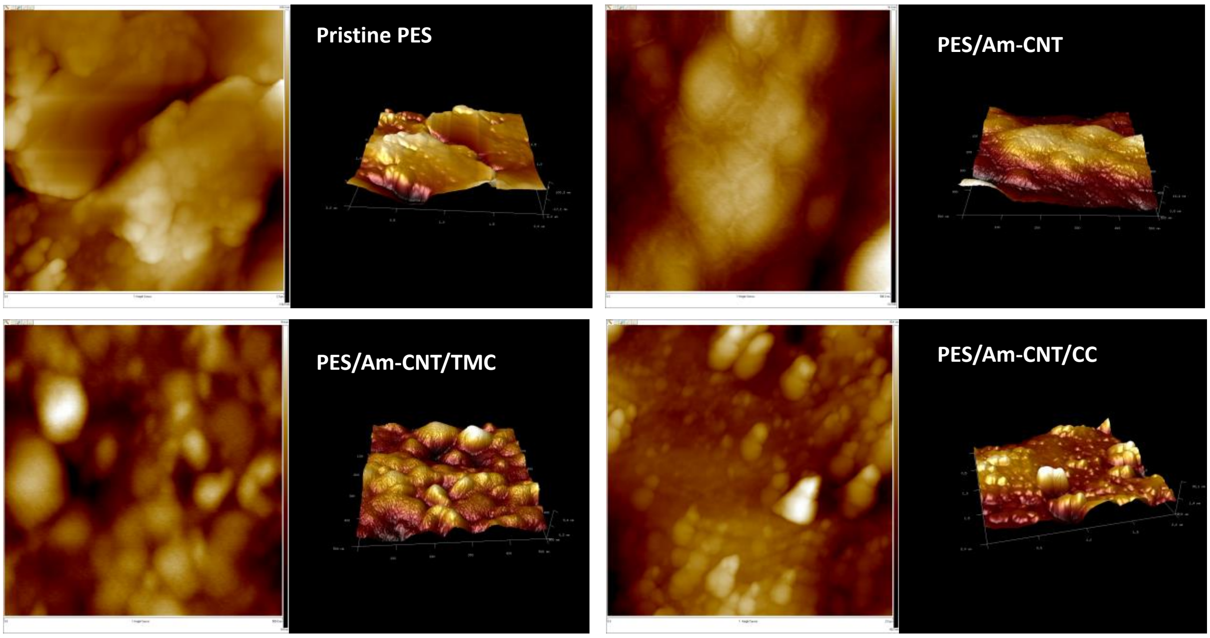


Figure 5.7. AFM images of pristine polyether sulphone, polyether sulphone/amine-MWCNTs, and modified polyether sulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

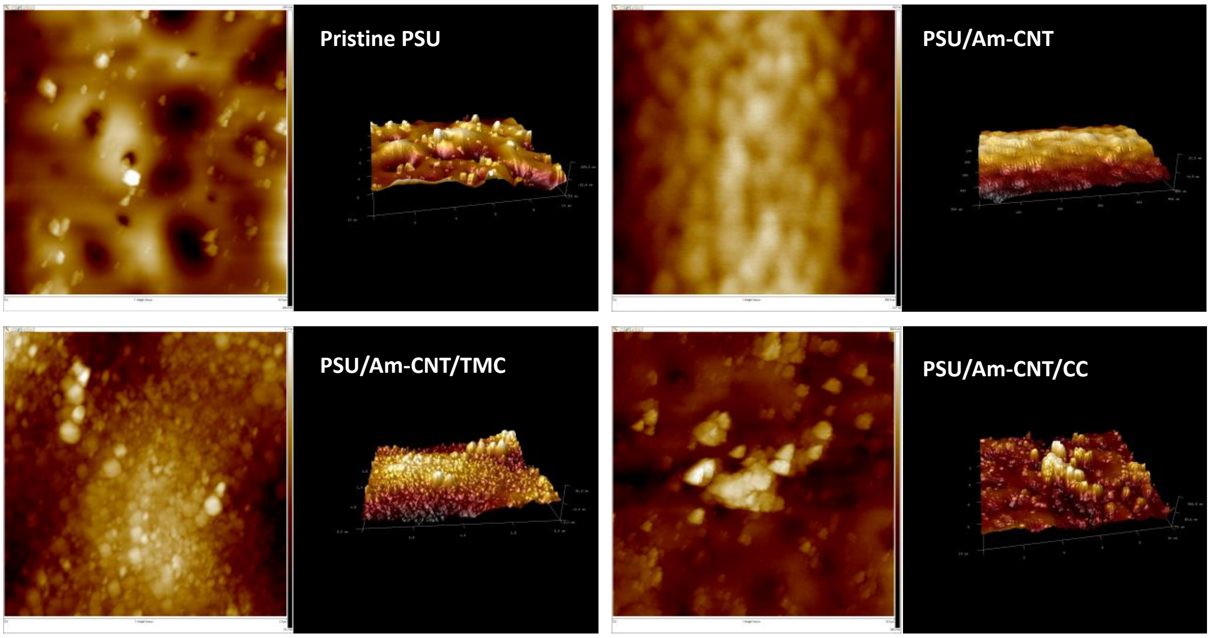


Figure 5.8. AFM images of pristine polysulphone, polysulphone/amine-MWCNTs, and modified polysulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

Table 5.3. Surface roughness parameter of pristine polysulphone, polysulphone/amine-MWCNTs, and modified polysulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

MEMBRANES	Average roughness, Sa (nm)	Root mean square, Sq (nm)
Pristine PES	21.93	29.29
PES/Am-CNT	8.03	13.03
PES/Am-CNT/TMC	10.14	18.13
PES/Am-CNT/CC	10.65	16.53

Table 5.4. Surface roughness parameter of pristine polysulphone, polysulphone/amine-MWCNTs, and modified polysulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

MEMBRANES	Average roughness, Sa (nm)	Root mean square, Sq (nm)
Pristine PSU	18.60	24.33
PSU/Am-CNT	8.59	11.03
PSU/Am-CNT/TMC	10.18	13.53
PSU/Am-CNT/CC	10.15	14.54

Table 5.3 and Table 5.4 present the results of the surface roughness study for different membrane samples using the key parameters of average roughness (Sa) and root mean square (Sq). The analysis implies that the pristine PSU and PES membranes have the highest values for both average roughness (18.60 nm and 21.93 nm) and root mean square (24.33 nm and 29.29 nm), indicating that these membranes have a relatively uneven surface with notable height variations. This result is expected since unmodified membranes often have inherent surface irregularities that contribute to higher roughness values. The PSU and PES/Am-CNT membranes show a noticeable decrease in both the average roughness (8.59 nm and 8.03 nm) and root mean square (11.03 nm and 13.03 nm) compared to the pristine membranes. This reduction in roughness values indicates that the incorporation of amine-functionalized MWCNTs has resulted in a significant smoothing effect on the membrane surface. The presence of Am-MWCNTs may have filled the surface defects and irregularities, resulting in a more uniform surface. This outcome is consistent with the properties of carbon nanotubes, which possess the ability to align and fill gaps due to their elongated and cylindrical structure. The PSU and PES/Am-CNT/TMC membranes showed significantly higher roughness values than the PSU and PES/Am-CNT membranes. Both the average roughness (10.18 nm and 10.14 nm) and root mean square (13.53 nm and 18.13 nm) values increased slightly. This indicates that the modification with trimesoyl chloride (TMC) on the membrane surface has caused changes in surface topography, such as the formation of amide linkages resulting from the reaction between trimesoyl chloride and amine groups on the membrane surface. The roughness values of the PSU and PES/Am-CNT/CC membranes are comparable to those of the PSU and PES/Am-CNT/TMC membranes. The average roughness values of the PSU and

PES/Am-CNT/CC membranes are 10.15 nm and 10.65 nm, respectively, while the root mean square values are 14.54 nm and 16.53 nm, respectively. These values indicate that the surface of the modified membranes is relatively similar in roughness to the previously modified membranes. This indicates that cyanuric chloride also reacts with amine functional groups on the membrane surface, similar to the previously modified membranes.

5.2.3 Contact angle measurement

The incorporation of amine-MWCNTs into PES and PSU membranes results in a significant enhancement of their hydrophilicity compared to the pristine PES and PSU membranes. This is evident from the contact angle measurements in Figures 5.9 and 5.10, which show a decreasing contact angle, indicating a more hydrophilic surface. The presence of amine-MWCNTs leads to increased porosity within the membrane, contributing to its improved hydrophilic properties. This increased porosity subsequently results in an increase in pure water flux, signifying that the membrane's surface has a greater affinity for water molecules. On the other hand, following surface modification with trimesoyl chloride and cyanuric chloride, the contact angle increases, indicating a decrease in hydrophilicity. This change is because of the surface reactions with trimesoyl chloride and cyanuric chloride, which result in the formation of amide linkages on the membrane surface. These chemical modifications resulted in a reduction in the pure water flux observed in these membranes.

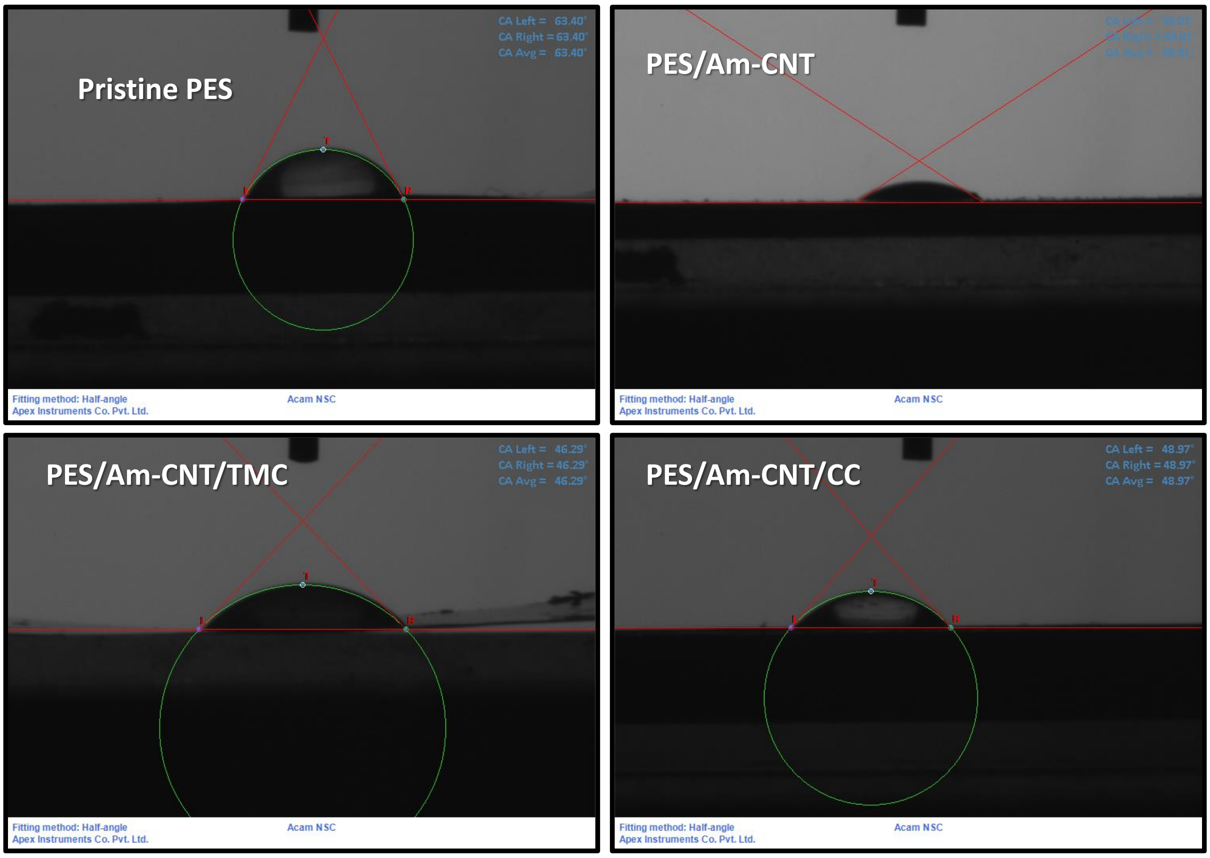


Figure 5.9. Contact angle measurement of pristine polyether sulphone, polyether sulphone/amine-MWCNTs, and modified polyether sulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

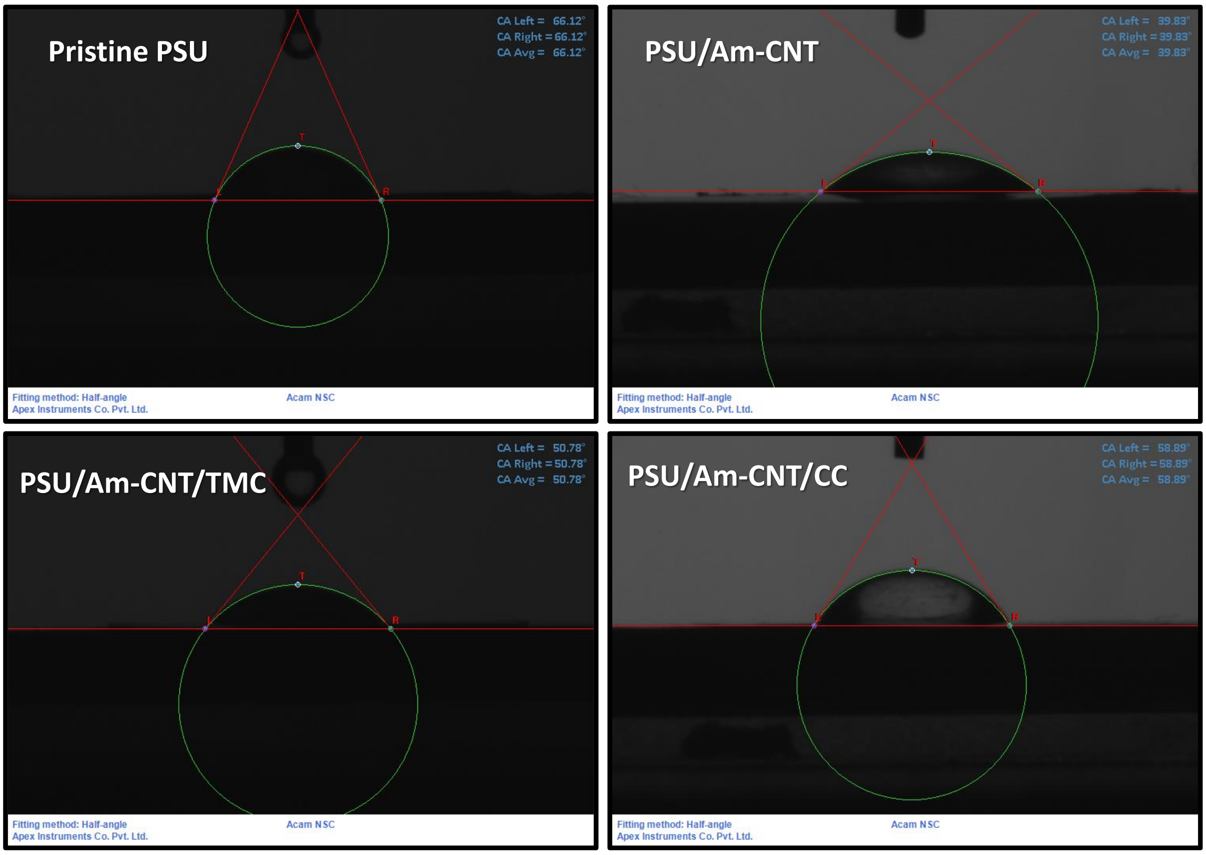


Figure 5.10. Contact angle measurement of pristine polysulphone, polysulphone/amine-MWCNTs, and modified polysulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC)

5.2.4 SANS

The membranes SANS profiles, both unmodified and modified, are shown in Figure 5.11. SANS is a novel technique for evaluating membranes, delivering insights into the pore size distribution and surface uniformity of the membrane. The SANS data for the different membrane samples are presented in arbitrary units and have been vertically shifted for clarity in the study. Two models were examined: the polydisperse sphere model, which assumes that the pores are spherical and surrounded by a matrix material, and the random two-phase model, which assumes that the pores are the first phase and the surrounding matrix material is the second phase. The SANS data for this membrane follow the second model and are depicted in Figure 5[85].

Table 5.5. Pore radius and Polydispersity of pristine polysulphone, pristine polyether sulphone, polysulphone/amine-MWCNTs, polyether sulphone/amine-MWCNTs and modified polysulphone/amine-MWCNTs and polyether sulphone/amine-MWCNTs mixed matrix membranes using trimesoyl chloride (TMC) and cyanuric chloride (CC) from SANS profile

MEMBRANES	Pore radius (nm)	Polydispersity (σ)
PSU/Am-CNT	10.4	0.4
PSU/Am-CNT/TMC	9.5	0.4
PSU/Am-CNT/CC	8.1	0.4
PES/Am-CNT	11.8	0.4
PES/Am-CNT/TMC	10.0	0.4
PES/Am-CNT/CC	8.6	0.4

The pore size and polydispersity of the membranes are presented in Table 5.5. Polysulphone membranes have smaller pores compared to polyether sulphone membranes due to differences in their morphology. This is because polysulphone is known for its higher glass transition temperature and more compact, amorphous structure, which limits the formation of larger pores during the membrane preparation process. Conversely, polyether sulphone, with its relatively more flexible and less densely packed polymer chains, allows for the formation of larger pores. After the addition of amine-functionalized MWCNTs into the polymer matrix, the pore size decreased and porosity increased. This reduction in pore size can be associated with the effects of the modification process, which typically involves chemical reactions on the membrane surface that can result in pore constrictions or blockages, causing a decrease in pore size. The presence of a range of pore sizes within a membrane structure is referred to as polydispersity[146,147]. Table 5.5 reveals that all the membranes exhibit the same level of polydispersity, despite having varying pore sizes. This indicates that they display a similar degree of non-uniformity in their size distribution, despite differences in their individual pore sizes. The presence of the same polydispersity in membranes with different pore sizes can result in similar effects on various transport properties, such as permeability and selectivity. For instance, a polydisperse membrane with larger average pore sizes may display higher overall permeability but lower selectivity compared to a polydisperse membrane with smaller average pore sizes. This is supported by the heavy metal rejection study of these membranes, which shows that the modified membranes with smaller pore sizes have higher heavy metal rejection compared to the unmodified and pristine membranes with larger pore sizes. The pore size of a membrane can be influenced by a variety of factors, including the synthesis or manufacturing process and the materials used. Understanding the relationship between the pore size and the polydispersity of the membrane can help in customizing the membrane performance for specific purposes. By regulating the polydispersity while adjusting the pore size, it is possible to achieve an optimal balance between permeability and selectivity, resulting in improved membrane performance[222,223].

5.3 Morphological Characterization of unmodified and modified polyether sulphone and polysulphone/oxidized-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

5.3.1 FE-SEM

The scanning electron microscope images in Figure 5.12 shows that the cross-section of polyether sulphone membranes displays a clear finger-like structure, while the polysulphone exhibits a sponge-like structure. These morphologies remain unchanged with the addition of oxidized-functionalized multi-walled carbon nanotubes and even after surface modification facilitated by PEI. This suggests that the bulk morphology of the membranes is not affected by surface modification. The complex phase-separation process during membrane formation results in two polymer structures with unique properties: finger-like patterns provide high surface area and improved selectivity, while sponge-like configurations offer robust mechanical stability and fluid flow through interconnected pores. The optimal choice between these structures depends on the specific application requirements, but it is crucial to note that finger-like structures might be more prone to fouling and have lower mechanical stability compared to their sponge-like counterparts[215,224].

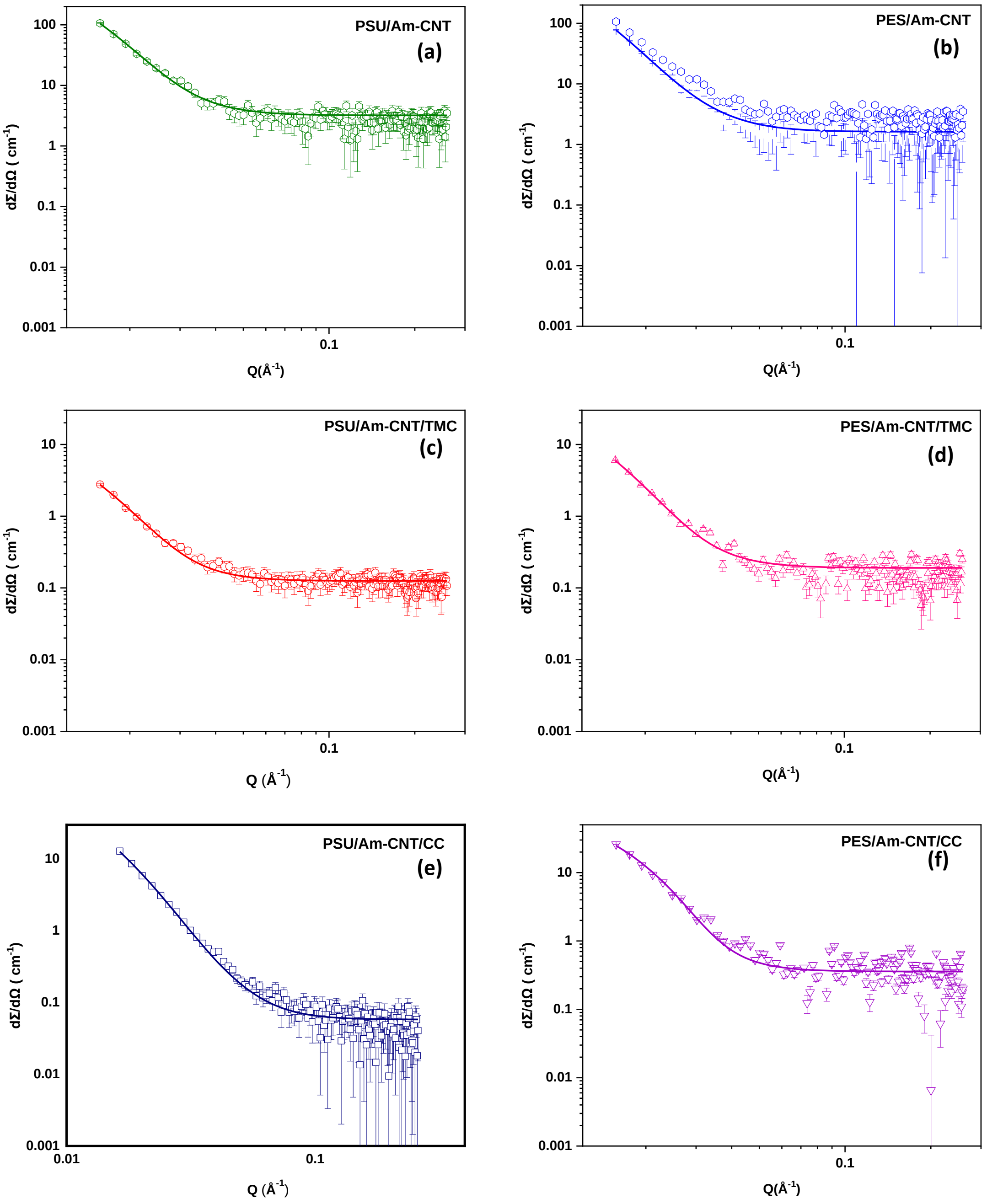


Figure 5.11. SANS profile of (a) polysulphone/amine-MWCNTs mixed matrix membrane and (b) polyether sulphone/amine-MWCNTs mixed matrix membrane (c) modified polysulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) (d) modified polyether sulphone/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) (e) modified polysulphone/amine-MWCNTs mixed matrix membrane using cyanuric chloride (CC) (f) modified polyether sulphone/amine-MWCNTs mixed matrix membrane using cyanuric chloride (CC)

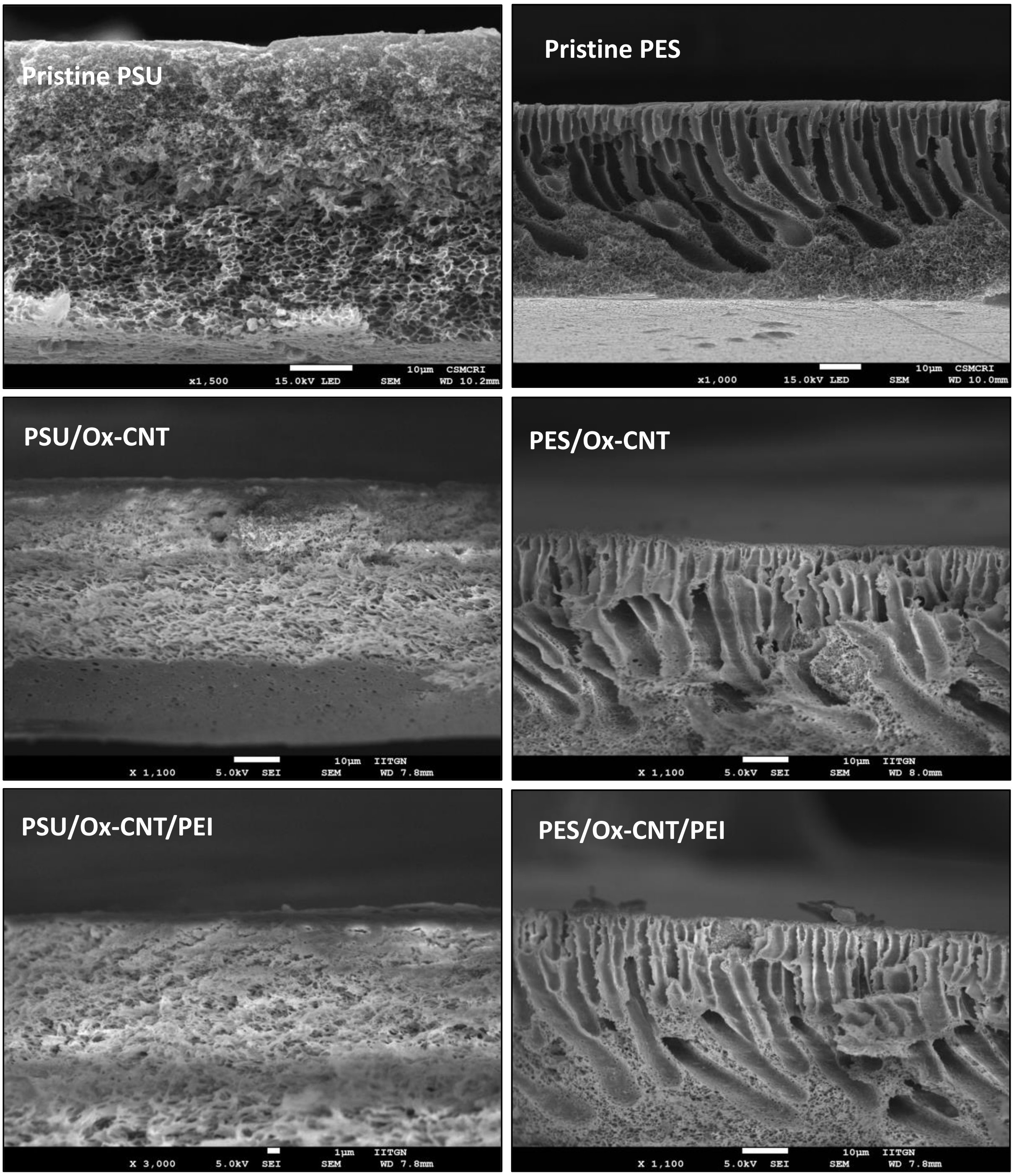


Figure 5.12. Cross-section SEM images of pristine polysulphone, pristine polyether sulphone, polysulphone/oxidized-MWCNTs and polyether sulphone/ oxidized -MWCNTs mixed matrix membrane and modified polysulphone/ oxidized -MWCNTs and polyether sulphone/ oxidized -MWCNTs mixed matrix membrane using polyethylenimine (PEI)

5.3.2 AFM

The surface roughness of both unmodified and modified membranes was determined using Atomic Force Microscopy (AFM). The results revealed a significant change in surface morphology upon the introduction of oxidized-functionalized multi-walled carbon nanotubes (MWCNTs) and subsequent treatment with Polyethylenimine. The addition of oxidized-functionalized MWCNTs to the membrane structure led to a significant decrease in surface roughness. This suggests that the nanotubes had a smoothening effect on the membrane surface. The decrease in roughness can be attributed to the exceptional properties of MWCNTs, which tend to align and fill in surface irregularities, resulting in a more even surface. This modification is likely to enhance the membrane overall performance, especially in applications where smooth surfaces are crucial, such as in separation processes. Although the treatment of polyethylenimine on the membrane with carboxylic functional groups had a contrasting outcome, the surface roughness of the membrane slightly increased following the treatment. This increase in surface roughness may be because of the chemical interaction between polyethylenimine and the membrane surface, resulting in the formation of amide linkages on the membrane surface[216,217].

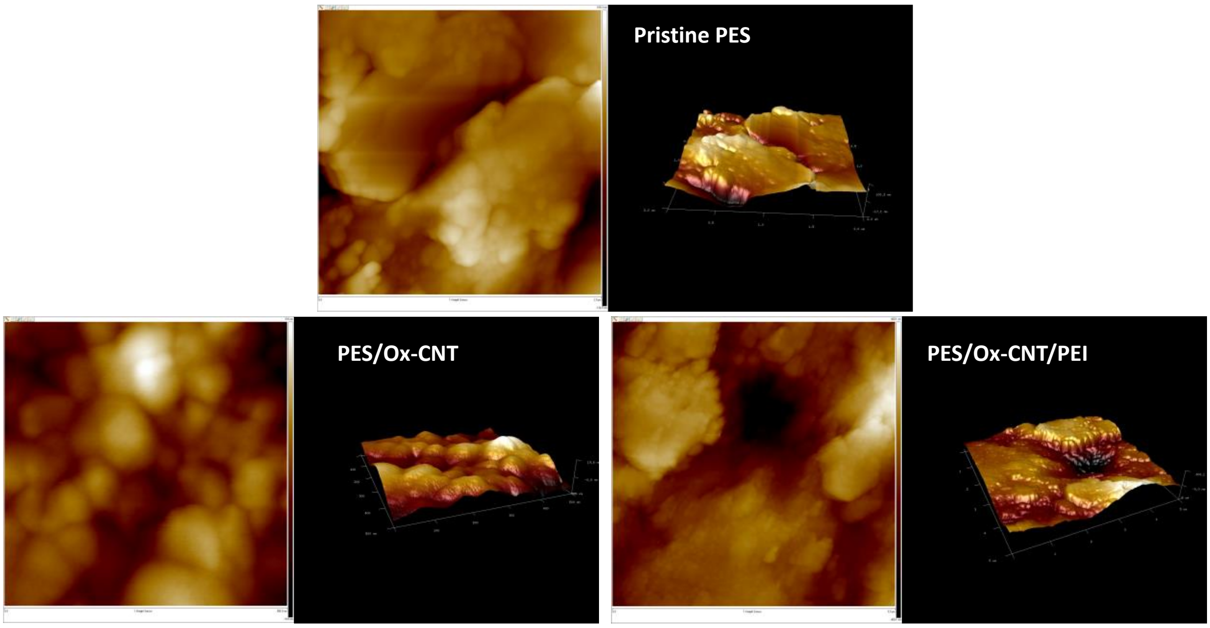


Figure 5.13. AFM images of pristine polyether sulphone, polyether sulphone/oxidized-MWCNTs, and modified polyether sulphone/ oxidized -MWCNTs mixed matrix membranes using polyethylenimine (PEI)

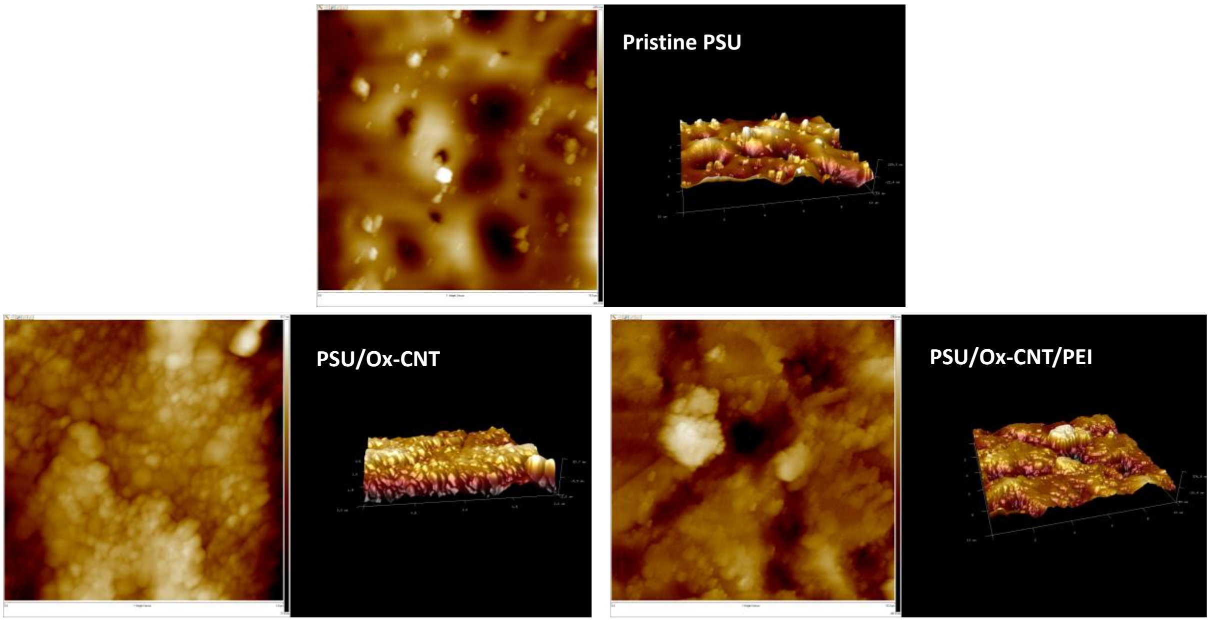


Figure 5.14. AFM images of pristine polysulphone, polysulphone/oxidized-MWCNTs, and modified polysulphone/ oxidized -MWCNTs mixed matrix membranes using polyethylenimine (PEI)

Table 5.6. Surface roughness parameter of pristine polyether sulphone, polyether sulphone/oxidized-MWCNTs, and modified polyether sulphone/ oxidized -MWCNTs mixed matrix membranes using polyethylenimine (PEI)

MEMBRANES	**Average roughness, Sa (nm)**	**Root mean square, Sq (nm)**
Pristine PES	21.93	29.29
PES/Ox-CNT	7.83	11.44
PES/Ox-CNT/PEI	11.26	17.83

Table 5.7. Surface roughness parameter of pristine polysulphone, polysulphone/oxidized-MWCNTs, and modified polysulphone/ oxidized -MWCNTs mixed matrix membranes using polyethylenimine (PEI)

MEMBRANES	Average roughness, Sa (nm)	Root mean square, Sq (nm)
Pristine PSU	18.60	24.33
PSU/Ox-CNT	8.55	10.63
PSU/Ox-CNT/PEI	11.51	16.30

The two tables, 5.6 and 5.7, present the results of the surface roughness analysis for various membrane types, using average roughness (Sa) and root mean square roughness (Sq). The analysis was conducted on membranes incorporated with oxidized carbon nanotubes (Ox-CNTs) and surface modified with polyethylenimine (PEI). The modifications are highlighted for two types of membranes: Pristine PES and Pristine PSU. The roughness values for the pristine PES membrane are relatively high, with an average roughness (Sa) of 21.93 nm and a root mean square roughness (Sq) of 29.29 nm. These values indicate a surface with significant height variations and irregularities. The inherent properties of the pristine material contribute to this roughness, likely due to surface imperfections and structural features. The PES/Ox-CNT membrane exhibits a marked decrease in both the average roughness (from 7.83 nm to 7.83 nm) and root mean square (from 11.44 nm to 11.44 nm) when compared to the pristine PES membrane. This significant reduction in roughness values suggests that the incorporation of oxidized MWCNTs has resulted in a considerable smoothening effect. The oxidized MWCNTs which possess carboxylic functional groups, seem to have filled in surface defects and irregularities, resulting in a more uniform surface. These findings are consistent with the properties of carbon nanotubes, which are able to align and fill gaps due to their elongated and cylindrical structure. The surface roughness of PEI-treated membranes was found to be higher than the unmodified membranes, with an average roughness (Sa) of 11.26 nm and a root mean square (Sq) of 17.83 nm. This change indicates that the introduction of PEI has modified the surface topography. PEI, known for its cationic nature and high density of amine groups, interacts with the membrane surface having carboxylic functional groups, leading to the formation of amide bonds. This interaction is believed to have contributed to the observed increase in roughness.

For the pristine PSU membrane, it initially has an average roughness (Sa) of 18.60 nm and a root mean square (Sq) of 24.33 nm, indicating a relatively uneven surface with notable height variations. However, after introducing oxidized MWCNTs to the PSU membrane (PSU/Ox-CNT), the roughness values decrease significantly. The average roughness (Sa) decreases to 8.55 nm, and the root mean square (Sq) decreases to 10.63 nm, showing the smoothening effect of oxidized MWCNTs, which align and fill surface irregularities, resulting in a more uniform surface morphology. However, when the membrane surface is treated with PEI, the roughness values increase. The average roughness (Sa) becomes 11.51 nm, and the root mean square (Sq) increases to 16.30 nm, suggesting that the modification with PEI forms amide linkages on the surface of the membrane, similar to the PES membrane.

5.3.3 Contact angle measurement

The PSU/Ox-CNT and PES/Ox-CNT composite membranes had a higher hydrophilicity than their pristine counterparts. This was due to the increased porosity resulting from the incorporation of oxidized MWCNT into the polymer matrix and the presence of carboxylic functional groups on the surface of the membrane. The addition of Ox-CNTs strengthened the interaction between the matrix and the CNTs, which affected the membrane porosity and hydrophilicity. An increase in hydrophilicity indicated a higher interaction between water molecules and the membrane surface, leading to a higher pure water flux compared to the pristine membranes[82,146,147,225]. The contact angle measurement provided a further explanation for the decrease in the pure water flux of the modified membranes, despite the reduction in pore size and blockage of the membrane surface following treatment with PEI on the membrane surface. This causes a decrease in hydrophilicity and an increase in the contact angle, indicating that the membrane interacts less with water molecules and retains less pure water.

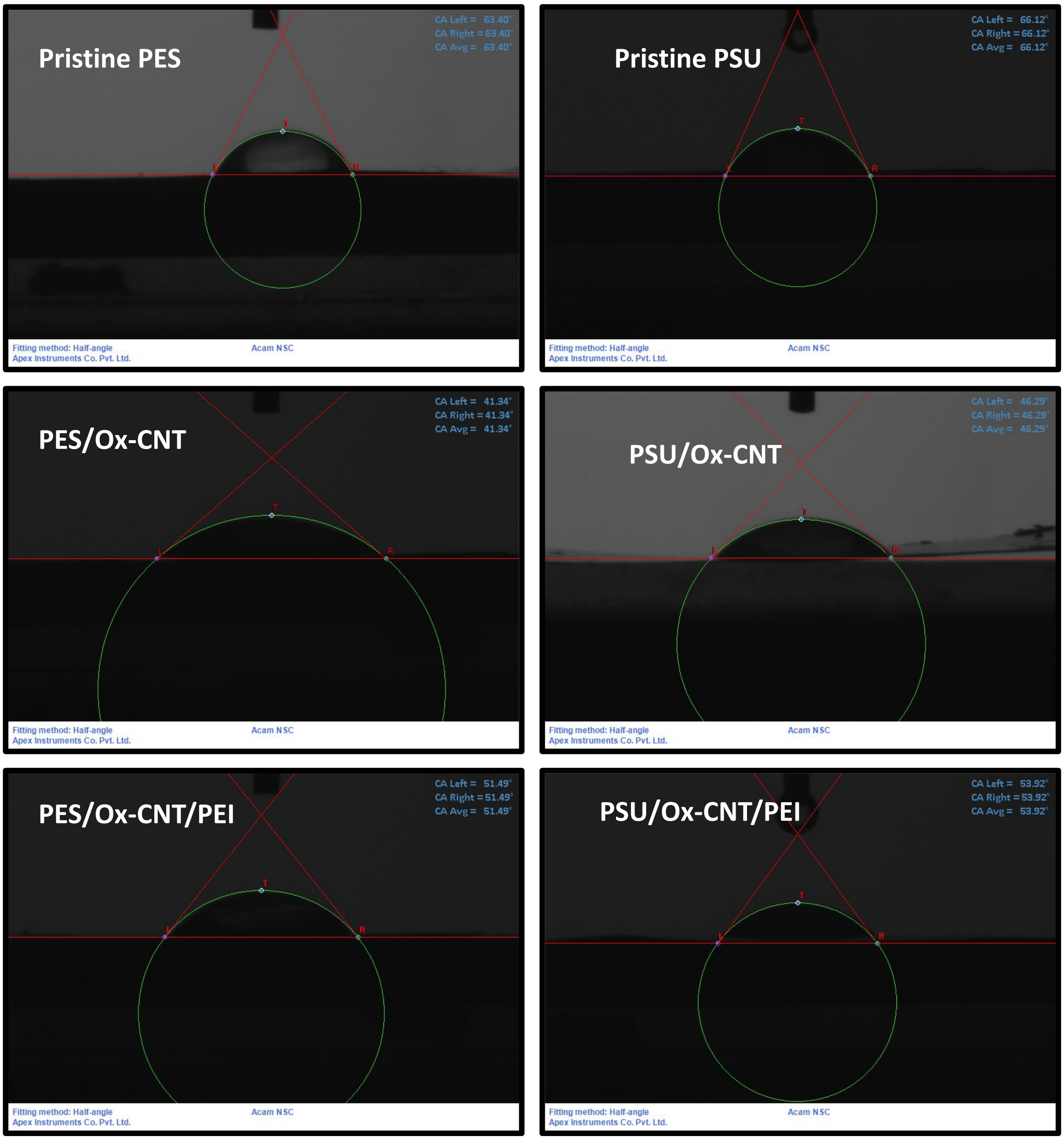


Figure 5.15. Contact angle measurement of pristine polysulphone, pristine polyether sulphone, polysulphone/oxidized-MWCNTs, polyether sulphone/oxidized-MWCNTs and modified polysulphone/ oxidized -MWCNTs and polyether sulphone/oxidized-MWCNTs mixed matrix membranes using polyethylenimine (PEI)

5.3.4 SANS

The SANS profiles of the unmodified and modified membranes are presented in Figure 5.16. SANS is a new technique for membrane characterization, providing insights into the pore size and pore distribution on the surface of the membrane. The SANS data displays the scattering intensities of different membrane samples in arbitrary units and has been adjusted to enhance clarity by shifting them vertically. In this study, two models were examined. The first model, called the polydisperse sphere model, assumed that the pores were spherical and surrounded by a matrix material. The second model, known as the random two-phase model, assumed that the first phase were the pores and the second phase was the surrounding matrix material. The SANS data for this membrane follows the second model, and the data are presented in Figure 5.16[85].

Table 5.8. Pore radius and Polydispersity of pristine polysulphone, pristine polyether sulphone, polysulphone/oxidized-MWCNTs, polyether sulphone/ oxidized-MWCNTs and modified polysulphone/oxidized-MWCNTs and polyether sulphone/oxidized-MWCNTs mixed matrix membranes using polyethylenimine (PEI) from SANS profile

MEMBRANES	Pore radius (nm)	Polydispersity (σ)
PSU/Ox-CNT	9.8	0.4
PSU/Ox-CNT/PEI	9.3	0.4
PES/Ox-CNT	10.0	0.4
PES/Ox-CNT/PEI	9.3	0.4

The pore size and polydispersity of the membranes are illustrated in Table 5.8. Polysulphone membranes have smaller pores compared to polyether sulphone membranes due to differences in their pore formation mechanisms. This is because polysulphone has a higher glass transition temperature and a more compact, amorphous structure, which hinders the formation of larger pores. In contrast, polyether sulphone has relatively more flexible and less densely packed polymer chains, which facilitate the formation of larger pores. After introducing oxidized- MWCNTs into the polymer matrix, the size of the pores decreased, and the porosity increased. When both membranes were surface modified with PEI, the pore size decreased, which can be assigned to the effects of the modification process, which involves chemical treatment of PEI on the membrane surface, leading to pore constrictions or blockages and resulting in a decrease in pore size. The concept of "polydispersity" encompasses the existence of a variety of pore sizes within a membrane structure. As demonstrated in Table 5.8, every membrane possesses the same value of polydispersity, regardless of their differing pore sizes, indicating a comparable degree of non-uniformity in their size distribution[150,226]. The polydispersity of membranes with varied pore sizes can result in comparable effects on multiple transport properties, such as permeability and selectivity. For example, a polydisperse membrane with larger average pore diameters may display elevated overall permeability, but reduced selectivity, compared to a polydisperse membrane having smaller average pore diameters. Conversely, the rejection of heavy metals by modified membranes with smaller pore sizes is higher than that of unmodified and pristine membranes having larger pore sizes. The synthesis or fabrication process of a membrane and the materials used play a role in determining its pore size distribution, which is known as polydispersity. Membranes with a more uniform pore size distribution tend to have better performance in terms of selectivity and permeability. By understanding the relationship between polydispersity and pore size, it is possible to tailor the membrane's properties for specific applications. This can be accomplished by controlling the polydispersity and adjusting the pore size to optimize the balance between permeability and selectivity, leading to improved membrane performance[222,223].

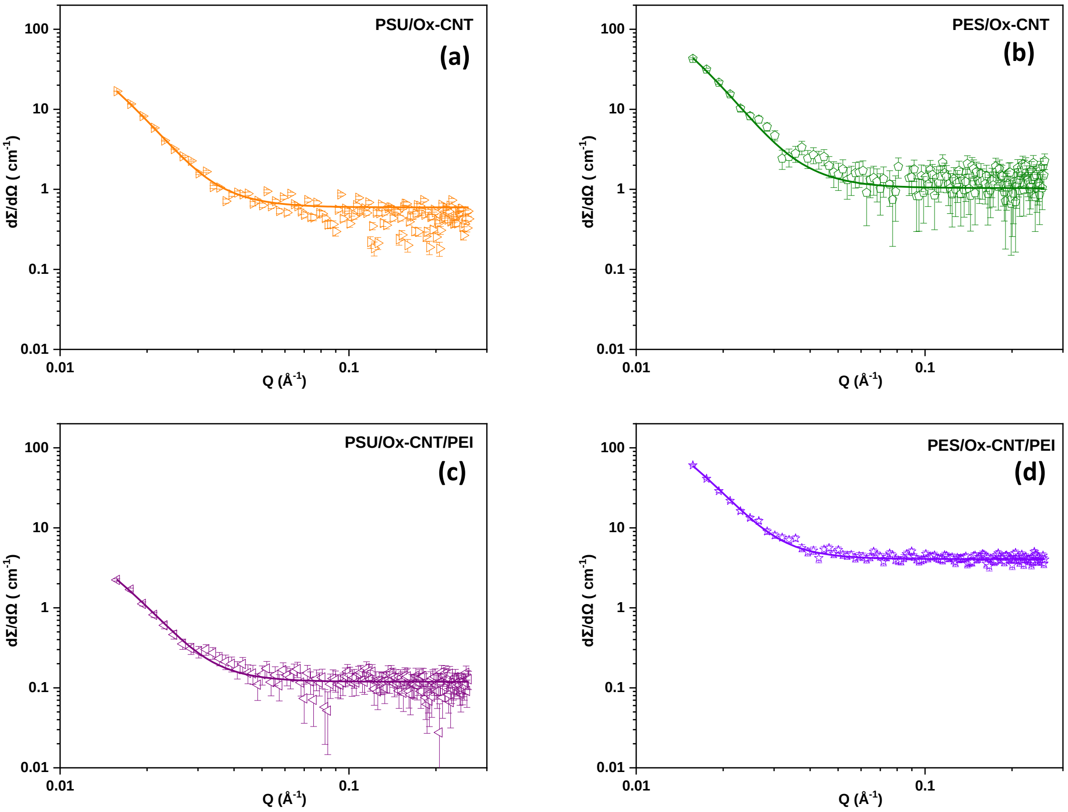


Figure 5.16. SANS profile of (a) polysulphone/oxidized-MWCNTs, (b) polyether sulphone/oxidized-MWCNTs and (c) modified polysulphone/ oxidized -MWCNTs and (d) polyether sulphone/oxidized-MWCNTs mixed matrix membranes using polyethylenimine (PEI)