5.1 Morphological characterization of f-MWCNT/PES mixed matrix membranes

5.1.1 Field Emission Scanning electron microscopy

The cross-section FESEM micrograph of mixed-matrix membranes were taken immediately after their cold fracture in liquid N_2. The three different images of the MMM give three essential information about them such as functionalization of nanotubes, the presence of network in the PES matrices and channelized arrangement of f-MWCNT for high water flux. Not only these, but it also supports the asymmetric nature and functionalization within the membranes. The Figure 5.1(a) of the mixed matrix membranes clearly show the formation of finger like pores that allow the pathway to the water molecules. The rich appearance of CNTs on the surface of the mixed matrix membranes is indicative for high degree of functionalization (Figure 5.1 b). Whereas the last image, Figure 5.1 c, is of an interconnected network of nanotubes exist inside the PES matrix. We consider that occurrence of CNTs perpendicular to the polyethersulfone matrix contributes to the enhancement in flux [275, 276]. Another analysis which makes the probabilities more for high water flux is through the enhanced hydrophilicity during the functionalization of CNTs.

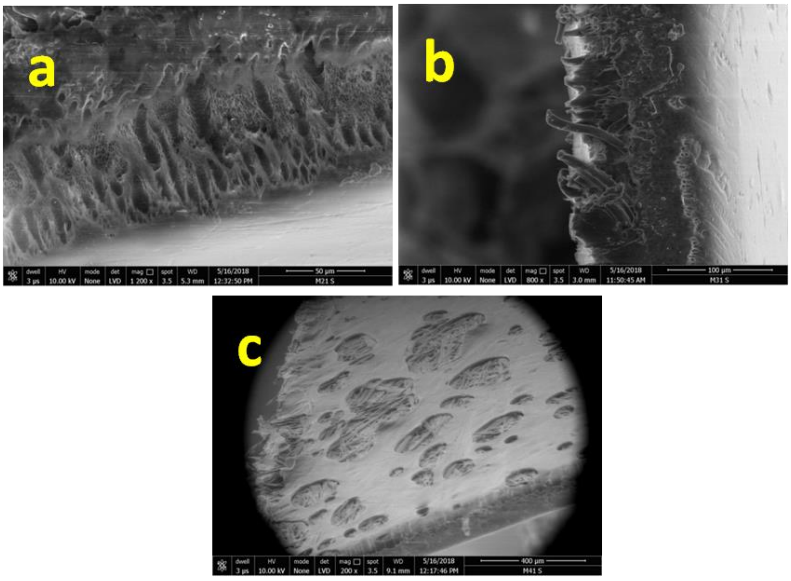


Figure 5.1 SEM micrograph of cross section of cold fractured membranes (a) M21 (b) M31 (b) (c) M41

FESEM images of the surface of the membranes were also taken (Figure 5.2), which clearly shows the change in the surface, pore dimensions as well as the porosity of the samples.

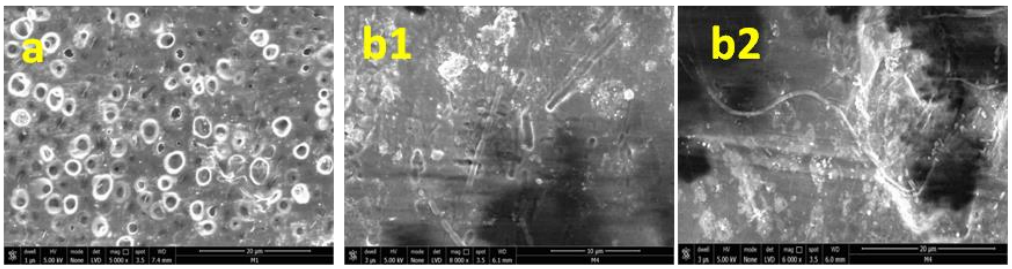


Figure 5.2 FE-SEM images of the surface of the membranes (a) M1 (b1) M41 (higher magnification) (b2) M41

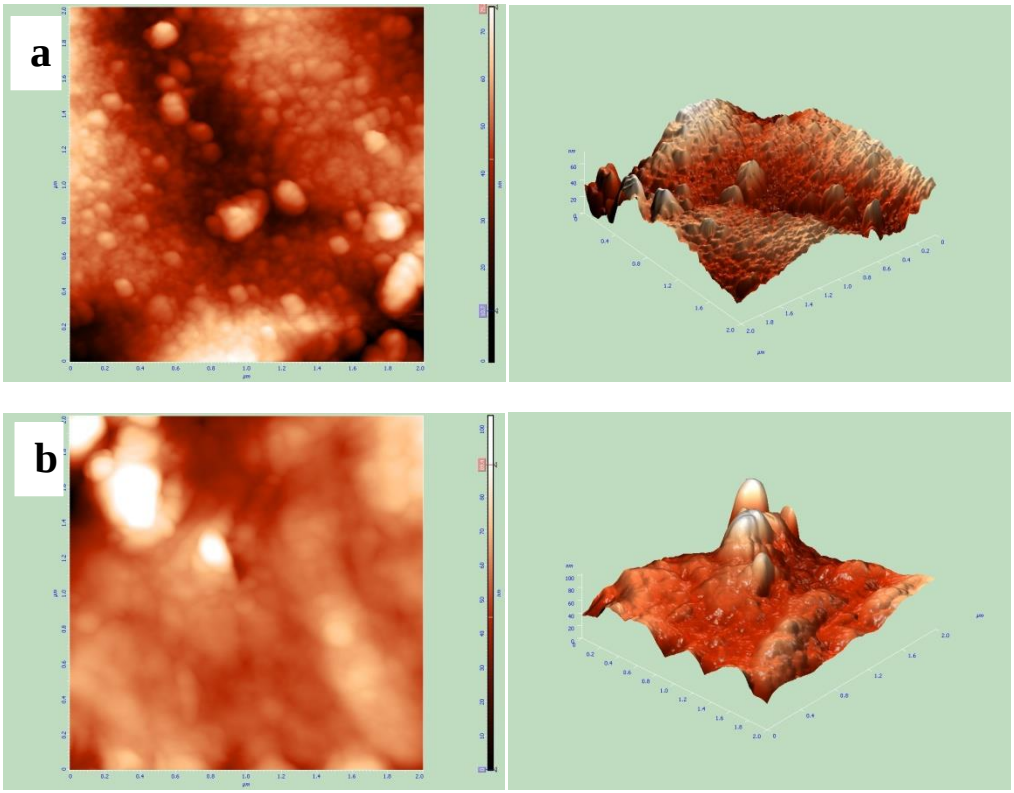
5.1.2 Atomic force microscopy

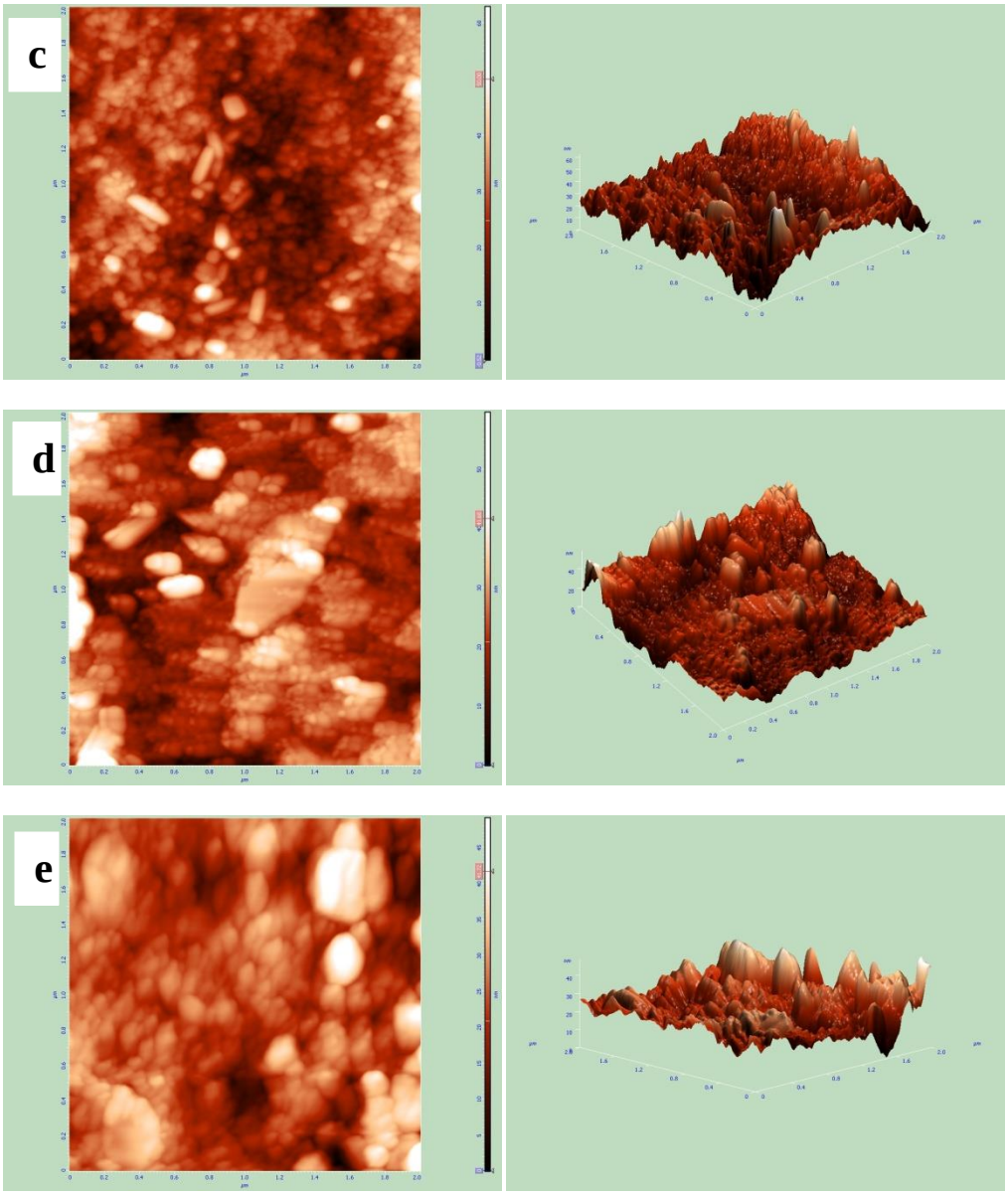
The additional information of the allocation of nanotubes into the PES matrix is studied with AFM topography images for different concentration of f-MWCNT in the membranes which can be seen in Figure 5.3. The highest point of the membrane surface is represented by the brightest area and the darker part shows valleys. The roughness parameters are calculated by SPM DME software and summarized in Table 5.1. It is observed that surface morphology of the prepared membranes drastically altered by the addition of f-MWCNT in the casting solution. The mean pore size and average roughness of the membranes is decreased with addition of MWCNT up to 1 wt %. At lower concentration of nanotubes, the effect of hydrophilicity accelerates the rate of exchange of solvent-non solvent during phase inversion process [277]. Thus large pore size and increased roughness is formed. While the higher concentration of f-MWCNT in the casting solution causes enhancement in the viscosity. The increased viscosity of casting solution obstruct the solvent-non solvent exchange which results the membrane with smooth surface, smaller pore size and dense structure. The mean roughness of the pristine PES membrane reduced from 9.81 nm to 2.10 nm for 1wt% Az-MWCNT membrane.

Table 5.1 Roughness parameter of Pristine PES, 0.03wt% Az-MWCNT/PES [M4003], 0.05wt% Az-MWCNT/PES [M4005], 0.07wt% Az-MWCNT/PES [M4007], 0.1wt% Az-MWCNT/PES [M401], 1wt% Az-MWCNT/PES [M41] mixed matrix membranes

	Average Roughness Sa (nm)	**Root Mean Square Sq (nm)**
M1	9.21	11.40

M4003	8.26	11.71
M4005	6.24	7.92
M4007	6.01	7.61
M41	5.08	6.55




c
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e

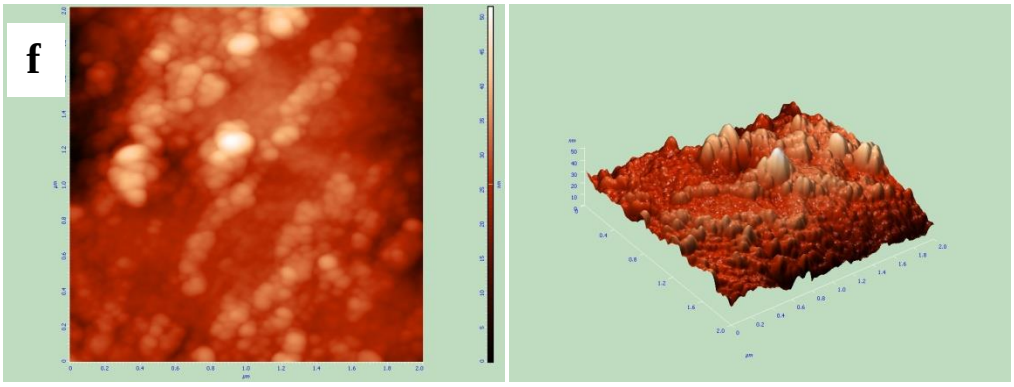


Figure 5.3 AFM images of Pristine PES (a) 0.03wt% Az-MWCNT/PES [M4003] (b) 0.05wt% Az-MWCNT/PES [M4005] (c) 0.07wt% Az-MWCNT/PES [M4007] (d) 0.1wt% Az-MWCNT/PES [M401] (e) 1wt% Az-MWCNT/PES [M41] (f) mixed matrix membranes

5.1.3 Contact angle

Figure 5.4 shows the disparity between the contact angle of pristine polyethersulfone and f-MWCNT (oxidized, amide and azide functional group) incorporated mixed matrix membranes. The contact angle of the pristine PES membrane is 73.3 ± 3^{o}. The contact angle of M21 (oxidized MWCNT incorporated mixed matrix membranes) is 65.3 ± 2^{o}, indicating the most hydrophilic surface (Table 5.2). Such a decrease in the contact angle could be the indication of the presence of functionalized nanotubes in the PES matrix as well as the indication of well aligned MWCNT structure in the membrane matrix which is in agreement with the literature [278]. The net charge on the membrane surface increases which implies that functional group attached to nanotubes are on the surface i.e nanotubes are aligned [279].

Table 5.2 Contact angle values of membranes

Membrane code	Contact angle(º)
M1	73.3±3.0
M2003	69.1±2.1
M2005	67.4±3.2
M2007	67.1±2.0
M201	66.9±1.5
M21	65.3±2.0
M3003	69.3±1.9
M3005	68.1±2.5
M3007	67.4±1.2
M301	67.0±2.3
M31	66.6±1.4
M4003	69.2±2.7
M4005	67.7±1.8
M4007	66.7±2.8
M401	66.1±2.5
M41	65.5±1.7

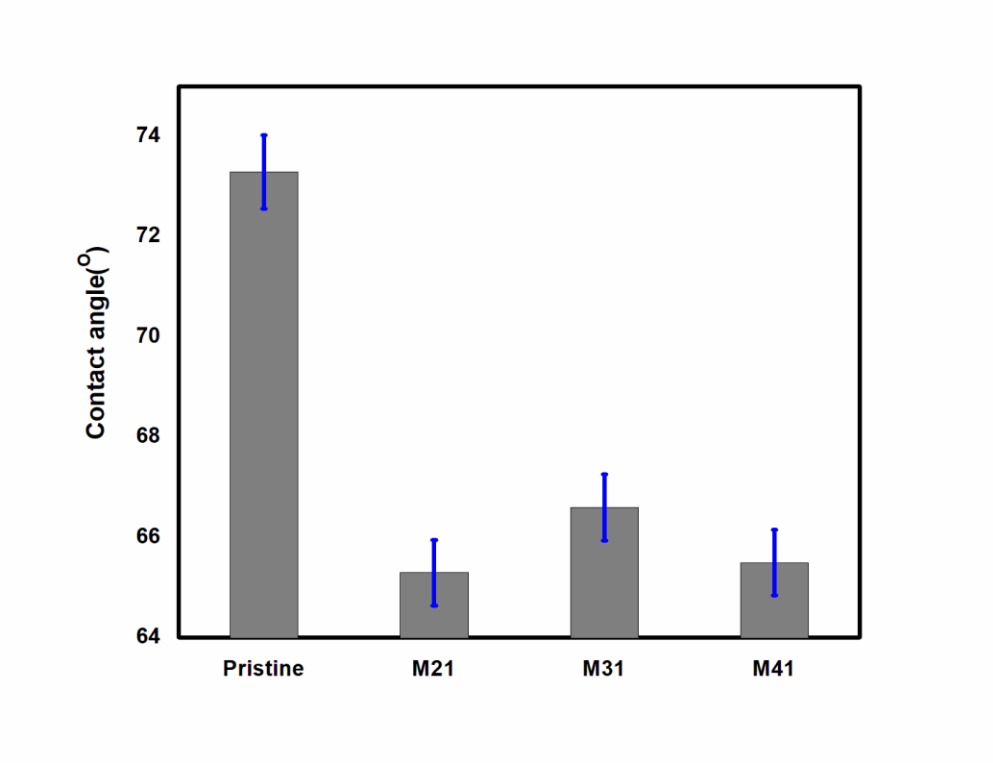


Figure 5.4 Contact angle of pristine PES as compared nanotubes incorporated membranes

5.1.4 Zeta Potential Measurement

Zeta potential measurement is essential characterization for membranes in order to avail the information of charge generated on the membrane surface leading to a better perceptive of membrane separation performance [280]. Zeta potential was analyzed from streaming current by streaming electrolyte KCl (0.001 M) in the pH range of 2.5 to 7.0. The pristine PES as well as MMMs containing functionalized nanotubes was found to be negatively charged from pH 2.5 to pH 7.0 (Figure 5.5), any iso-electric point could not be identified. The charge evaluated on the surface of pristine PES membrane is in agreement with earlier

report [281]. The zeta potential values at lower pH are less negative due to the presence of protonated carboxylic group. At higher pH the deprotonated carboxylic group gives rise to more negative zeta potential [282]. The zeta potential values for amide functionalized MWCNT containing PES mixed matrix membranes (MMMs) are comparatively less negative due to the presence of terminal amine groups which are protonated. Azide functionalized MWCNT incorporated PES MMMs are having negatively charged surface.

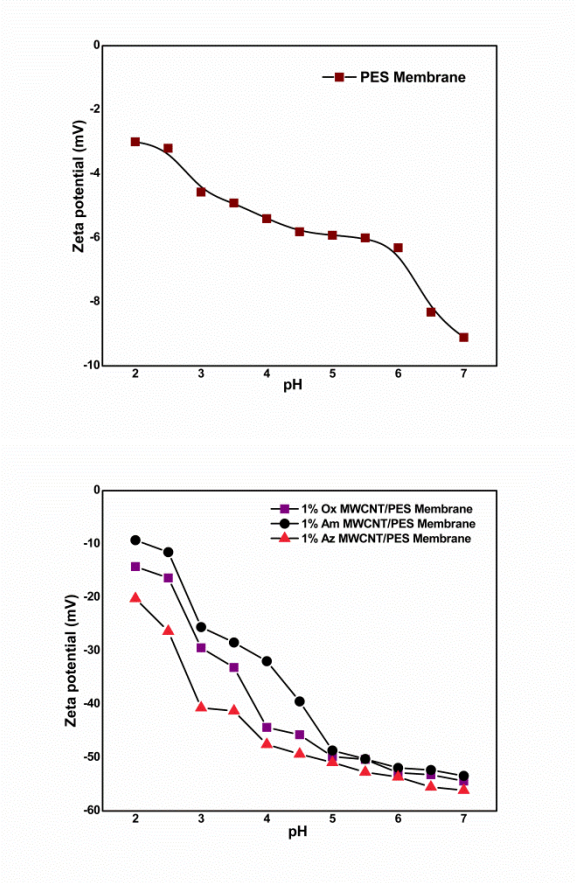


Figure 5.5 The zeta potential value of pristine PES and mixed matrix membranes as a function of pH

5.1.5 Capillary flow porometry

Capillary flow analysis reveals the pore dimensions of the membranes. The study shows the dimensions of the pores of membranes vary with the addition of MWCNT in the polymer matrix. The largest pore of the membranes was detected by bubble point as by applying the pressure, the pores are emptied of the Galwick liquid. On applying higher pressure, this liquid was expelled from the other smaller pores also. The bubble point pressure obtained was 33.5 psi and bubble point diameter obtained was 0.19 µ. This data is summarized in Table 5.3. Comparing the mean flow pore pressure and bubble point pressure for the pristine as well as for the mixed matrix membranes, we can see that the pressure for mixed matrix membrane decreased significantly. Thus, we can conclude that the pores are much more uniform in MWCNT impregnated mixed matrix membranes than in pristine membranes.

Table 5.3 Variation of pore diameter and required pressure of membranes having 1% concentration of MWCNT, M1 (Pristine), M21 (oxidized), M31 (Amide), M41 (Azide)

Parameter	M1	M21	M31	M41
Mean flow pore pressure (psi)	47.61	37.55	36.35	39.28
Mean flow pore diameter (µ)	0.14	0.17	0.18	0.16
Bubble point pressure (psi)	33.50	33.21	35.82	33.50
Bubble point diameter (µ)	0.19	0.19	0.18	0.19

5.1.6 Small angle neutron scattering

To overcome the limitation of detection of small pores by capillary flow porometer, much more detailed structural information of the inorganic filler incorporated polymeric membranes was studied by the neutron scattering technique namely the Small Angle Neutron Scattering (SANS). This technique makes use of wave properties of neutron to probe the structure of the material.

In the SANS study, the differential scattering cross section per unit volume ($d\Sigma/d\Omega$) for mono-disperse particles is represented by the expression [283],

$$\frac{d\Sigma}{d\Omega} = nP(Q)S(Q) + B \qquad (4)$$

Where n is the number density of the particles, P(Q) is the intraparticle structure factor, S(Q) is the inter-particle structure factor and B is a constant term. P(Q) depends on the shape and size of the particles and S(Q) is decided by the spatial distribution of the particles. For dilute system, S(Q) is considered to be unity. B accounts for the incoherent scattering background that occurs mainly due to the presence of hydrogen in the sample.

For spherical particles/pores of radius R, P(Q) can be given by

$$P(Q) = \frac{16\pi^2}{9}(\rho_p - \rho_s)^2 R^6 \left[3\frac{sin(QR) - (QR)cos(QR)}{(QR)^3}\right]^2$$

(5)

Where ρ_p and ρ_s are the scattering length densities of particle/pore and solvent/matrix, respectively.

The $P(Q)$ of randomly oriented cylindrical particles with the radius R and length L (=2l) is given by

$$P(Q) = \pi^2 R^4 L^2 \left(\rho_p - \rho_s\right)^2 \int_0^{\pi/2} \frac{4 j_1^{\,2}(QR\sin\theta)}{Q^2 R^2 \sin^2\theta} \frac{\sin^2(Ql\cos\theta)}{Q^2 l^2 \cos^2\theta} \sin\theta d\theta \qquad (6)$$

where j_1 (x) is first order Bessel function and θ is the angle subtended by the principal axis of the cylinder with Q.

For polydispersed systems, $d\Sigma/d\Omega$ in equation (4) can be expressed as

$$\frac{d\Sigma}{d\Omega}(Q) = \int \frac{d\Sigma}{d\Omega}(Q,R) f(R) dR + B \qquad (7)$$

where $f(R)$ is the size distribution and usually accounted by log normal distribution as given by

$$f(R) = \frac{1}{R\sigma\sqrt{2\pi}} \exp\left[-\frac{\left(\ln R/R_{med}\right)^2}{2\sigma^2} \right] \qquad (8)$$

where R_{med} and σ are the median value and standard deviation respectively. The mean (R_m) and median values are related as $R_m = R_{med} \exp(\sigma^2/2)$.

For non-particular structures, randomly distributed two-phase system, the scattering intensity can also be modeled using Ornstein Zernike model where [284]

$$I(Q) = I_0 \frac{1}{\left[1 + \left(Q\xi\right)^2\right]} \qquad (9)$$

Where I_0 is the forward scattering and ξ is the correlation length. The above equation characterizes the exponential decay of the composition fluctuations correlation function, with correlation length ξ.

The data is analyzed using SASFIT software. Throughout the data analysis corrections were made for instrumental smearing. The calculated scattering profiles were smeared by the appropriate resolution function to compare with the measured data. Figures 5.6, 5.7, 5.8 show the scattering profile of the pure as well as functionalized membranes soaked in the D_2O.

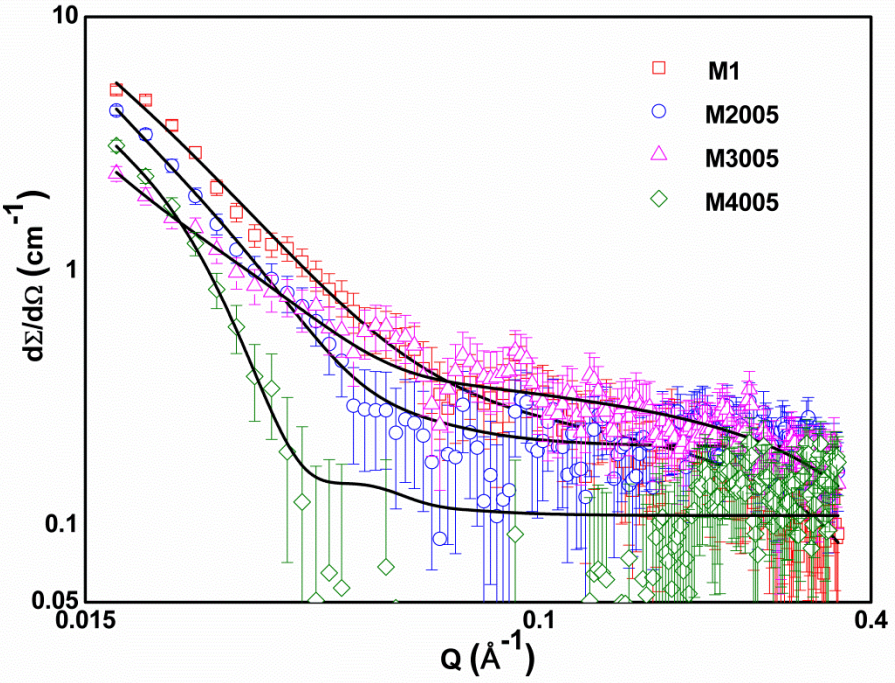


Figure 5.6 SANS profile of Pristine PES (M1), 0.05 wt % Ox/PES (M2005), 0.05 wt % Am/PES (M3005) and 0.05 wt % Az/PES (M4005) membrane soaked in D_2O

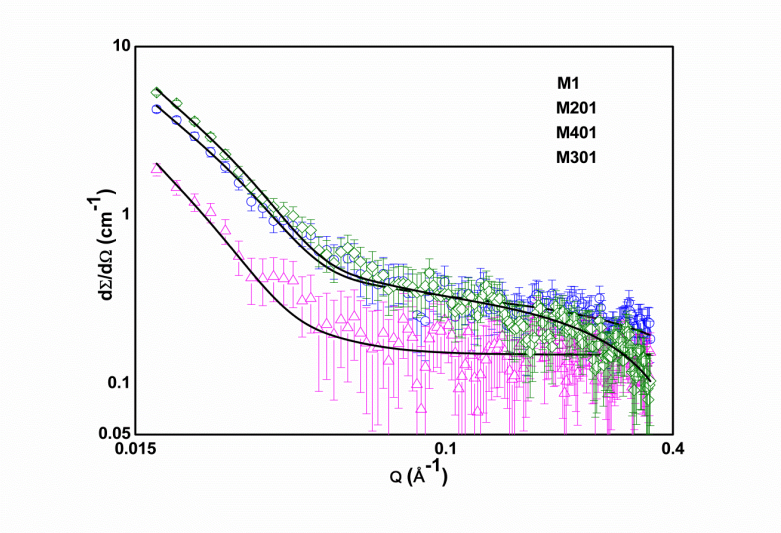


Figure 5.7 SANS profile of Pristine PES (M1), 0.1 wt % Ox/PES (M201), 0.1 wt % Am/PES (M301) and 0.1 wt % Az/PES (M401) membrane soaked in D_2O

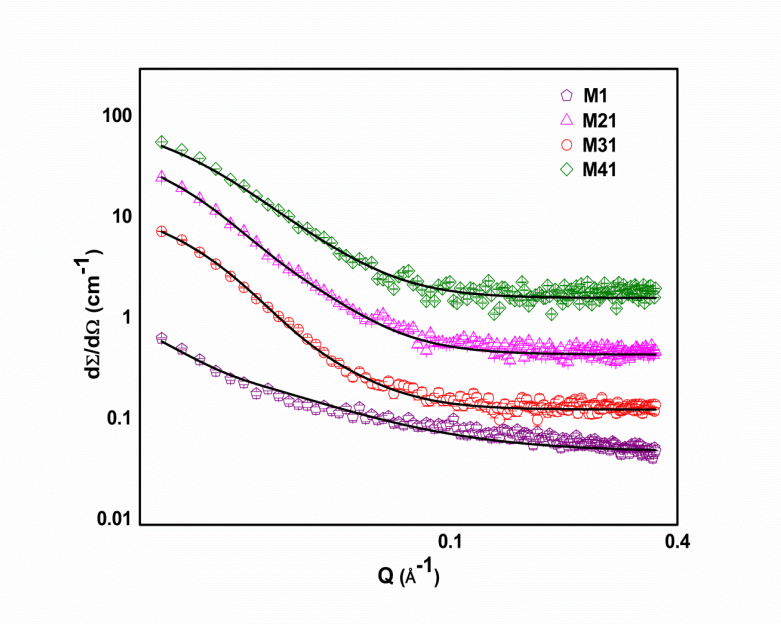


Figure 5.8 SANS profile of Pristine PES (M1), 1 wt % Ox/PES (M21), 1 wt % Am/PES (M31) and 1 wt % Az/PES (M41) membrane soaked in D_2O

The scattering intensities for the different membrane samples are presented in the arbitraty unit and shifted vertically for the clarity of the presentation. There are two models that are considered: (i) the polydispersed sphere model where the pores are considered to be spherical and surrounded by a matrix material and (ii) the random two-phase model, where first phase is the pores and the second phase the surrounding matrix material. These data are presented in Table 5.4.

Table 5.4 SANS data of membrane soaked in D_2O.

Sample	Pore Radius (nm)	Polydispersity (σ)	Correlation length (nm)
M1	14.8	0.27	3.9
M2003	6.2	0.2	4.8
M2005	10.9	0.20	4.8
M2007	15.8	0.20	4.8
M201	13.0	0.20	4.8
M21	9.7	0.27	3.9
M3003	9.1	0.20	4.9
M3005	9.1	0.20	4.9
M3007	5.2	0.20	4.9
M301	14.0	0.20	4.9
M31	8.3	0.29	3.9
M4003	11.3	0.20	4.9
M4005	11.0	0.20	4.9
M4007	10.5	0.20	4.9
M401	10.5	0.20	4.9
M41	7.4	0.27	3.9

Our data were better fit to the second model where the scattering from the distributed polydispersed spherical pores is combined with OZ equation to fit the experimental data. The correlation length is found to be about 3.9 nm. The addition of the MWCNT influences the SANS data in the intermediate Q range. All these data have been analyzed by considering the scattering contributions from the CNTs along with that from the distributed pores. The MWCNT radius is found to be about 4 nm while the length of the CNTs (in microns) cannot be estimated due to the limited Q range of the data. A fixed value of the MWCNT length (~ 100 nm) more than the $2\pi/Q_{min}$ has been used through the data analysis. It may be pointed out that the distribution of the pores does not change with addition of the MWCNT while the pore radius reduces significantly.

The correlation length is 3.9 nm in the pristine PES membrane as well as in the mixed matrix membrane containing 1 weight percentage of MWCNT and in the membranes containing smaller percentage of nanotubes the value is about 4.8 nm. As it is the most repeated distance between the pores and is same for both pristine and mixed matrix membrane however pore radius is decreased in later case which implies that porosity of the membrane is increased with the addition of the 1 weight percentage of nanotubes which is in agreement with enhanced porosity of membranes containing nanotubes reported in our previous work [279] (Figure 5.9). However lower percentage of addition of nanotubes does not affect the porosity. The addition of the CNTs influences the SANS data in the intermediate Q range.

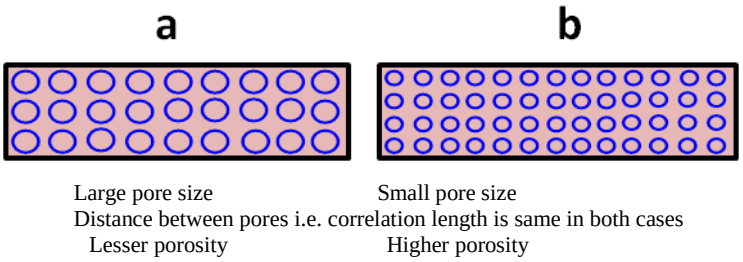


Figure 5.9 Schematic representation of arrangement of pores in the (a) pristine membrane and (b) mixed matrix membrane

5.2 Characterization of SPES/f-MWCNT membranes

5.2.1 FE-SEM

The surface and cross-section of the SPES as well as f-MWCNT containing mixed matrix membranes is observed using Field emission scanning electron microscopy. The surface morphology is showing the smooth surface and there is not much change in morphology with addition of functionalized nanotubes (Figure 5.10).

The cross-section of the 1wt% Am-MWCNT/SPES membranes showed the figure like macro voids (Figure 5.11). The addition of MWCNT in the polymer matrix changed membrane upper layer by eliminating the wider layer and there is formation of thin skin layer on the membrane surface.

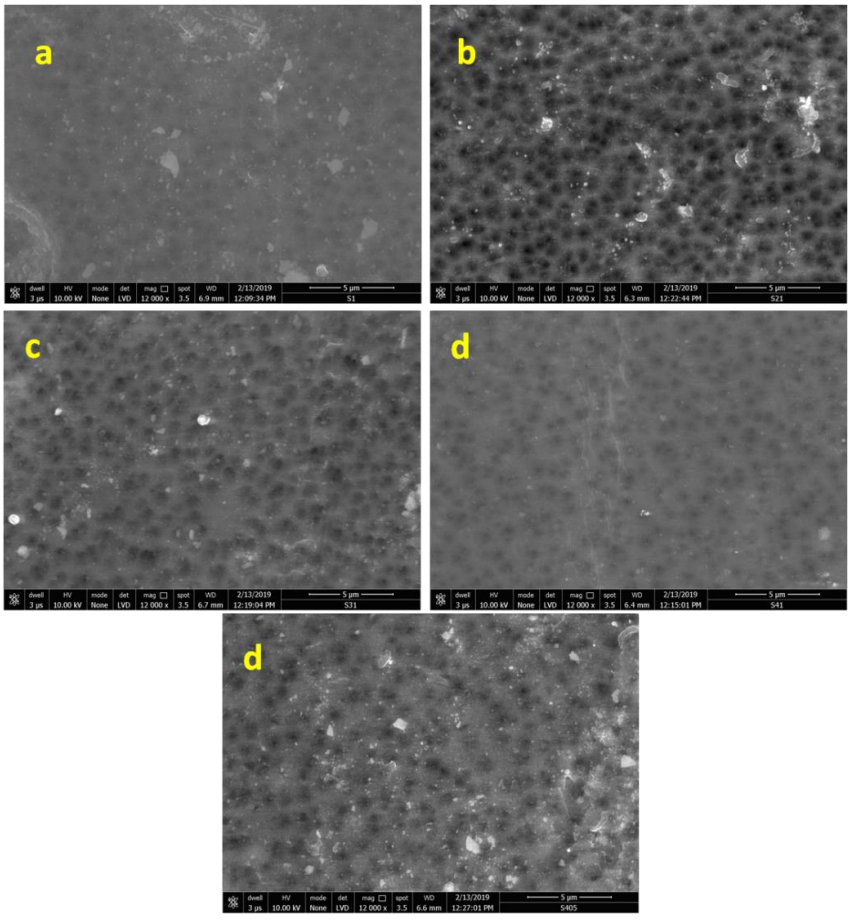


Figure 5.10 FE-SEM image of the surface of the Pristine SPES (a) 1wt% Ox-MWCNT/SPES (b) 1wt% Am-MWCNT/SPES (c) 1wt% Az-MWCNT/SPES (d) 0.5wt% Az-MWCNT/SPES

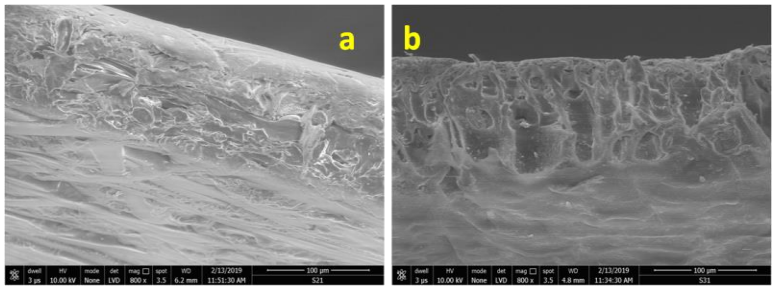


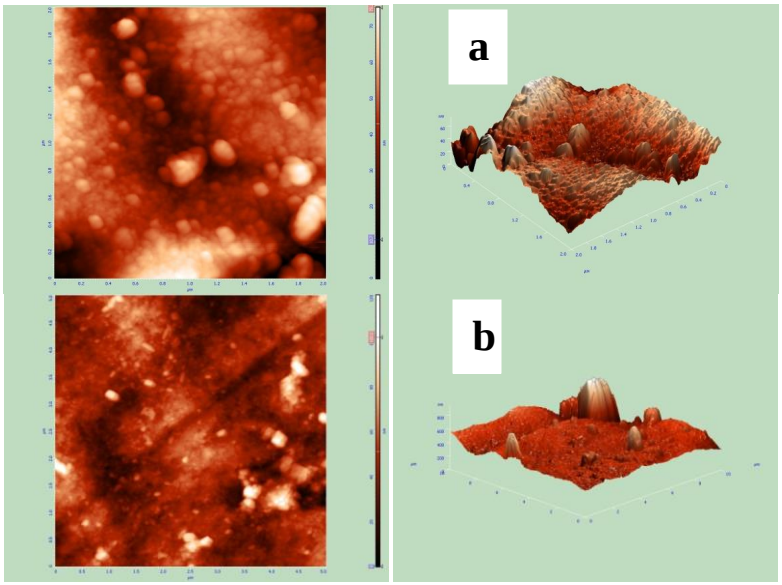
Figure 5.11 FE-SEM image of cross-section of Pristine SPES (a) and 1wt% Am-MWCNT/SPES membranes

5.2.2 Atomic Force Microscopy (AFM)

The AFM images of pristine PES, pristine SPES, Az-MWCNT/SPES membranes are shown in Figure 5.12, which revealed that membrane surface roughness mainly depends on the composition of casting solution. In case of pristine PES and pristine SPES the viscosity of the sulfonated polyethersulfone dope solution is less compared to the PES solution, which speedup the solvent-non solvent exchange rate of SPES membrane, thus the surface roughness increases. Average roughness value for PES is 9.21 nm which is increased to 11.02 nm for SPES membranes. Furthermore, the addition of functionalized nanotubes increases the viscosity of Az-MWCNT/SPES dope solution thus slow down the solvent-non solvent exchange rate and formation of smooth surface (Table 5.5).

Table 5.5 Roughness parameters of Pristine PES [M1], Pristine SPES [S1], 0.1wt% Az-MWCNT/SPES [S401], 0.5wt% Az-MWCNT/SPES [M405], 1wt% Az-MWCNT/SPES [M41] mixed matrix membranes

	Average Roughness Sa (nm)	**Root Mean Square Sq (nm)**
M1	9.21	11.41
S1	11.02	14.35
S401	4.02	5.09
S405	4.87	6.61
S41	4.17	5.33



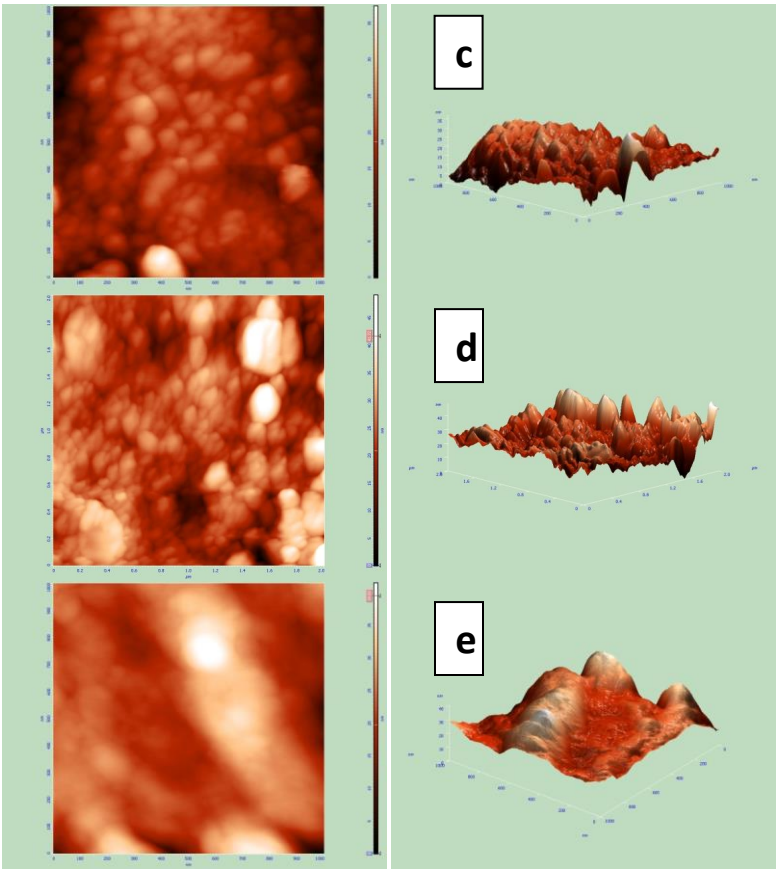


Figure 5.12 AFM images of pristine PES (a) pristine SPES (b) 0.1wt% Az-MWCNT/SPES (c) 0.5wt% Az-MWCNT/SPES (d) 1wt% Az-MWCNT/SPES (e)

5.2.3 Contact angle

The limitation of polyethersulfone membranes are their hydrophobic nature which gives rise to fouling of the membrane, thus reducing the life of the membranes [285, 286]. The contact angle of sulfonated polyethersulfone membrane and functionalized nanotubes containing mixed matrix membranes are measured to observe the change in the surface properties and hydrophilicity. The contact angle values are given in Table 5.6. Pristine SPES membranes are having 49.13^{o}, which is the indication of improved hydrophilicity of the membrane due to sulfonation

of PES. The lower contact angle i.e. higher hydrophilicity of SPES membranes may be accredited to the polar groups of SPES polymer, having SO_3H groups which are strongly hydrophilic. The contact angles are much reduced for the mixed matrix membranes containing f-MWCNT and reached to the value of 38.84 for 1wt% Az-MWCNT/SPES membranes. Furthermore, for all the functionality of nanotubes the contact angle is decreased with increasing the content of nanotubes in the polymer matrix.

Table 5.6 Contact angle values of pristine SPES and f-MWCNT/SPES mixed matrix membranes

Membranes	Contact angle (º)
S1	49.13±1.3
S201	41.51±2.4
S205	40.72±3.1
S21	39.47±1.7
S301	43.69±5.2
S305	41.11±2.9
S31	39.70±1.2
S401	40.75±3.0
S405	40.56±1.1
S41	38.84±1.0

5.2.4 Zeta Potential measurement

The evaluation of the charge generated on the membrane surface is a vital parameter to understood antifouling performance of the membranes. The

sulfonated PES membranes are retaining negative charge on the membrane surface as in case of PES membranes (Figure 5.13 a), however the SPES membranes are showing higher negative charge which is in agreement with previous report [287]. The mixed matrix membranes containing oxidized, amide and azide MWCNT are showing negative zeta potential in the pH range of 2.5 to 7.0 (Figure 5.13 b) and no isoelectic point could be observed. The negative charge is decreasing at the lower pH value.

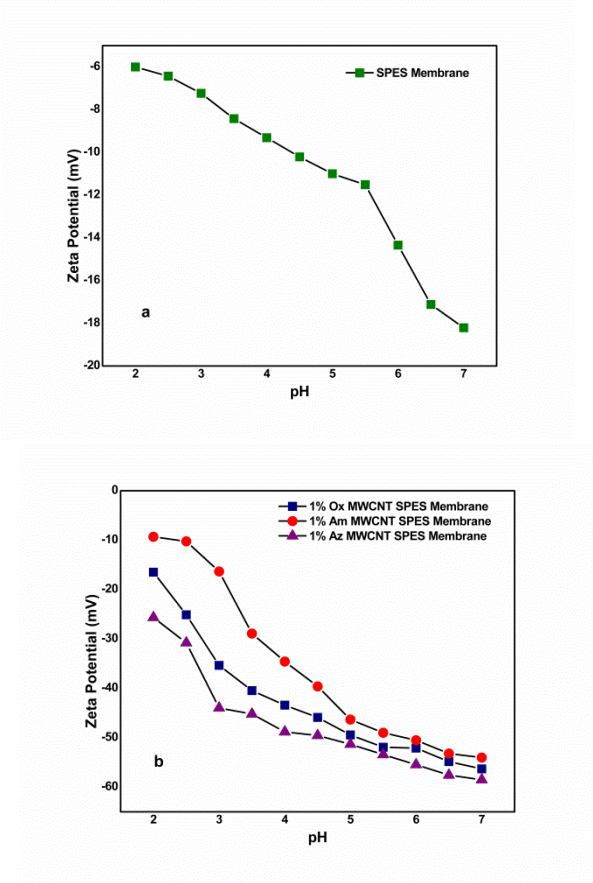


Figure 5.13 The zeta potential value of pristine PES (a) and mixed matrix membranes (b) as a function of pH

5.2.5 Small angle neutron scattering

Small angle neutron scattering (SANS) is the technique to probe the morphology of the porous materials. In this technique, wave properties of neutron are used to probe the structure of the material. Detailed discussion regarding the principle of the instrument is already described in the previous section. Corrections were performed through whole duration of data analysis for instrumental smudging. The calculated scattering profiles were smeared by the appropriate resolution function to compare with the measured data. The SANS profile of pristine SPES membrane and 0.1wt%, 0.5 wt % and 1wt% all the functionalized (oxidized, amide and azide) MWCNT mixed matrix membranes are shown in Figure 5.14, 5.15 and 5.16 respectively.

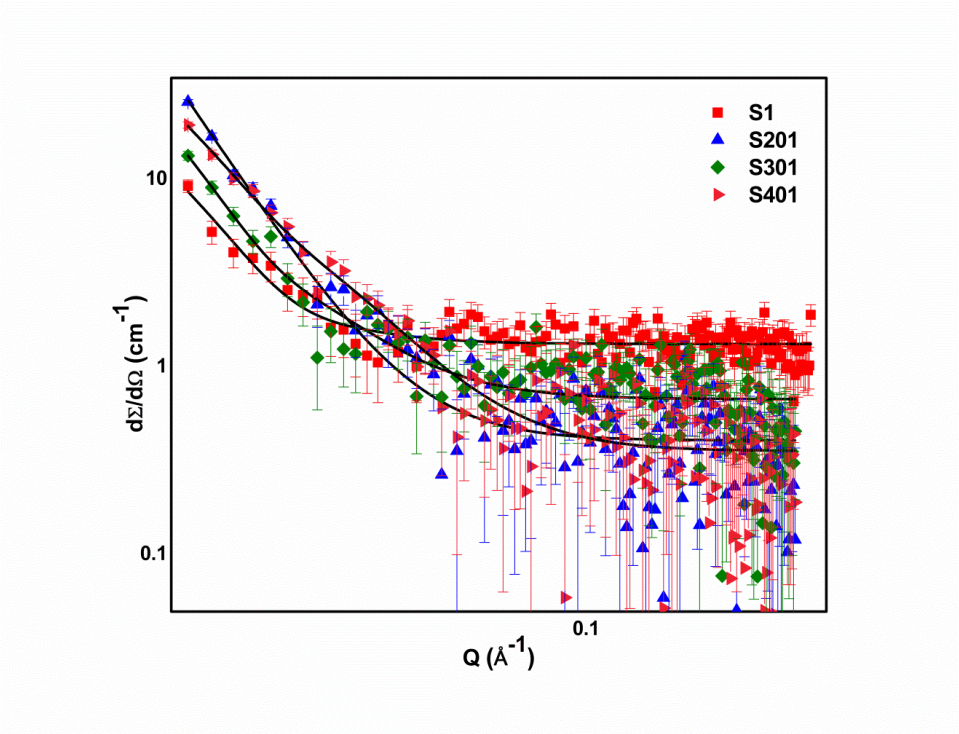


Figure 5.14 SANS profile of Pristine SPES (S1), 0.1 wt % Ox/SPES (S201), 0.1 wt % Am/SPES (S301) and 0.1 wt % Az/SPES (S401) membrane soaked in D_2O

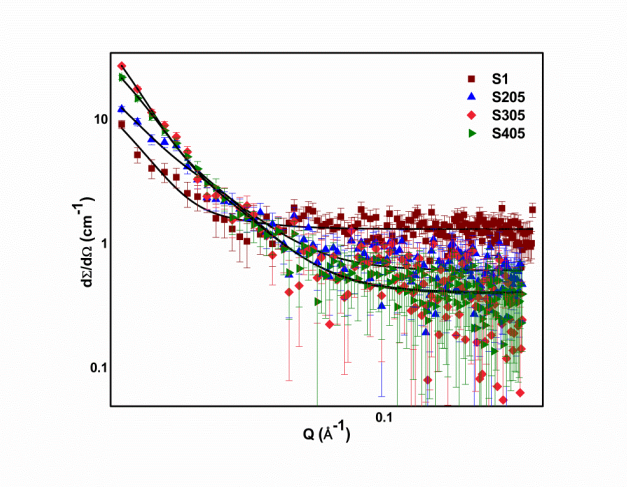


Figure 5.15 SANS profile of Pristine SPES (S1), 0.5 wt % Ox/SPES (S205), 0.5 wt % Am/SPES (S305) and 0.5 wt % Az/SPES (S405) membrane soaked in D_2O

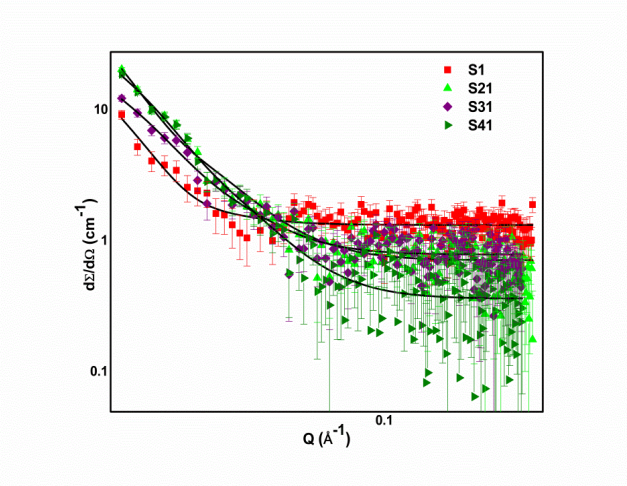


Figure 5.16 SANS profile of Pristine SPES (S1), 0.5 wt % Ox/SPES (S205), 0.5 wt % Am/SPES (S305) and 0.5 wt % Az/SPES (S405) membrane soaked in D_2O

The data was interpreted using SASFIT software. There are two models that are considered: (i) the polydispersed sphere model where the pores are considered to be spherical and surrounded by a matrix material and (ii) the random two-phase model, where first phase is the pores and the second phase the surrounding matrix material. Here is this case also our data is better fitted to the second model, which confirms the presence of nanotubes in the polymer matrix.

Table 5.7 SANS data of membrane soaked in D_2O

Sample	Pore Radius (nm)	Polydispersity (σ)	Correlation length (nm)
M1	14.8	0.27	3.9
S1	15.4	0.25	3.9
S201	15.2	0.24	3.9
S205	14.7	0.25	3.9
S21	14.1	0.27	3.9
S301	14.8	0.26	3.9
S305	14.3	0.28	3.9
S31	14.0	0.29	3.9
S401	13.7	0.30	3.9
S405	13.7	0.30	3.9
S41	13.7	0.30	3.9

The correlation length of pristine SPES membrane as well as mixed matrix membranes prepared from sulfonated SPES is 3.9 nm (Table 5.7), which is identical to the correlation length of PES membranes. This implies that the porosity of SPES membranes is decreased as the correlation length is most repeated distance between the pores. The pore size of the azide functionalized MWCNT/SPES membranes is least, thus giving the best filtration results.

5.3 Characterization of click reaction modified PES/Az-MWCNT membranes

5.3.1 FE-SEM

Figure 5.17 shows the FESEM images of the unmodified and modified mixed matrix membranes. One can see no difference in the surface of the membrane containing 1,2,3, triazole moiety in comparison to the unmodified membrane. At the low magnification of 3000X, the difference in the surface morphology cannot be distinguished. However, cross section of both the membranes gives similar unsymmetrical finger like pores indicating that the chemical modifications carried out only changed the surface morphology and did not alter the bulk morphology.

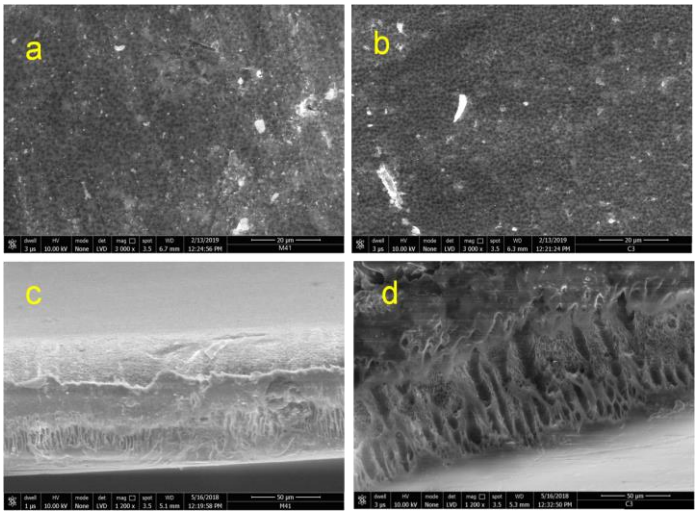


Figure 5.17 FESEM images of azide functionalized MWCNT incorporated PES membrane (a) surface (c) cross section and click reaction modified membrane (b) surface (d) cross section

5.3.2 AFM

The membrane surface topography was analyzed with Atomic force microscopy in semi contact mode and Nova 1.0.26.1424 software was used to evaluate various roughness parameters. The surface roughness of 1% Az-MWCNT/PES membrane is 2.1 nm (Table 5.8). The surface roughness of click reaction modified membrane is 2.2 nm indicative of the uniform addition of triazole moiety on azide membrane surface without any significant change of the surface roughness (Figure 5.18). On the whole, our observations indicate that the click modification on 1% Az-MWCNT/PES membranes significantly increased the hydrophilicity but showed little impact on the surface roughness of the modified membrane.

Table 5.8 Roughness parameters of 1wt% Az-MWCNT/SPES [M41] and click reaction modified membranes

	Average Roughness Sa (nm)	**Root Mean Square Sq (nm)**
M41	2.1	2.6
C3	2.2	2.8

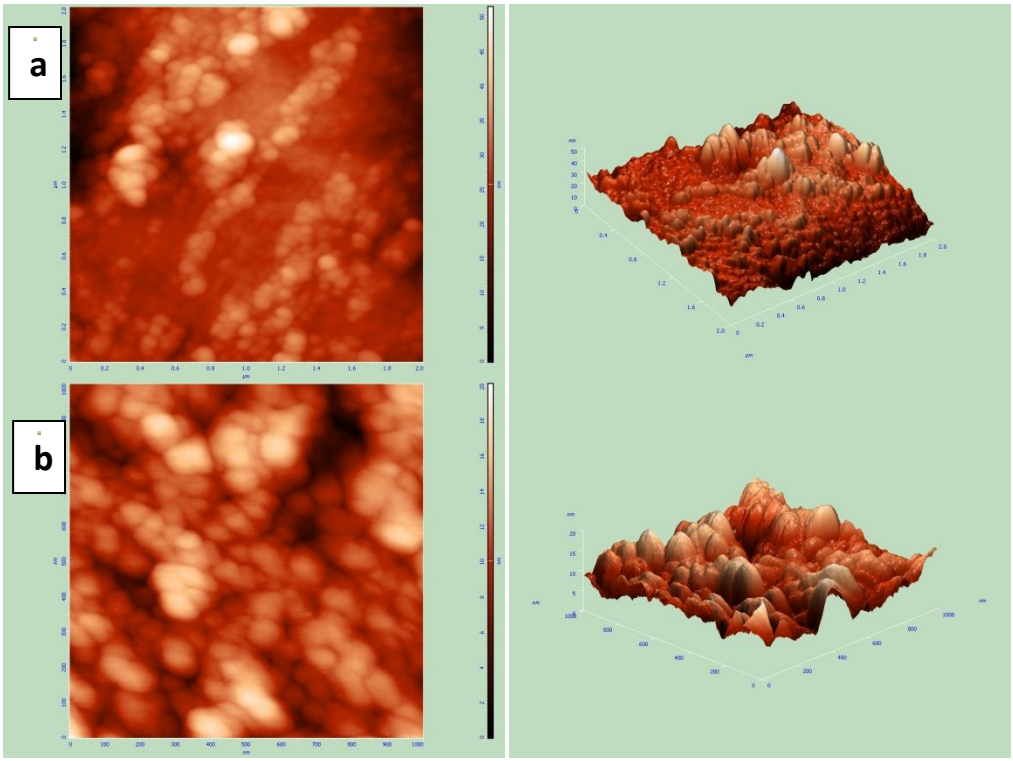


Figure 5.18 AFM images of 1wt% Az-MWCNT/PES [M41] (a) and Click reaction modified mixed matrix membranes

5.3.3 Contact angle measurement

Contact angle of water droplet with the membrane surface is shown in Figure 5.19. As can been seen the water droplet is flat in the case of the modified membrane as compared to that of the unmodified membranes. The values of contact angle are summarised in Table 5.9. The membrane surface after click reaction became more hydrophilic in comparison to the unmodified membranes.

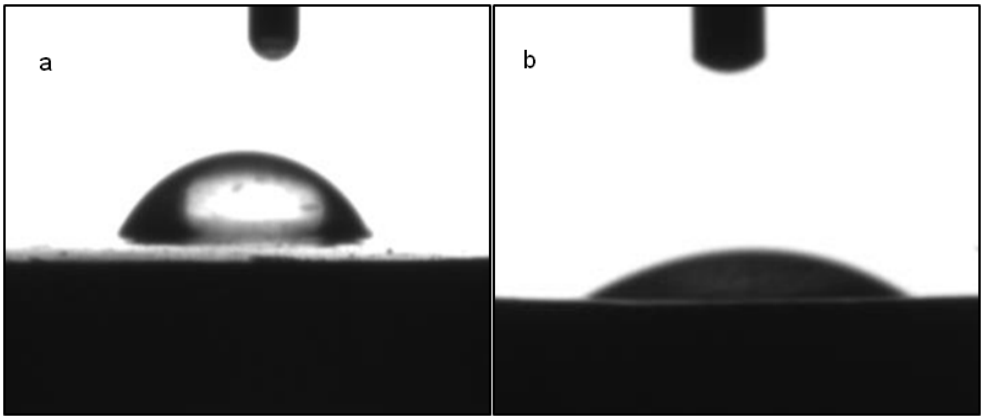


Figure 5.19 Contact angle of azide functionalized MWCNT incorporated PES membrane (a) and click reaction modified membrane (b)

Table 5.9 Contact angle values of membranes

Sr. No.	Membrane code	Membrane details	Contact angle (º)
1	M1	Polyether sulfone (PES)	73.3
2	M41	Az-MWCNT (PES)	65.5
3	C3	Modified (PES)	35.9

5.3.4 Zeta potential measurement

The zeta potential of 1 wt% Az-MWCNT/PES and click reaction modified membranes are measured from streaming potential by streaming electrolyte KCl (0.001 M) in the pH range of 2.5 to 7.0. The zeta potential of click reaction modified membranes was found to be more negative than the 1 wt% Az-MWCNT/PES membrane which is in agreement with the result reported by Lahmar et al [288]. The zeta potential values were less negative at lower pH due to protonation. The zeta potentials were represented in Figure 5.20. Higher

negative charges on the membrane surface stimulate better electrostatic repulsion between the membrane surface and negatively charged foulants [289, 290].

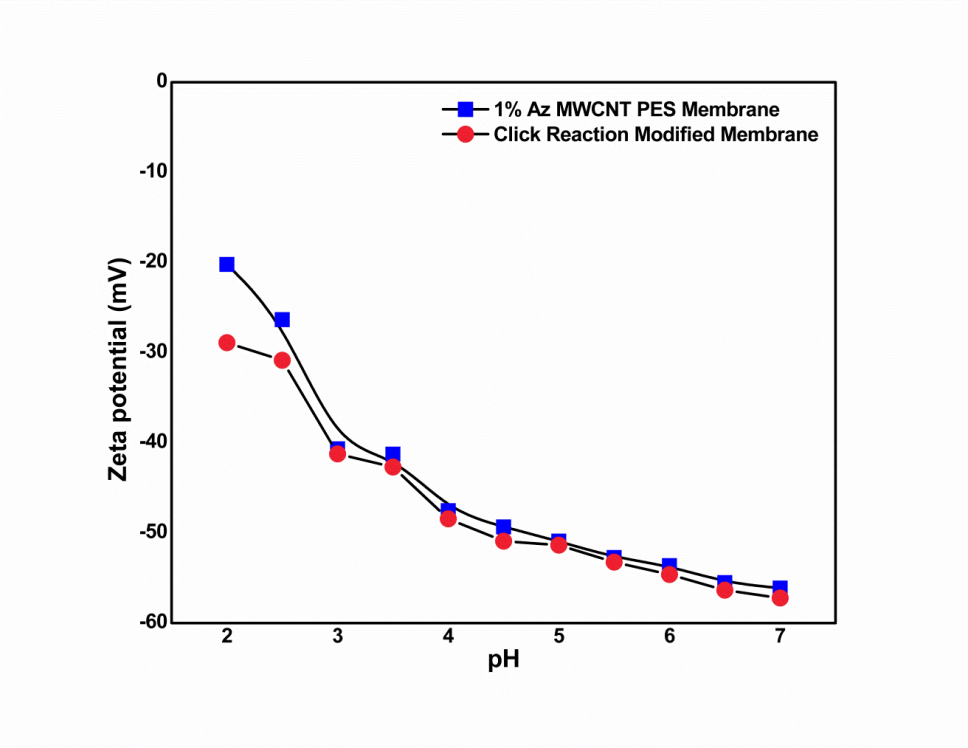


Figure 5.20 The zeta potential value of pristine PES (a) and mixed matrix membranes (b) as a function of pH

5.3.5 Small angle neutron scattering

Small angle neutron scattering data, where we have measured the pore dimension of membrane in neutral condition, gives larger pore dimensions in comparison to unmodified membranes (Figure 5.21). The SANS profiles obtained from the diffractometer are fitted using SASFIT software. This gives the pore dimensions, polydispersity and correlation length of the membranes samples. All these values are presented in the Table 5.10.

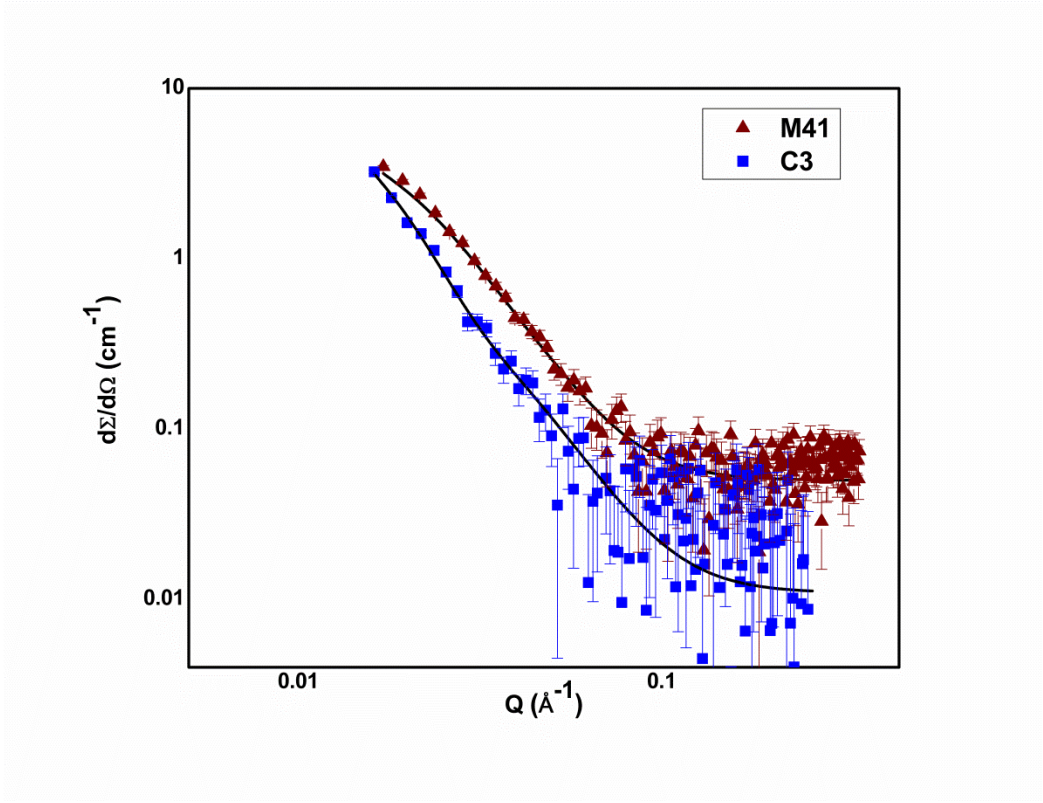


Figure 5.21 SANS profile of 1 wt % Az-MWCNT/PES (M41) and click reaction modified membrane (C3) soaked in D_2O

Table 5.10 SANS data of membrane soaked in D_2O, M1 (pristine PES), M41 (azide), C3 (click modified)

Sample	Pore Radius (nm)	Polydispersity (σ)	Correlation length (nm)
M41	7.4	0.27	3.9
C3	13.3	0.27	2.9

The pore radius of 1wt% Az-MWCNT/PES membrane is found to be 7.4 nm, which is changed to13.3 nm in case of click reaction modified membranes. The correlation length is decreased to 2.9 nm from 3.9 nm for click reaction modified membranes as the pore size is increased. From the previous FESEM study (Figure 5.17), the bulk pore dimensions look similar in the modified and the unmodified membranes, however the SANS is a much more sensitive technique and can detect the pores dimensions better due to the scattering from the heavy water present in the pores. Therefore the modification leads to the opening of the pores.