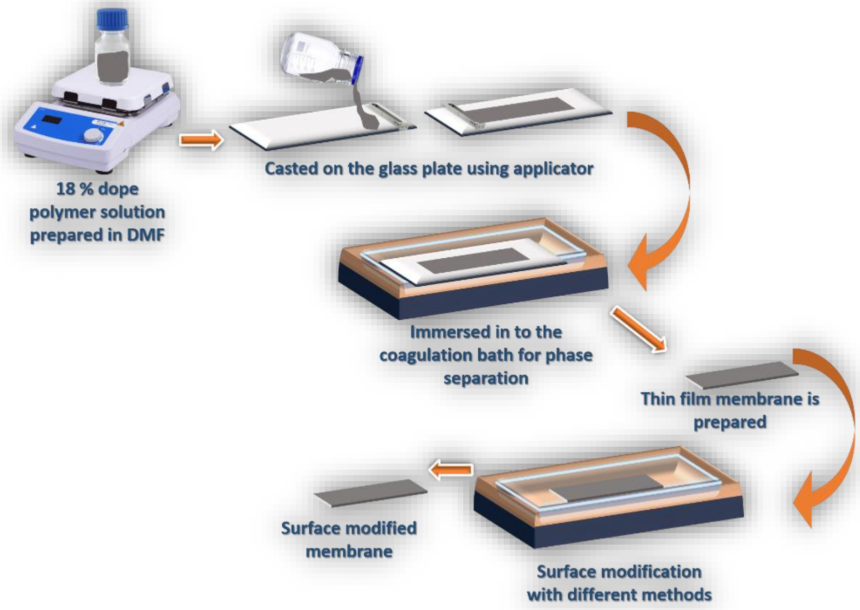
Chapter 3

Experimental route



3.1 Materials

Polysulphone (PSU) (ULTRASON S6010 with Mw 62000 g mol^{-1}) and Polyether sulphone (PES) (ULTRASON E6020 with Mw 72000 g mol^{-1}) purchased from Permionics Membranes Pvt. Ltd. Vadodara, India. Multiwalled Carbon nanotubes (MWCNT) (Purity: >99%, Average Diameter: 10-15 nm, Average length: 5 µm surface area: 400 m^2/g) purchased from Ad-nano technologies private limited, Shimoga, Karnataka, India. Concentrated HCl, Concentrated H_2SO_4, Concentrated HNO_3, Thionyl chloride (>99%, Sigma Aldrich), Ethylenediamine (>99%, Sigma Aldrich), Sodium Azide (>99%, Sigma Aldrich), 1-Pentyne (>99%, Sigma Aldrich), Copper Bromide (>99%, Sigma Aldrich), Trimesoyl Chloride (TMC, 98%) and Cyanuric chloride (CC, 99%) were purchased from Sigma-Aldrich. Polyethyleneimine (PEI) (Thermoscientific, branched, M.W. 10,000, 99%). Dimethyl Formamide (>99%, Sigma Aldrich) were used as received. Hexane were purchased from Loba Chemie Pvt Ltd.

3.2 Purification and functionalization of multiwalled carbon nanotubes

3.2.1 Purification of multiwalled carbon nanotubes (MWCNTs)

To obtain pure multiwalled carbon nanotubes (MWCNTs), it was necessary to eliminate impurities like amorphous carbon and metal ions present in commercial MWCNTs. Various methods are available for purifying MWCNTs, including the modified method employed, which effectively removed amorphous carbon soot and heavy metals. To purify MWCNTs, 2 g of MWCNT was sonicated in a 50% HCl solution for about 3 hours at room temperature (33°C). The metal ions in MWCNTs react with HCl to form soluble metal chlorides. Then, the MWCNTs were thoroughly washed with distilled water to remove acid. The purified CNTs do not attract magnetic needles, and unwanted carbonaceous material and metal ions are removed by purification and washing. After the complete washing with distilled water, the purified MWCNTs are dried in a vacuum oven and used for further functionalized[82–84,86].

3.2.2 Functionalization of multiwalled carbon nanotubes (MWCNTs)

The functional groups on MWCNTs are important because they facilitate interactions with polymers. Specifically, carboxylic groups were introduced onto the MWCNTs because they can be easily converted into other functional groups. Oxidation was performed to introduce carboxylic functional groups by treating purified and dried MWCNTs with a (3:1) mixture of concentrated HNO_3 and concentrated H_2SO_4 for 24 h at 33 °C. After the completion of the reaction, the MWCNTs were washed with distilled water until the pH was neutral. All the acids were removed by washing with distilled water. After complete washing, the oxidized MWCNTs having carboxylic functional groups were dried in a vacuum oven. These oxidized multi-walled carbon nanotubes were subjected to acylation, where the carboxylic functional groups were then converted into acyl chlorides. To accomplish this conversion, the oxidized MWCNTs were treated with thionyl chloride ($SOCl_2$) in dimethyl formamide (DMF) as a solvent for 36 hours at 60 ℃. The acylated-MWCNTs were then washed with toluene to remove excess thionyl chloride. The resulting acylated MWCNTs were dried in a vacuum oven and then subjected to further functionalization with amine and azide groups.

For amine functionalization, the acetylated MWCNTs were sonicated with ethylenediamine for 16 hours at 33 °C. Then, methanol was added to the sonicated reaction mixture for dilution. The amine- MWCNTs were washed and dried in a vacuum oven. Next, the acylated MWCNTs were converted into azide-MWCNTs by reacting with sodium azide (NaN_3) in dimethyl formamide (DMF) as a solvent for 24 hours at 60 ℃. The azide-MWCNTs were finally washed with distilled water and dried in a vacuum oven. The functionalization of MWCNTs was confirmed through FTIR and their morphology was examined by TEM. Following this, all functionalized MWCNTs were utilized as fillers for the production of polysulphones-based mixed matrix membranes. Figure 3.1 gives the details of various functional groups on MWCNTs[82,83].

3.3 Preparation of polysulphones/f-MWCNTs mixed matrix membrane

An 18% dope solution of polysulphone and polyether sulphone was prepared by dissolving the polymers in dimethyl formamide as a solvent. The polymers were added slowly to the solvent to form a homogenous dope solution. Afterwards, 1% of functionalized MWCNTs, which were oxidized, amine- and azide-, were added to the polymeric dope solution and kept in sonication for 12 hours to disperse the carbon nanotubes evenly in the solution. The solution was then cast on a glass plate with the help of an applicator with a gap size of 200 µm. The glass plate was placed in a coagulation bath containing a mixture of distilled water and isopropanol, which is a nonsolvent for both polymers. A thin-film membrane was formed through phase separation, which involved solvent and nonsolvent exchange, resulting in the formation of a porous asymmetric membrane.

The prepared mixed matrix membrane was then washed with water to remove any traces of solvent and stored in distilled water until further use. Figure 3.2 shows the preparation of mixed matrix membrane via phase inversion technique.

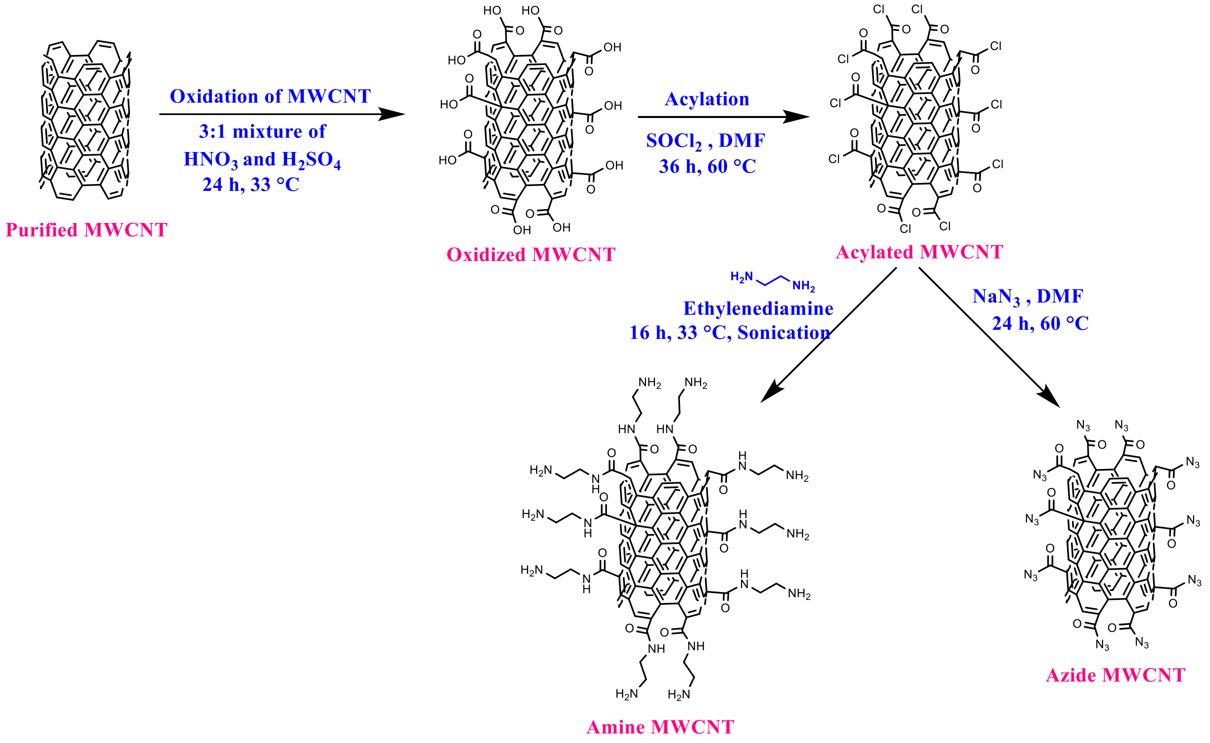


Figure 3.1. Functionalization of multiwalled carbon nanotubes (MWCNTs)

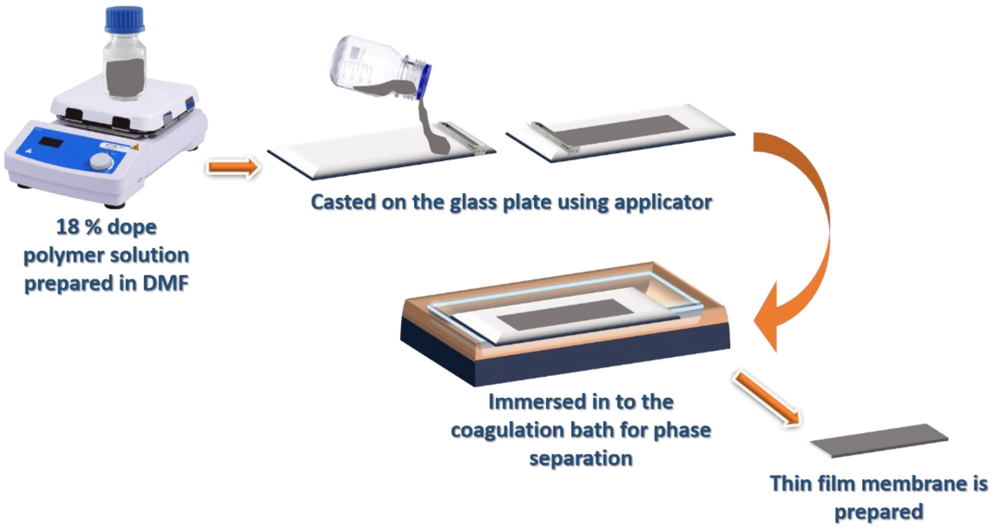


Figure 3.2. Preparation of polysulphones mixed matrix membrane via phase inversion process

3.4 Surface Modification of polysulphone/azide-MWCNT mixed matrix membrane via click reaction

A PSU/azide functionalized MWCNT mixed matrix membrane with azide functional groups on its surface was reacted with 1-pentyne in the presence of copper bromide (CuBr). During the reaction, the azide functional group was converted to a triazole ring. The membrane was initially submerged in water in a 500 ml round-bottom flask, and an inert atmosphere was maintained. CuBr was added, followed by the dropwise addition of 1-pentyne using an additional funnel at low temperature. The reaction was continued for approximately 3 hours for the complete conversion of the azide to triazole. The colour of the solution changed from light yellow to green, indicating a change in the oxidation state of Cu(I) to Cu(II). The membrane was then washed several times with distilled water to remove excess CuBr and 1-pentyne and air dried for 24 hours before further characterization. The reaction scheme for the surface modification of polysulfone/azide-MWCNT mixed matrix membrane via click reaction is shown in Figure 3.3[146,147].

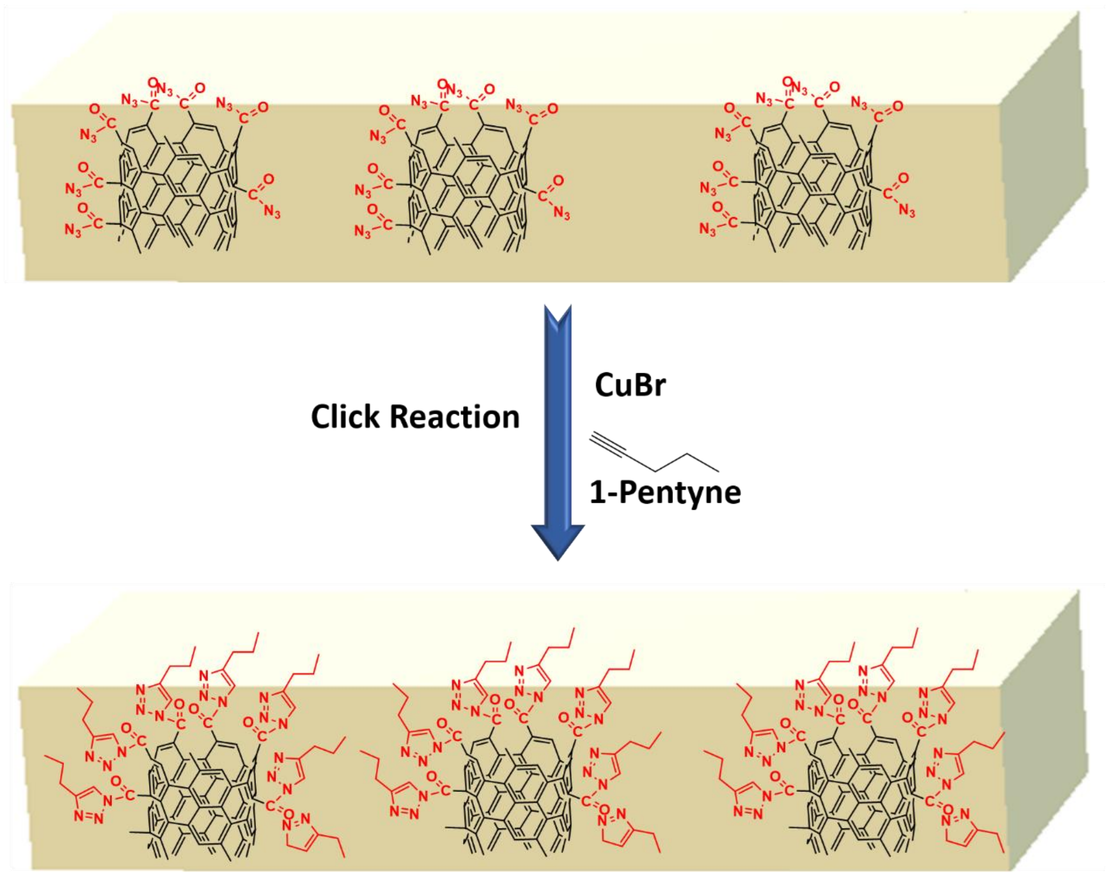


Figure 3.3. Scheme for the surface modification of polysulphone/azide-MWCNT mixed matrix membrane via click reaction

3.5 Surface Modification of polysulphones/amine-MWCNT mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

The process of surface modification for polysulphone and polyether sulphone/amine-MWCNT mixed matrix membranes involves the use of trimesoyl chloride (TMC) and cyanuric chloride (CC). To begin, the mixed matrix membranes are immersed in a 0.01 M NaOH solution, which acts as an acid receptor to deprotonate the amine groups on the membrane surface. This makes the groups more nucleophilic, enabling them to react with TMC and CC[175]. Afterward, the membrane is removed from the NaOH solution and excess NaOH solution is removed using a rubber roller. Then, an organic solution containing 1% TMC or CC is poured onto the membrane surface and left to soak for approximately 24 hours. The excess organic solution is removed from the membrane surface using a rubber roller, after which the membrane is allowed to air dry at room temperature to evaporate the organic solvent. The resulting modified membrane is washed with distilled water and stored in distilled water until use.

The reaction between trimesoyl chloride and an amine involves nucleophilic addition and elimination. The amine functional groups on the membrane surface act as nucleophiles, attacking the electrophilic carbonyl carbon of trimesoyl chloride. This leads to the formation of an amide linkage on the membrane surface. In contrast, the reaction between cyanuric chloride and amines follows a nucleophilic substitution mechanism. Amine groups on the membrane surface act as nucleophiles, easily displacing chloride ions in cyanuric chloride. The reaction scheme for the surface modification with trimesoyl chloride and cyanuric chloride is depicted in Figure 3.4.

3.6 Surface Modification of polysulphones/oxidized-MWCNT mixed matrix membrane using polyethylenimine (PEI)

The polysulphones/oxidized-MWCNTs mixed matrix membranes with carboxylic functional groups on their surfaces underwent a treatment with polyethylenimine (PEI) by the following procedure: After soaking the membranes in water overnight, excess water was drained. The wet membranes were then immersed in 1% PEI solution in water in one necked round bottom flask and kept at 100°C for 6 hours. Following this treatment, the membranes were washed thoroughly with distilled water to remove excess PEI from the surface. The resulting modified membranes were stored in distilled water. The amines within polyethyleneimine (PEI) act as nucleophiles, initiating a reaction by attacking the carbonyl carbon present on the mixed matrix membrane surface. This leads to the formation of amide linkages on the membrane surface. The surface modification process using PEI is illustrated in Figure 3.5, including the reaction scheme.

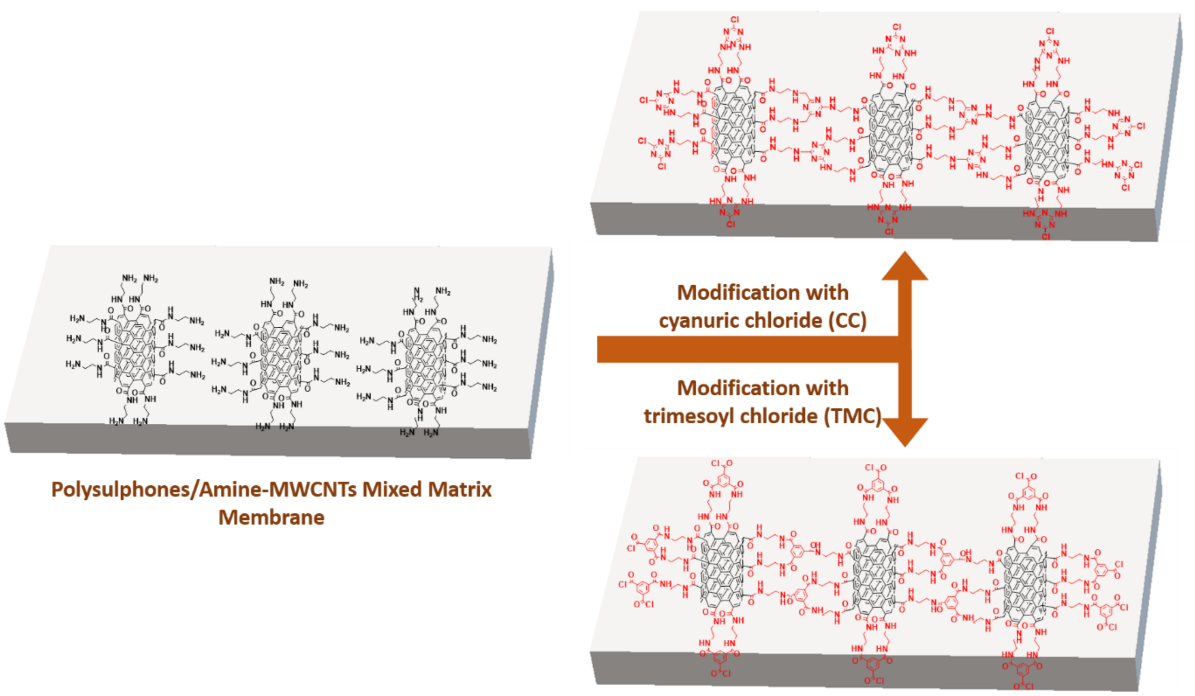


Figure 3.4. Scheme for the surface modification of polysulphones/amine-MWCNT mixed matrix membrane using TMC and CC

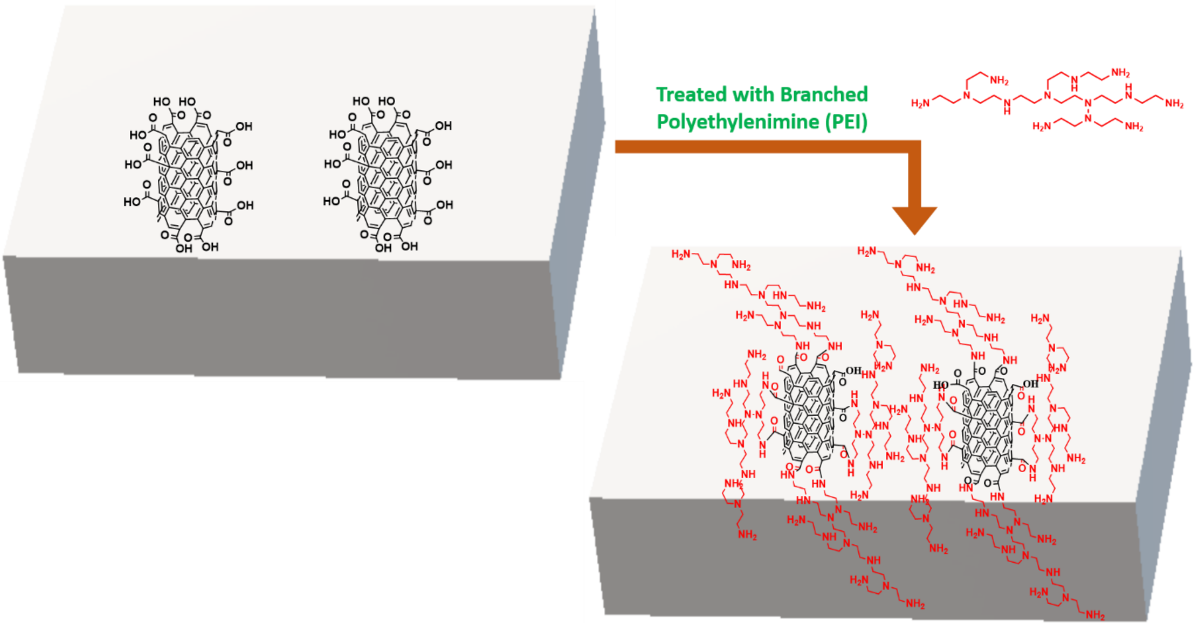


Figure 3.5. Scheme for the surface modification of polysulphones/oxidized-MWCNT mixed matrix membrane with PEI

Table 3.1. Composition of prepared membrane

Membranes	Composition
Pristine PES	Pristine polyether sulphone
Pristine PSU	Pristine polysulphone
PSU/Az-CNT	Polysulphone mixed matrix membrane incorporated with azide functionalized multiwalled carbon nanotubes
PSU/TAz-CNT	PSU/Az-CNT membrane modified via click reaction having a triazole moiety
PES/Am-CNT	Polyether sulphone mixed matrix membrane incorporated with amine functionalized multiwalled carbon nanotubes
PSU/Am-CNT	Polysulphone mixed matrix membrane incorporated with amine functionalized multiwalled carbon nanotubes
PES/Ox-CNT	Polyether sulphone mixed matrix membrane incorporated with oxidized functionalized multiwalled carbon nanotubes
PSU/Ox-CNT	Polysulphone mixed matrix membrane incorporated with oxidized functionalized multiwalled carbon nanotubes
PES/Am-CNT/TMC	PES/Am-CNT membrane modified with trimesoyl chloride (TMC)
PSU/Am-CNT/TMC	PSU/Am-CNT membrane modified with trimesoyl chloride (TMC)
PES/Am-CNT/CC	PES/Am-CNT membrane modified with cyanuric chloride (CC)
PSU/Am-CNT/CC	PSU/Am-CNT membrane modified with cyanuric chloride (CC)
PES/Ox-CNT/PEI	PES/Ox-CNT membrane modified with polyethylenimine (PEI)
PSU/Ox-CNT/PEI	PSU/Ox-CNT membrane modified with polyethylenimine (PEI)

3.7 Characterization

3.7.1 Characterization of f-MWCNTs

Fourier Transform Infrared Spectroscopy (FTIR) was utilized to characterize the functionalized multiwalled carbon nanotubes (f-MWCNTs), and their morphology was analyzed using transmission electron microscopy (TEM).

3.7.2 Characterization of unmodified and modified mixed matrix membranes

The surface properties of modified and unmodified polysulphones mixed matrix membranes were analyzed using X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) to identify surface functional groups. Cross-sectional studies of the membranes were examined using Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) and Field Emission Scanning Electron Microscope (FE-SEM). The roughness of the unmodified and modified membranes was characterized using Atomic Force Microscopy (AFM), and the surface charge was measured using a zeta potential study. Small-angle neutron scattering (SANS) was used in order to investigate the arrangement and size of pores within the membranes, while the hydrophilicity of the membranes was determined by measuring the contact angle using a contact-angle meter.

3.7.3 Fourier Transform Infrared Spectroscopy (FTIR)

PerkinElmer Spectrum Two™ (FTIR) spectrophotometer was used to detect functional groups on the functionalized multiwalled carbon nanotubes, as well as the surface functional groups of both modified and unmodified mixed matrix membranes.

3.7.4 Transmission electron microscopy (TEM)

A Transmission Electron Microscope (TEM) with a resolution of up to 0.38 nm (point image) and 0.2 nm (lattice image), an accelerating voltage of up to 120 kV, and a magnification of x1,200,000 was used to examine the morphology of functionalized multiwalled carbon nanotubes (MWCNTs).

3.7.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to characterize the modified and unmodified mixed matrix membrane, including identifying surface functional groups and confirming the formation of a triazole moiety from an azide group via click reaction, as well as the conversion of amine to amide after treatment with trimesoyl chloride and cyanuric chloride. The presence of amine functional groups was also confirmed after treatment with polyethylenimine (PEI). XPS is a quantitative method for evaluating the elemental composition on the surface of the material, and it characterizes the modified molecular structure and determines its binding energy. The modified and unmodified membranes, with a sample size of 8 mm x 2 mm, were analyzed using a Physical Electronics PHI 5000 VersaProbe III X-ray Photoelectron spectrophotometer.

3.7.6 Field Emission Scanning Electron Microscope (FE-SEM)

Field Emission Scanning Electron Microscope (FE-SEM) JSM7600F (Jeol) (CIF, IIT Gandhinagar) and Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) (IIT, Bombay) used to study the cross section of the modified and unmodified membranes. A cross-section field emission-scanning electron (FE-SEM) micrograph of the mixed-matrix membranes was taken immediately after their cold fracture in liquid N_2.

3.7.7 Atomic Force Microscopy (AFM)

Surface Roughness and other surface parameters analyzed by Atomic Force Microscopy using INTEGRA Scanning Probe microscope with modules including Atomic Force Microscopy (AFM) (IIT Roorkee, Uttarakhand India).

3.7.8 Small-angle neutron scattering (SANS)

Small-angle neutron scattering experiments were performed at the SANS diffractometer at Guide Tube Laboratory, Dhruva Reactor, Bhabha Atomic Research Centre, Mumbai, India[176]. The intensity of scattered neutrons is measured as a function of magnitude of wave vector transfer Q ($= 4\pi \sin\theta/\lambda$), where λ is the wavelength of the incident neutrons and 2θ is the scattering angle). The mean wavelength of the monochromatized beam from neutron velocity selector is 5.2 Å with a spread of Δλ/λ ~ 15%. The angular distribution of neutrons scattered by the sample is recorded using a number of 1 m long one-dimensional He3 position-sensitive detectors (PSDs) in crossed-geometry. The instrument covers a Q-range of 0.01–0.3 Å-1. The data have been corrected for the contributions from background.

3.7.9 Zeta potential

The zeta potential is a measurement of the strength of the electrostatic force between particles, either repelling or attracting them. It is the electric potential at the interface between the liquid and the solid particles, specifically at the location where the particles are moving relative to the bulk fluid. This potential is determined by the amount of electric charge within the region between the slipping plane and the surface of the liquid, and it varies based on the position of the plane. The zeta potential, a measure of electrokinetic potential represented by the Greek letter zeta (ζ), is used to determine the membrane zeta potential through the Helmholtz-Smoluchowski equation by calculating the streaming potential[177].

The determination of the zeta potential of porous membranes can be inferred from measurements of the electrolyte conductivity within the pores. The separation performance of membranes is usually described in terms of size exclusion, but in some cases, the electrical double layer near the pore walls plays a critical role. When an electrolyte solution is passed through a capillary under pressure, an electrical potential called streaming potential is generated. The surface or pore charge modification is then evaluated by measuring streaming potential to observe related modifications[178].

Polymeric membranes possess a surface charge because of the presence of functional groups on the surface. When these membranes come into contact with an aqueous solution, they form an electrical double layer, with the compensation of the membrane's surface charge through counter ions in the solution near the surface. The characteristic of the electrical double layer is that the surface charge is balanced by the counter ions, some of which are located very close to the surface in the Stern layer, and the remaining ones are distributed at a distance from the surface in the Diffuse layer. The potential at the boundary between the Stern and Diffuse layers is known as the Stern potential, which cannot be directly measured. However, the zeta potential is often considered a satisfactory alternative to the Stern potential. The potential at the plane of shear between the solid surface and the solution, where relative movement occurs between them, is the zeta potential. There are four basic types of electro kinetic effects that can be utilized to measure zeta potential based on the given conditions. These include Electrophoresis, Electro-osmosis, Sedimentation potential, and Streaming potential. The Streaming potential method is most appropriate for membranes. The Liquid sedimentation balance method is a new technique for measuring zeta-potential that utilizes test samples and a liquid sedimentation balance. Streaming current measurements involve measuring membrane zeta potential at different membrane thicknesses and using a parallel ohmic resistance model to eliminate the influence of thickness. The Streaming potential analyzer is useful for measuring the zeta potential of reverse osmosis membrane surfaces. The Electrophoresis method offers a significant insight into the ion transport properties of pristine and modified nanofiltration membranes. The Electrolyte conductivity inside pores can be used to determine the zeta potential of porous membranes, such as ceramic microfiltration membranes[179–182].

Zeta potential studies of unmodified and modified membranes were conducted with an adjustable-gap cell. The membranes were soaked in 0.1 M KCl water for 1 h. The membranes were cut to 2x1 cm size and fixed on the measurement holder using double-sided adhesive tape. 0.1 M KCl was used as the electrolyte. The pH of the electrolyte was increased to 11 by adding 1 M NaOH and was titrated against 0.05 M HCl for a sweep to pH 2-3. The streaming potential was measured by pumping the electrolyte by a pair of syringe pumps through the adjustable gap cell in both flow directions. The rinsing and flow check was performed at an increasing pressure of up to 300 mbar and the measurement was performed at 200 mbar. The pH and conductivity sensors were calibrated before the measurement. The zeta potential was obtained from the measured streaming potential in the SurPass software Attract (Anton Paar GmbH) based on Helmholtz–Smoluchowski equation.

3.7.10 Contact-angle meter

The hydrophilicity of the membranes was measured by measuring the contact angle using a contact angle meter (ACAMNSC 03, Apex Instruments Pvt. Ltd.) via the sessile water drop method.

3.8 Characterization of functionalized MWCNTs (f-MWCNTs)

3.8.1 FTIR

The FTIR spectra of oxidized-MWCNTs (shown in Figure 3.6), amine-MWCNTs (shown in Figure 3.7), and azide-MWCNTs (shown in Figure 3.8) confirm the functionalization of these multiwalled carbon nanotubes. The FTIR spectrum of the oxidized MWCNTs displays a sharp band at 3276 cm^{-1} because of the presence of hydroxyl (-OH) groups, which is accompanied by a band at 1739 cm-1 resulting from the C=O stretching in the carboxyl groups. Similarly, the FTIR spectrum of amine-MWCNTs shows a new band at 1690 cm^{-1}, along with the disappearance of the 1739 cm^{-1} band, indicating the formation of amide bonds through the reaction with amines. Another weak band at 3560 cm^{-1} appears to indicate N-H amide stretching in the amide linkages. In the case of azide-MWCNTs, the bands at 2135 cm^{-1} and 1598 cm^{-1} correspond to the asymmetric stretching and weak stretching of the azide functional groups, respectively. In all the functionalized MWCNTs, the band at 2930 cm^{-1} is because of the carbon bonded to hydrogen, while the 1074 cm-1 associated with the aromatic C=C stretching vibrations in the graphene structure of CNT. Therefore, the FTIR spectra confirm the functionalization of multiwalled carbon nanotubes[82,83].

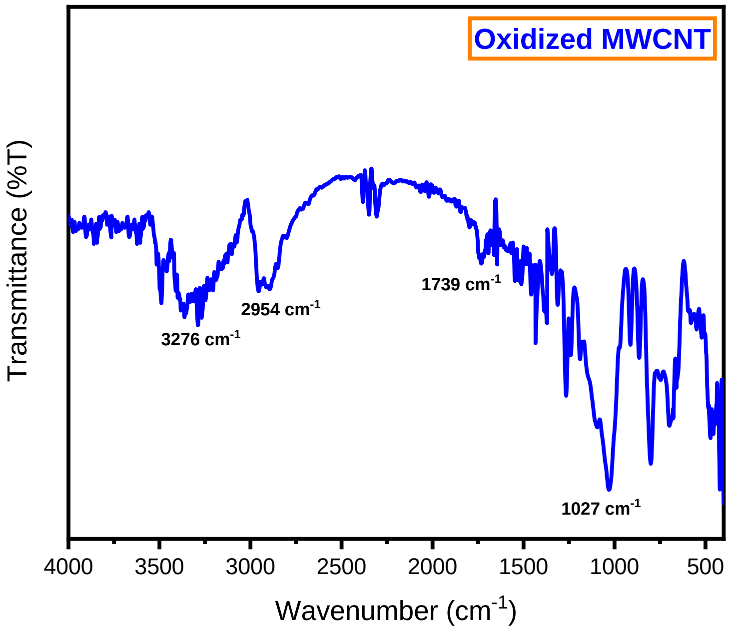


Figure 3.6. FTIR spectra of Oxidized-MWCNTs

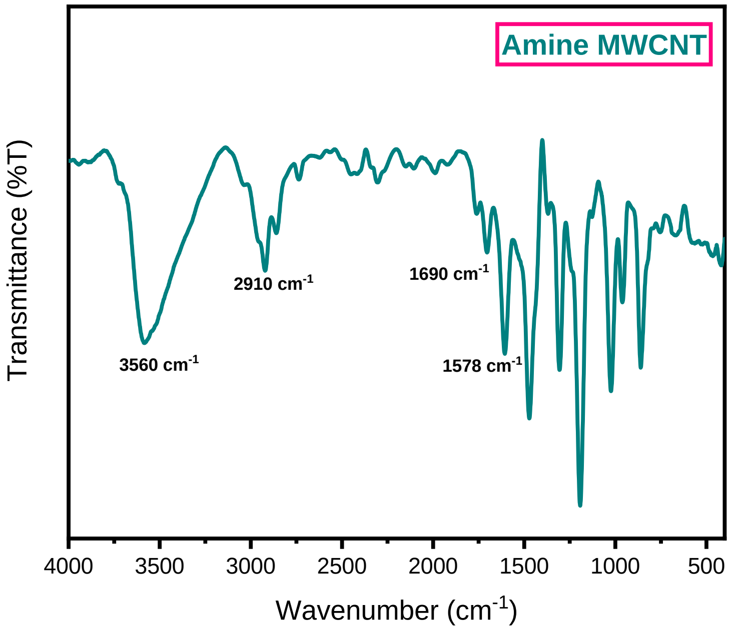


Figure 3.7. FTIR spectra of Amine-MWCNTs

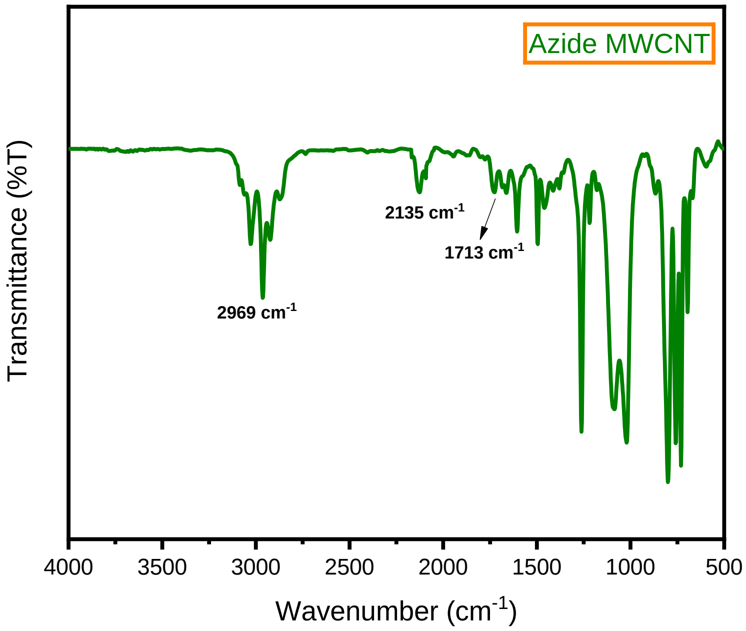


Figure 3.8. FTIR spectra of Azide-MWCNTs

3.8.2 TEM

TEM micrographs of functionalized multiwalled carbon nanotubes (MWCNTs) show that the structure of the resulting carbon nanotubes remains consistent, regardless of the specific functional groups attached. This is due to the inherent structural stability of MWCNTs. The unique tubular structure of MWCNTs minimizes disruptions caused by functionalization, preserving the overall appearance of the CNTs. Consequently, while functionalization alters the surface properties and functionalities, it does not significantly affect the macroscopic morphology of CNTs, allowing for consistent structural integrity across different functionalization. This stability is beneficial for maintaining membrane performance in various applications.

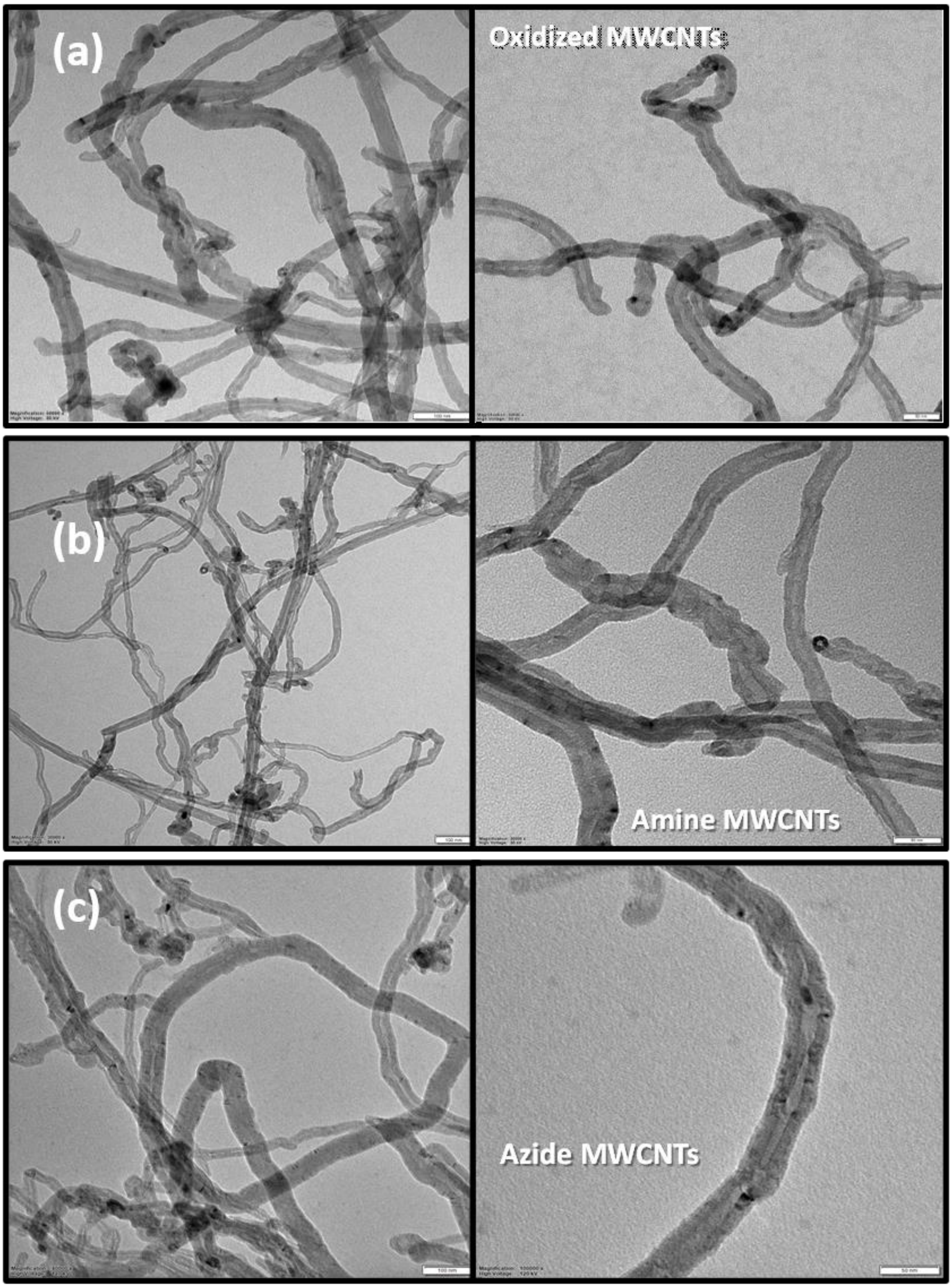


Figure 3.9. TEM images of (a) Oxidized-MWCNTs, (b) Amine-MWCNTs, (c) Azide-MWCNTs

3.9 Surface Characterization of unmodified and modified polysulphones/azide-MWCNTs mixed matrix membrane via click reaction

3.9.1 XPS

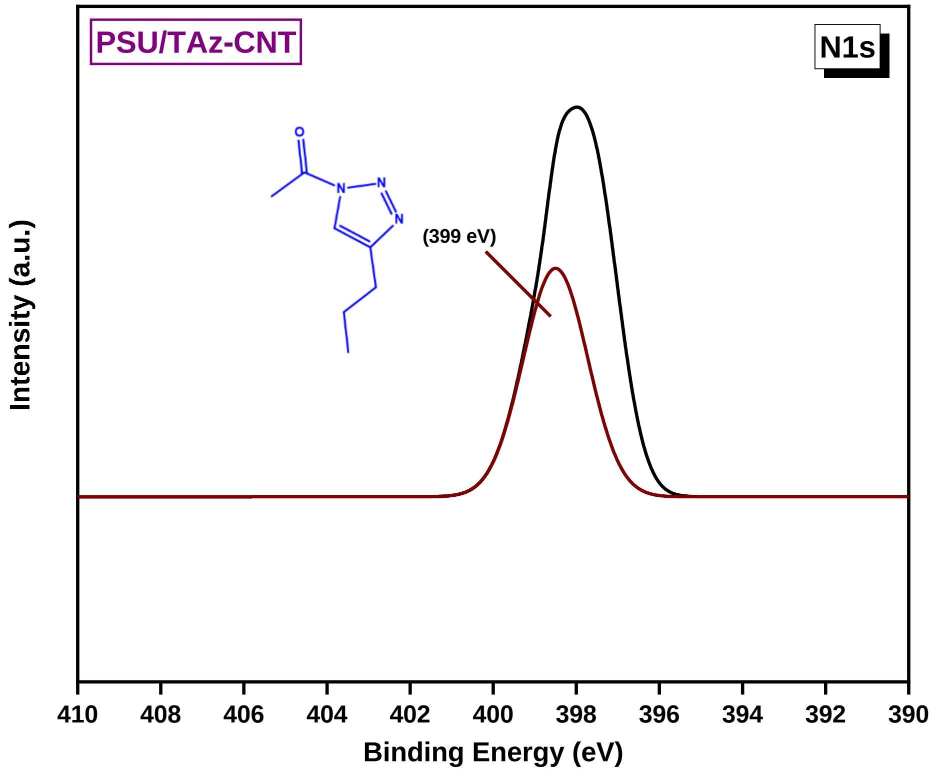


Figure 3.10. N1s XPS spectra of modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

Both the unmodified and click reaction-modified mixed matrix membranes were characterized using X-ray photoelectron spectroscopy (XPS) to identify surface groups and confirm the effectiveness of the click reaction on the membrane surface.

Figure 3.10 and 3.11 show N1s XPS spectra of modified and unmodified membranes. Unmodified membrane had two peaks in XPS spectra at 399 eV and 403 eV, due to azide functional groups on surface. One peak at 399 eV was due to two terminal nitrogen atoms, while the other at 403 eV was due to the central, electron-deficient nitrogen atom. The latter peak was less intense and higher in energy, which is quite abnormal for the organic nitrogen atom therefore that peak consider for the central nitrogen in azide[183]. In the modified membrane, a single peak was observed at 399 eV, indicating formation of triazole ring and disappearance of the peak at 403 eV. The peak at 399 eV was broad and suggested that different nitrogen atoms present were chemically different. The areas under the peaks were similar (Figure 3.11) to the area under 399 eV in the spectra, indicating successful conversion of triazole ring from the azide functional group on the membrane surface[184–186].

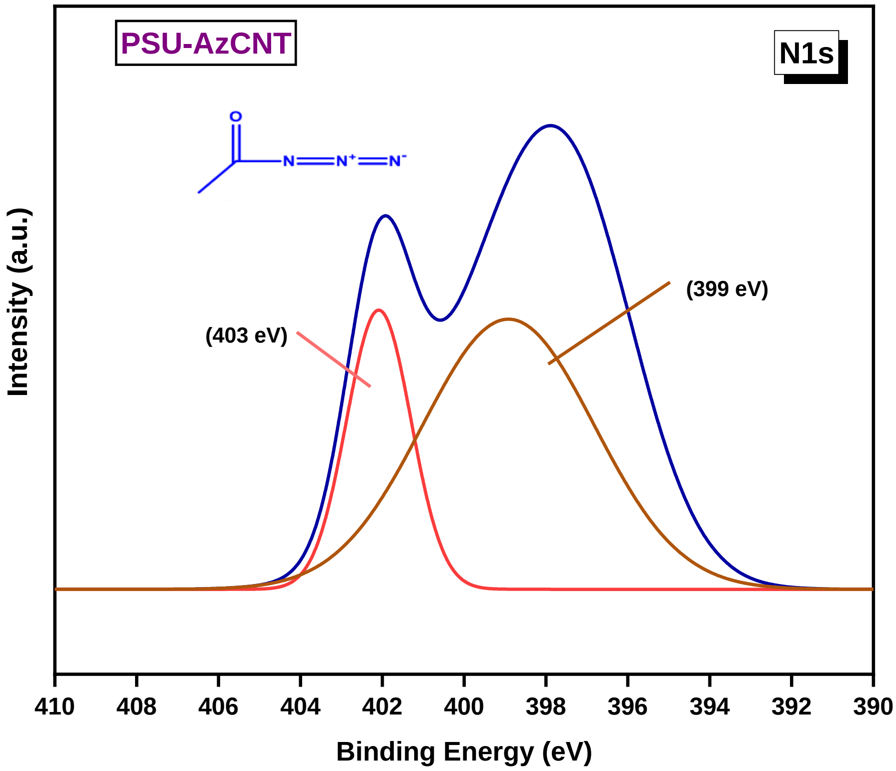


Figure 3.11. N1s XPS spectra of unmodified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction

XPS is a technique that uses X-rays to irradiate a surface, and the spectrum is obtained by analyzing the intensity of electrons that escape from the surface and the binding energy. In this case, the azide functional group produced two distinct peaks at 399 eV for two electron-rich nitrogen atoms and 403 eV for an electron-deficient nitrogen atom. These peaks also contribute to the resonance structure of the azide groups. Following conversion into the stable aromatic triazole ring, a single peak was observed at 399 eV.

In this study, only the nitrogen atom environment altered due to ring formation. Nevertheless, the oxidation state and binding energy of carbon and oxygen remained unchanged because the click reaction is a straightforward cycloaddition process occurring between the azide group and 1-pentyne.

3.9.2 Zeta potential

In Figure 3.12 and Figure 3.13, the zeta potential data for the unmodified and modified polysulphone/azide-MWCNTs mixed matrix membrane via click reaction are presented at different pH levels. The observed increase in the negative zeta potential of the click reaction-modified membranes compared to that of the unmodified membrane was attributed to the presence of triazole groups resulting from the click reaction on the membrane surface[187]. At acidic pH, protonation of the triazole groups occurs, leading to a decrease in the negative charge on the membrane surface. This reduction in the surface charge is due to the increased concentration of positively charged hydrogen ions (H^+) in the solution, which compete with the triazole groups for binding to the membrane surface. Consequently, the membrane became less negatively charged under acidic conditions. Conversely, at a basic pH, the concentration of hydroxide ions (OH^-) in the solution increased, which resulted to the deprotonation of the triazole groups and an increase in the negative charge on the membrane surface. A negatively charged surface is advantageous for repelling heavy metals and foulants[188,189].

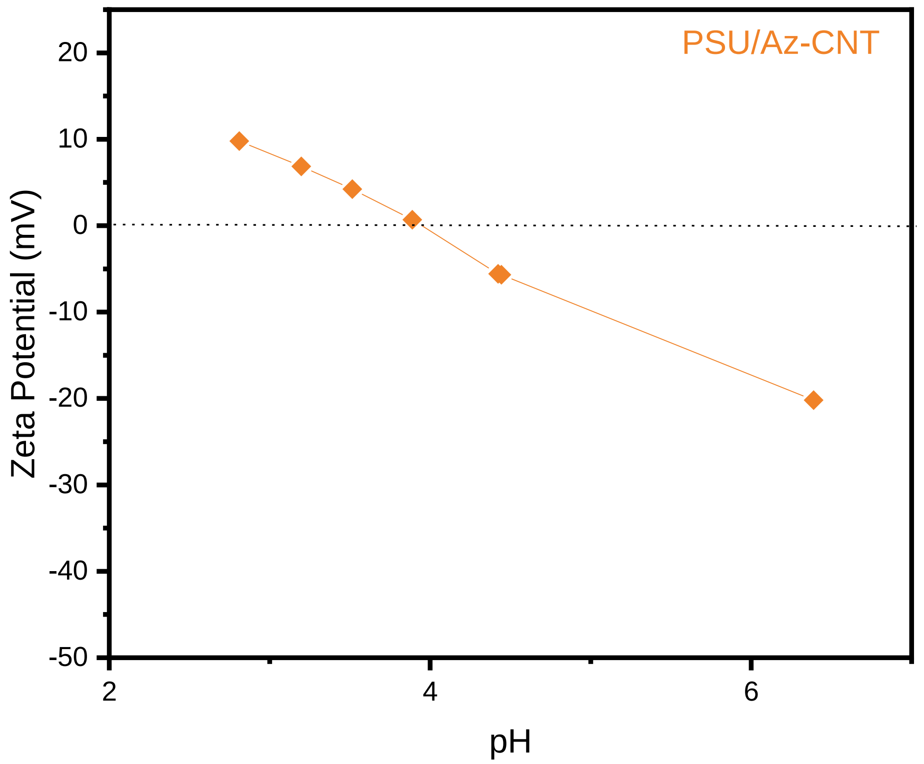


Figure 3.12. Zeta potential values of polysulphone/azide-MWCNT mixed matrix membrane

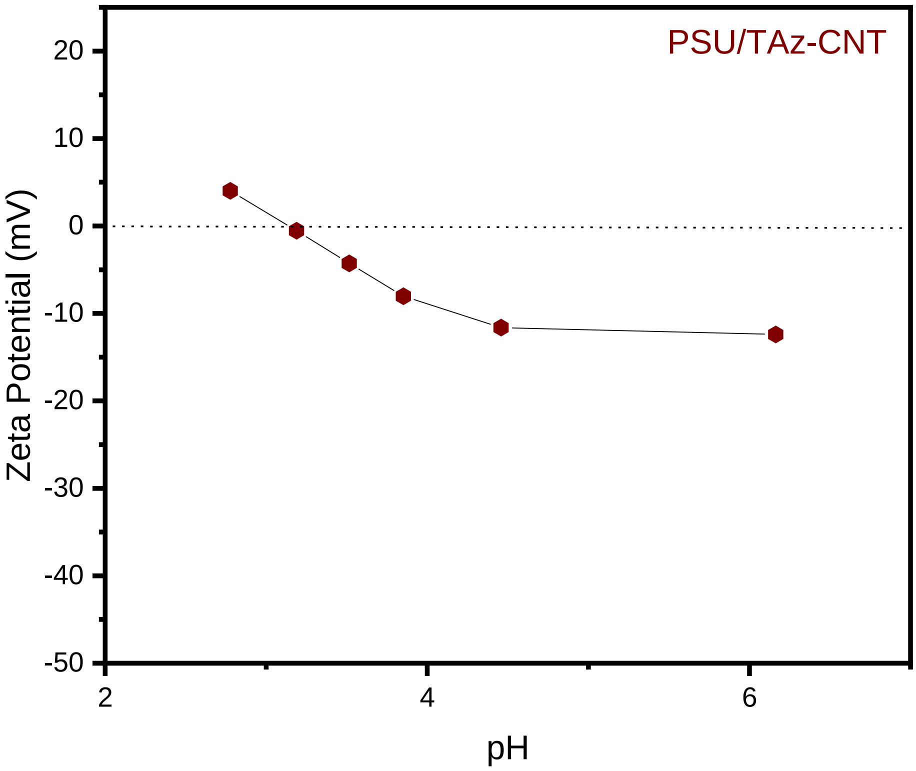


Figure 3.13. Zeta potential values of modified polysulphone/azide-MWCNT mixed matrix membrane via click reaction

3.10 Surface Characterization of unmodified and modified polysulphones/amine-MWCNTs mixed matrix membrane using trimesoyl chloride (TMC) and cyanuric chloride (CC)

3.10.1 FTIR

FT-IR analysis of the mixed matrix membranes (MMMs) shows distinct differences between the modified and unmodified membranes. The unmodified membranes exhibited characteristic bands at 3095 cm^{-1} (Figure 3.14(a)) and 3094 cm^{-1} (Figure 3.15(a)) due to the stretching of N-H amine groups present on the polysulphones mixed matrix membrane surfaces, which were incorporated with amine-functionalized multi-walled carbon nanotubes (MWCNTs) as fillers. However, the amine stretching bands gradually decreased or disappeared after modification with trimesoyl chloride and cyanuric chloride. The modified membranes treated with trimesoyl chloride showed bands at 1679 cm^{-1} (Figure 3.14(b)) and 1694 cm^{-1} (Figure 3.15(b)) indicating the presence of the C=O group in the amide linkage, as well as bands at 1808 cm^{-1} (Figure 3.14(b)) and 1723 cm^{-1} (Figure 3.15(b)) suggesting the presence of C=O stretching in the acid chloride groups. These observations reveal that some acid chloride groups in trimesoyl chloride did not react with amines. Similarly, the modified membranes treated with cyanuric chloride exhibited bands at 1574 cm^{-1}, 1403 cm^{-1}, and 719 cm^{-1} (Figure 3.14(c)), and 1584 cm^{-1}, 1410 cm^{-1}, and 720 cm^{-1} (Figure 3.15(c)). These bands were attributed to ring stretching and deformation vibration caused by the triazine ring present in cyanuric chloride. The triazine ring itself displayed IR bands near 1574 cm^{-1} and 1584 cm^{-1}, derived from the quadrant ring stretch, while the bands at 1403 cm^{-1} and 1410 cm^{-1} indicated the presence of C=N in the triazine ring. Furthermore, a moderately intense band in the 700-800 cm^{-1} region indicated the involvement of ring-sextant out-of-plane deformation, which involved the movement of carbon and nitrogen atoms in opposite directions. The unreacted chloride groups in cyanuric chloride are indicated by bands at 797 cm^{-1} (Figure 3.14(a)) and 769 cm^{-1} (Figure 3.15(a)) for the C-Cl stretch[190–193].

The FT-IR spectra revealed that the membranes had been modified through the reaction with cyanuric chloride and trimesoyl chloride. However, not all the chloride groups in these compounds reacted with the amine functional groups on the membrane surface. The reaction extent relied on the availability of amine functional groups, which is crucial for determination

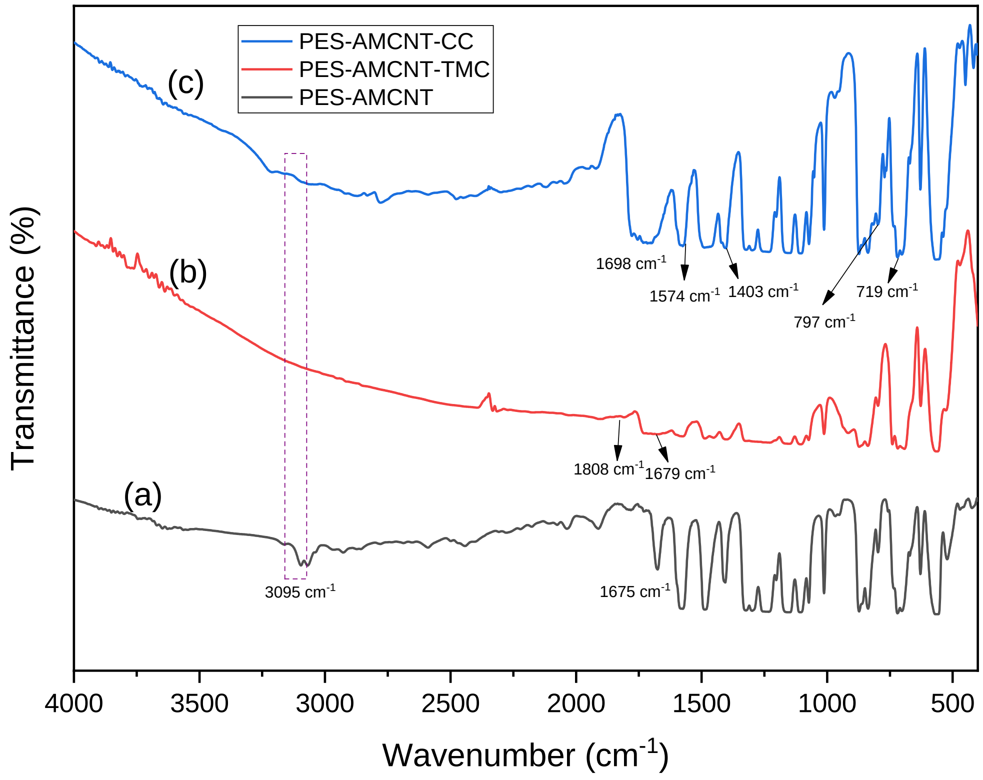


Figure 3.14. FTIR spectra of polyether sulphone/amine-MWCNT mixed matrix membrane, (a) unmodified, (b) modified with trimesoyl chloride (TMC), (c) modified with cyanuric chloride (CC)

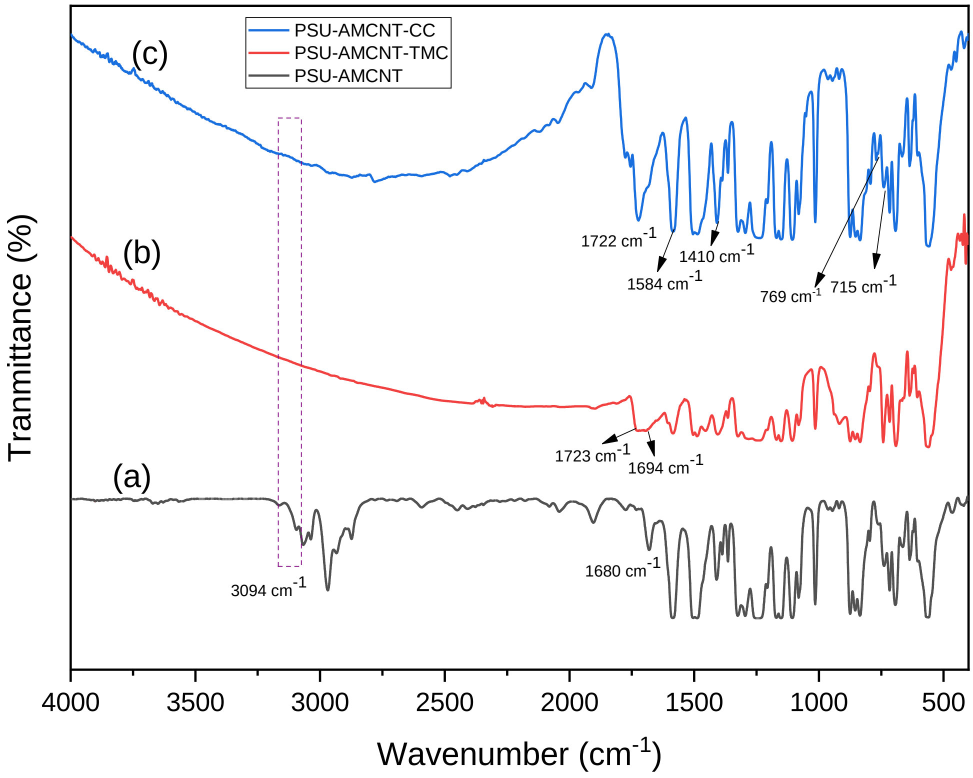


Figure 3.15. FTIR spectra of polysulphone/amine-MWCNT mixed matrix membrane, (a) unmodified, (b) modified with trimesoyl chloride (TMC), (c) modified with cyanuric chloride (CC)

3.10.2 XPS

The unmodified poly ether sulphone/amine-MWCNT mixed matrix membrane exhibits four distinct peaks in the X-ray photoelectron spectroscopy (XPS) analysis:399.3 eV for O=C-N*, 398.9 eV for C-N*, 400.0 eV for O=C-N*H$^-$, and 401.0 eV for protonated NH_2 ($-NH_3^+$). same with the unmodified polysulphone/amine-MWCNT mixed matrix membrane exhibits four distinct peaks:399.6 eV for O=C-N*, 399.2 eV for C-N*, 400.3 eV for O=C-N*H$^-$, and 401.3 eV for protonated NH_2 ($-NH_3^+$) [161,194]. The N1s XPS spectra of the unmodified and modified mixed-matrix membranes are presented in Figures 3.16, 3.17, 3.18, 3.19, and 3.20, as well as in Figure 3.21.

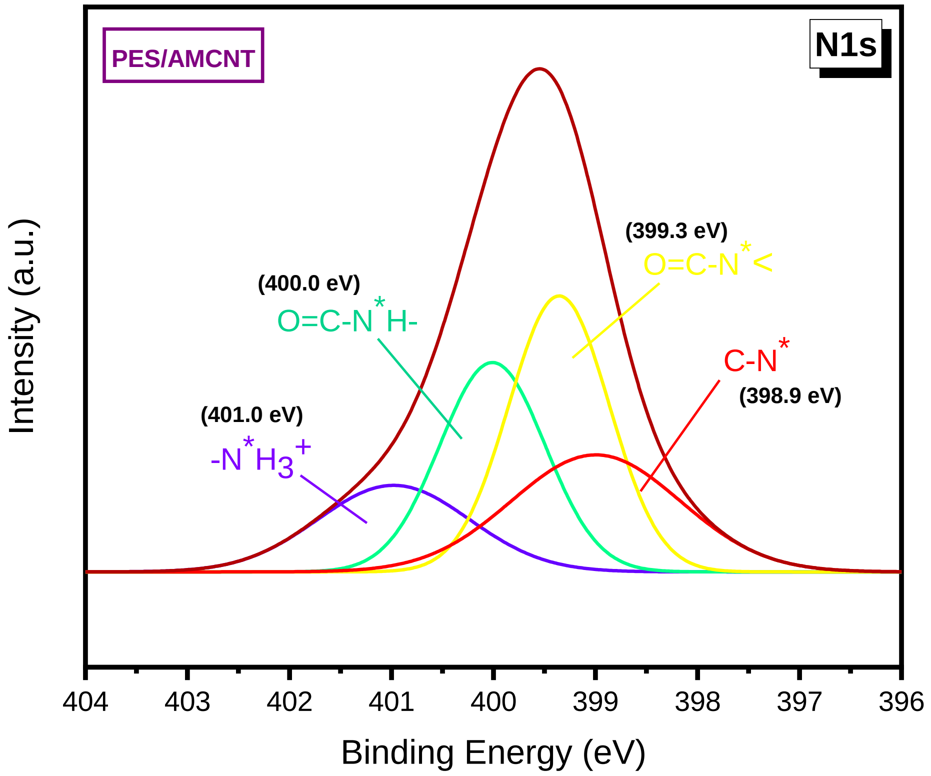


Figure 3.16. N1s XPS spectra of polyether sulphone/amine-MWCNT mixed matrix membrane

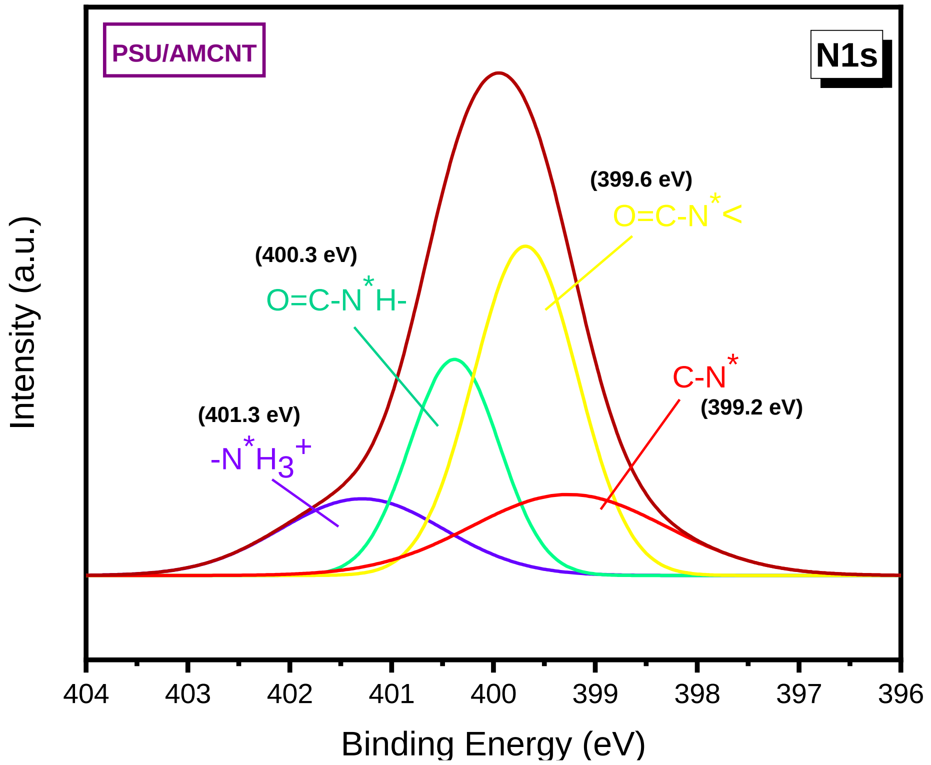


Figure 3.17. N1s XPS spectra of polysulphone/amine-MWCNT mixed matrix membrane

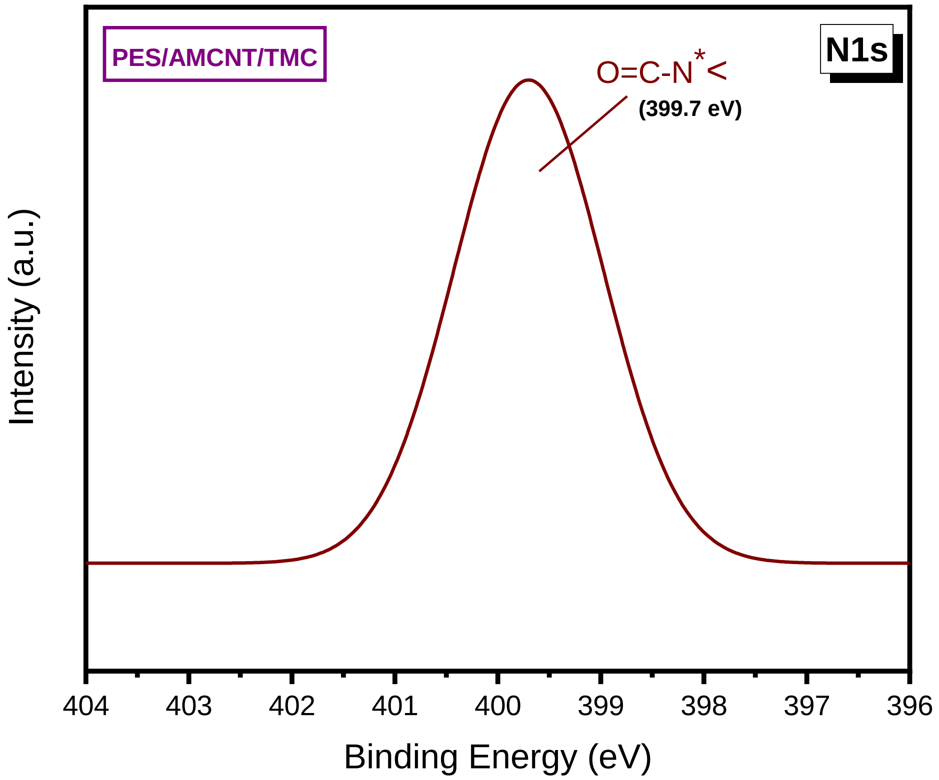


Figure 3.18. N1s XPS spectra of polyether sulphone/amine-MWCNT mixed matrix membrane modified using trimesoyl chloride (TMC)

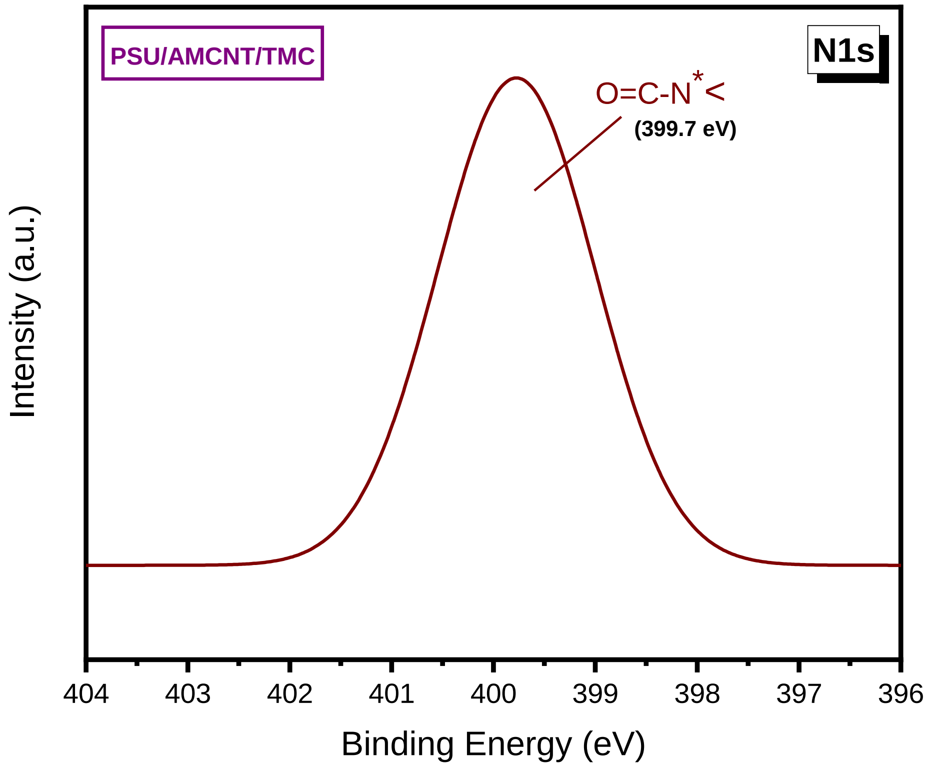


Figure 3.19. N1s XPS spectra of polysulphone/amine-MWCNT mixed matrix membrane modified using trimesoyl chloride (TMC)

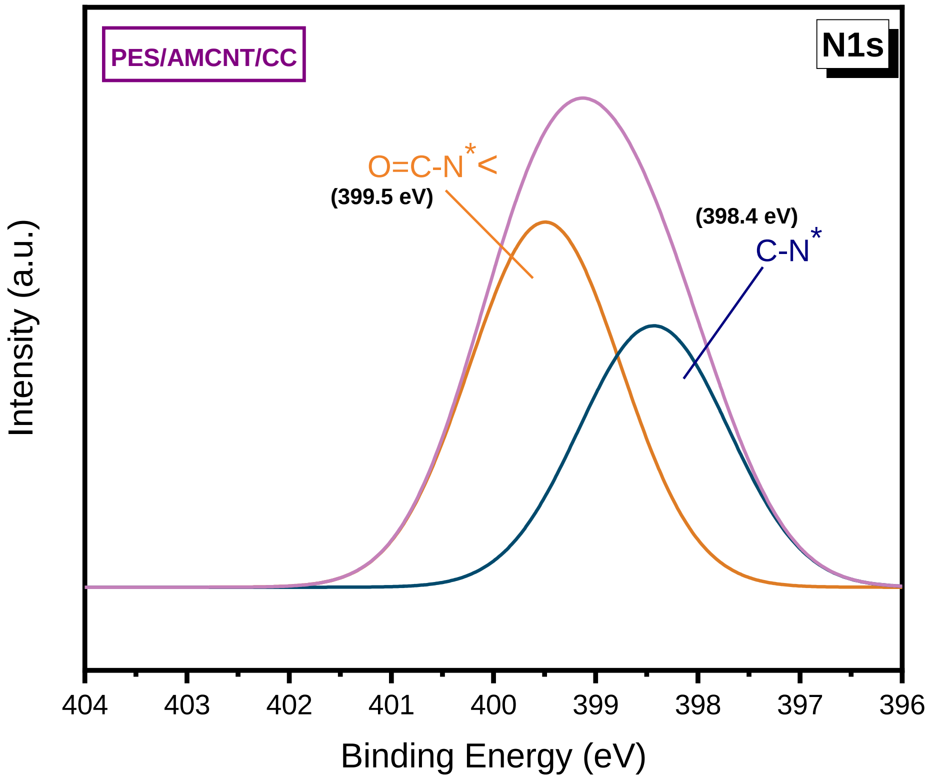


Figure 3.20. N1s XPS spectra of polyether sulphone/amine-MWCNT mixed matrix membrane modified using cyanuric chloride (CC)

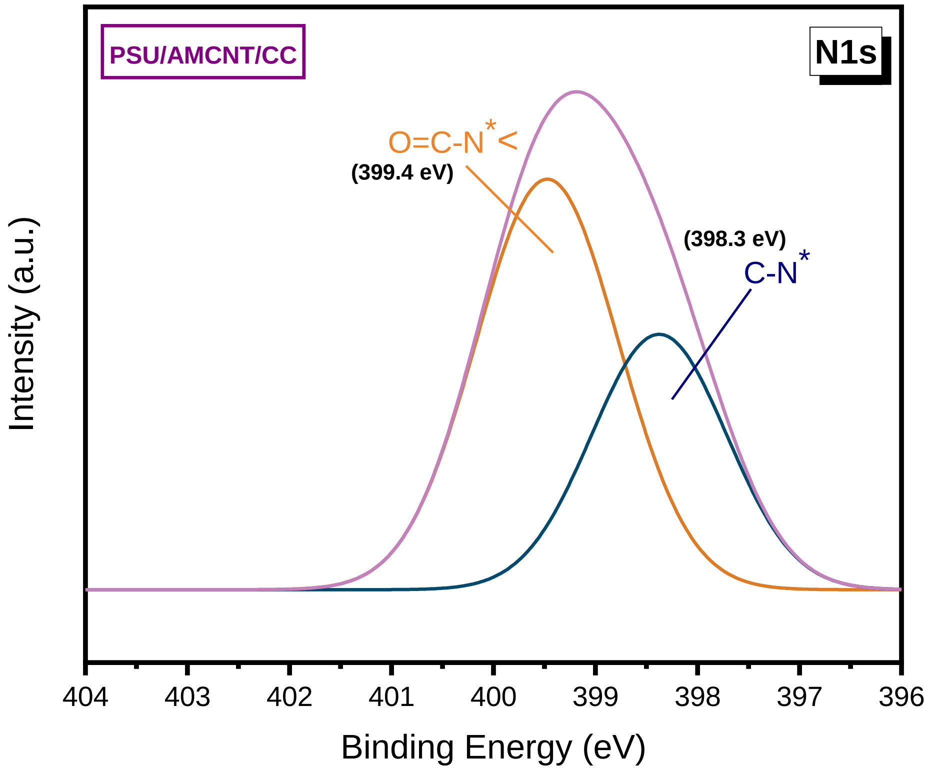


Figure 3.21. N1s XPS spectra of polysulphone/amine-MWCNT mixed matrix membrane modified using cyanuric chloride (CC)

After undergoing modification with trimesoyl chloride and cyanuric chloride, the peaks at 400.0 eV and 401.0 eV in the case of the polyether sulphone/amine-MWCNT membrane and 400.3 eV and 401.3 eV in the case of the polysulphone/amine-MWCNT membrane disappear. When examining the modified membranes, the trimesoyl chloride-treated membrane displayed a single peak at 399.7 eV (figure 3.18 and 3.19), attributed to O=C-N*, indicating the formation of an amide bond on the surface. On the contrary, the membrane treated with cyanuric chloride shows two peaks at 399.5 eV and 398.4 eV (Figure 3.20) and 399.4 eV and 398.3 eV (Figure 3.21), attributed to O=C-N* from the amide linkage and C-N* arising from the triazine ring of cyanuric chloride respectively [195]. This suggests that the membrane surface containing amine functional groups has been successfully modified using trimesoyl chloride and cyanuric chloride. The XPS spectra provide a clear understanding of the modification that occurs on the membrane surface.

3.10.3 Zeta potential

The zeta potential of PSU/Am-CNT became positively charged at low pH levels, which can be attributed to the protonation of amine groups on the membrane surface. As the pH level increased, the number of available protons decreased, causing a gradual decrease in the positive zeta potential. This pH-dependent behaviour is explained by the principles of acid-base equilibria, in which amine groups are more likely to be protonated under acidic conditions[86]. The PSU/Am-CNT membranes underwent a substantial change in their zeta potential when treated with trimesoyl chloride, as a result of the introduction of acyl functional groups to the membrane surface. These groups are prone to hydrolysis, resulting in the formation of carboxylic acid groups, which exhibited less positive zeta potentials, particularly at acidic pH values. This alteration in zeta potential can be attributed to changes in the charge distribution caused by the conversion of amine groups to carboxylic acid groups, resulting in a reduction of the membrane surface charge under acidic conditions. On the other hand, when the PSU/Am-CNT membranes were modified with cyanuric chloride, a different zeta-potential change was observed. The introduction of the cyanuric chloride resulted in the formation of a nitrogen-containing triazine ring structure on the membrane surface. This unique structure possesses protonatable sites that can interact with protons, leading to an enhanced positive surface charge at low pH. This behaviour is consistent with the principles of pH-dependent protonation, in which triazine ring protonation enhances positive zeta potential. As a result, cyanuric chloride modification imparts a higher degree of positive charge to the membrane surface than those modified with trimesoyl chloride[175,179,190,193,196].

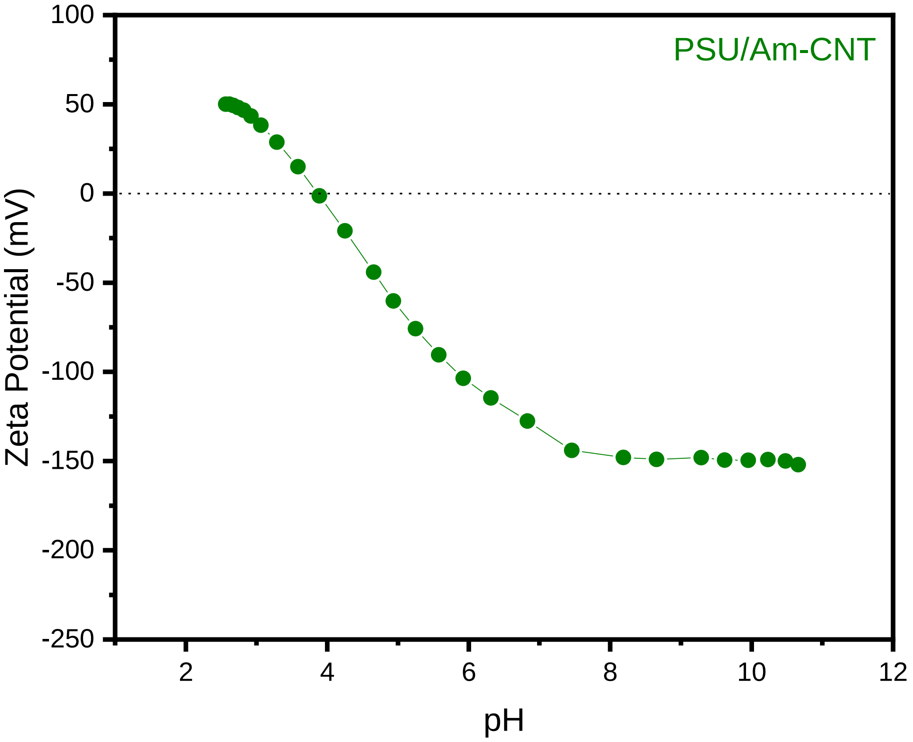


Figure 3.22. Zeta potential values of polysulphone/amine-MWCNT mixed matrix membrane

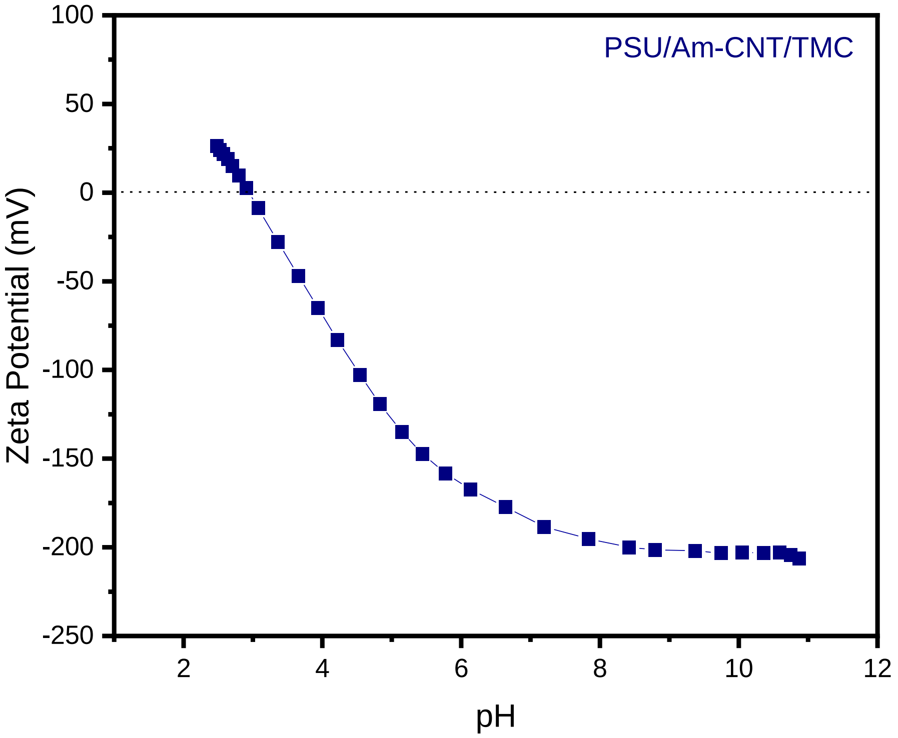


Figure 3.23. Zeta potential values of polysulphone/amine-MWCNT mixed matrix membrane modified using trimesoyl chloride (TMC)

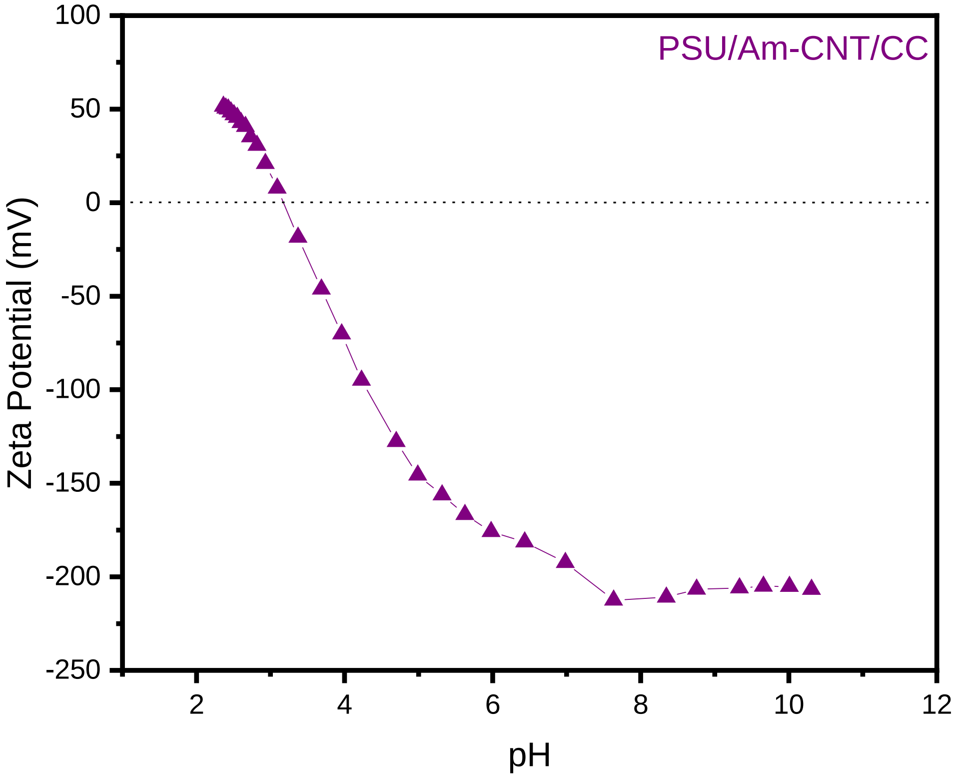


Figure 3.24. Zeta potential values of polysulphone/amine-MWCNT mixed matrix membrane modified using cyanuric chloride (CC)

3.11 Surface Characterization of unmodified and modified polysulphones/amine-MWCNTs mixed matrix membrane using polyethylenimine (PEI)

3.11.1 FTIR

The FT-IR spectra of the modified membranes revealed characteristic bands associated with the membranes. In particular, bands at 1582 cm^{-1} and 1252 cm^{-1} were observed for N-H bending and C-N stretching, respectively, as shown in Figures 3.25 and 3.26. Similarly, bands at 1584 cm^{-1} and 1233 cm^{-1} were observed in Figures 3.25 and 3.26 for N-H bending and C-N stretching, respectively. The bands at 1674 cm^{-1} in Figure 3.25 and 1680 cm^{-1} in Figure 3.26 were attributed to C=O stretching in the amide linkages, although this band was also observed in the unmodified membranes due to C=O stretching in the carboxylic groups on the membrane surface. The modified membranes showed bands at 3068 cm^{-1} and 3064 cm^{-1} after treatment with PEI, which can be assigned to N-H stretching. Additionally, new bands at 3630 cm^{-1} and 3696 cm^{-1} in Figures 3.25 and 3.26 indicated N-H amide stretching, suggesting the formation of amide linkages on the membrane surface. In contrast, the unmodified membrane showed bands at 3094 cm^{-1} and 3088 cm^{-1} due to O-H stretching, with the amine stretching band appearing weak and sharp, while the hydroxyl stretching band was strong and broad[197,198].

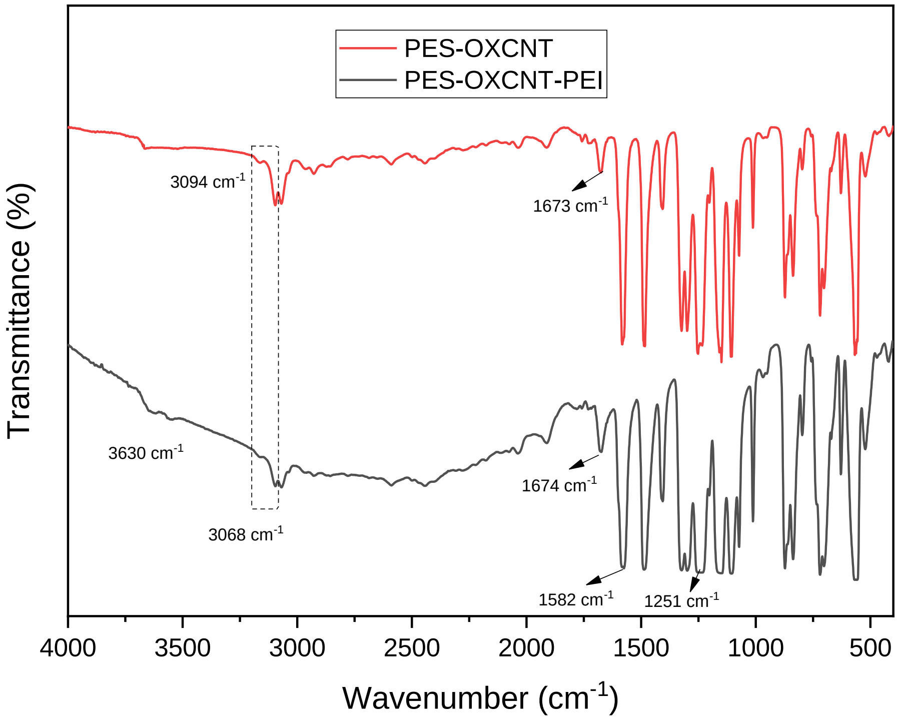


Figure 3.25. FTIR spectra of polyether sulphone/oxidized-MWCNT mixed matrix membrane, (a) unmodified, (b) modified using polyethylenimine (PEI)

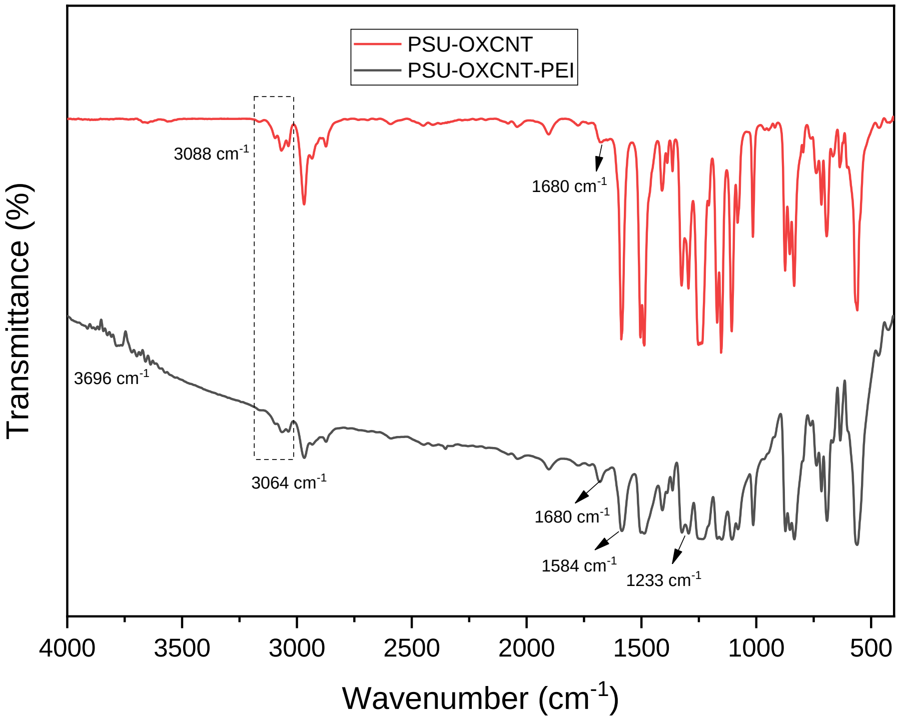


Figure 3.26. FTIR spectra of polysulphone/oxidized-MWCNT mixed matrix membrane, (a) unmodified, (b) modified using polyethylenimine (PEI)

3.11.2 XPS

In Figures 3.27 and 3.28, the XPS spectra of the unmodified polyether sulphone/oxidized-MWCNT mixed matrix membrane display two prominent peaks at 531.6 eV and 533 eV, which correspond to double-bonded oxygen in the carbonyl group and single-bonded oxygen in the hydroxyl group, respectively[199]. Similar for the polysulphone/oxidized-MWCNT mixed matrix membrane. The formation of amide linkages on the membrane surface through the reaction of carboxylic groups with amines led to the decrease in the intensity of the peak at 533 eV after treatment with PEI (Figure 3.29). A similar pattern was observed for both the unmodified polysulfone/oxidized-MWCNT and PEI-modified membranes (Figure 3.30). The decrease in the intensity of single-bonded oxygen in both mixed-matrix membranes suggests that some carboxylic groups were present on the membrane surface following modification. The N1s XPS spectra of both modified polymeric mixed-matrix membranes displayed four distinct peaks, as depicted in the figures 3.31 and 3.32. The N1s spectra of Polyether sulphone/oxidized-MWCNT modified with PEI showed four peaks at 399.6 eV for -C=N* <, 398.9 eV for -C=N*, 400.3 eV for O=C-N*H-, and 401.2 eV for $-NH_2$ (protonated). Similarly, the modified polysulphone/oxidized-MWCNT with PEI also showed four peaks at 399.7 eV for -C=N* <, 398.9 eV for -C=N*, 400.6 eV for O=C-N*H-, and 401.7 eV for $-NH_2$ (protonated), The aforementioned modifications on the membrane surface, including the creation of carboxylic functional groups through PEI, the formation of amide linkages, and the presence of amine groups, have been confirmed[161,200].

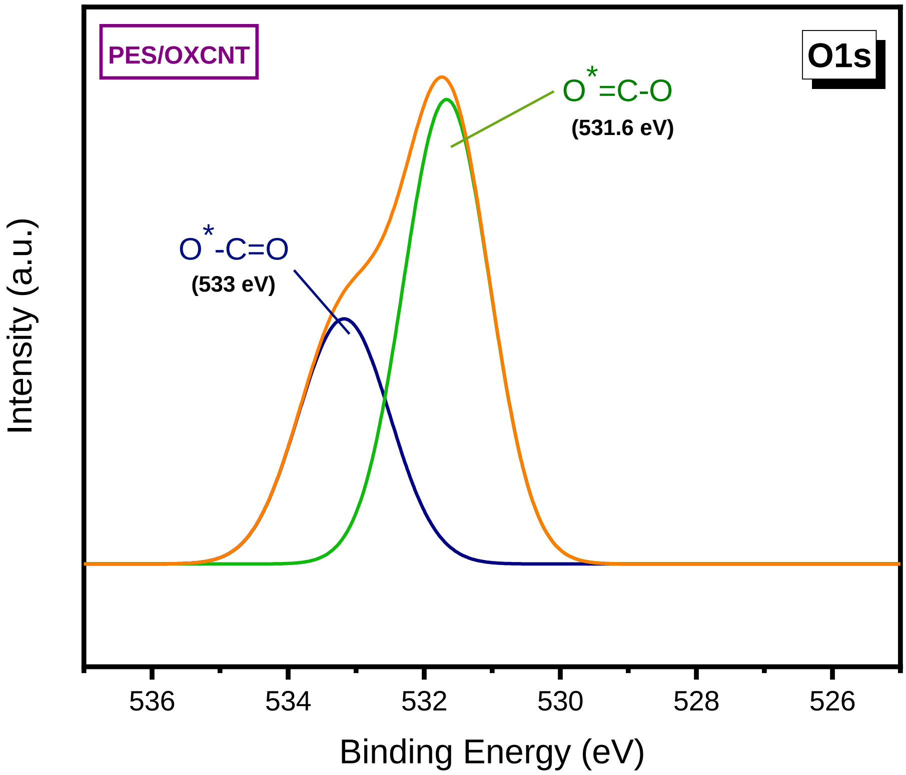


Figure 3.27. O1s XPS spectra of polyether sulphone/oxidized-MWCNT mixed matrix membrane

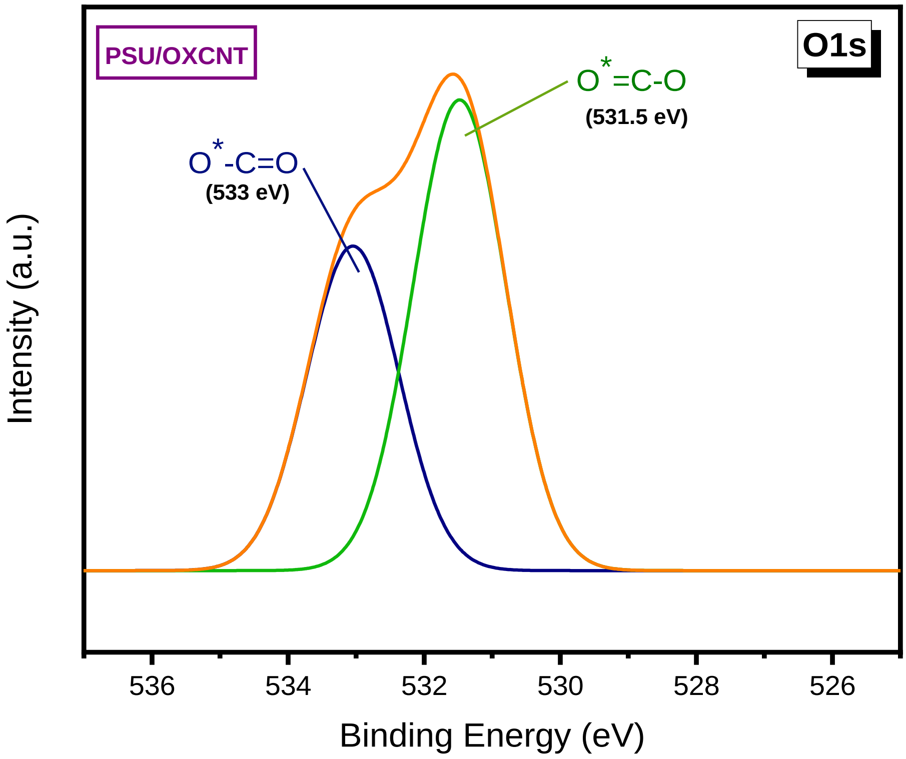


Figure 3.28. O1s XPS spectra of polysulphone/oxidized-MWCNT mixed matrix membrane

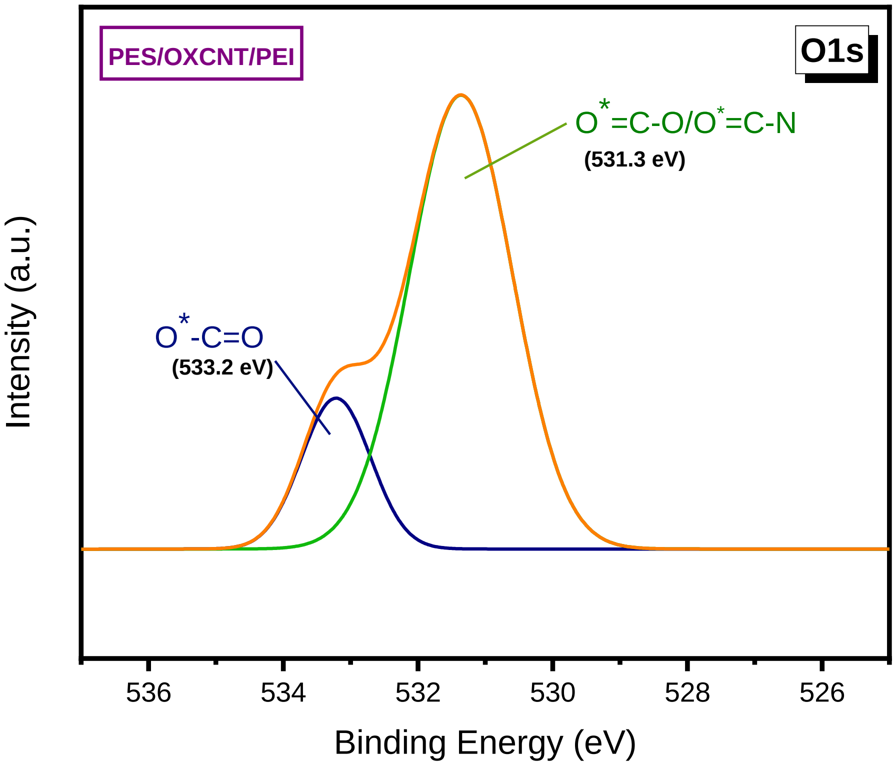


Figure 3.29. O1s XPS spectra of polyether sulphone/oxidized-MWCNT mixed matrix membrane modified using polyethylenimine (PEI)

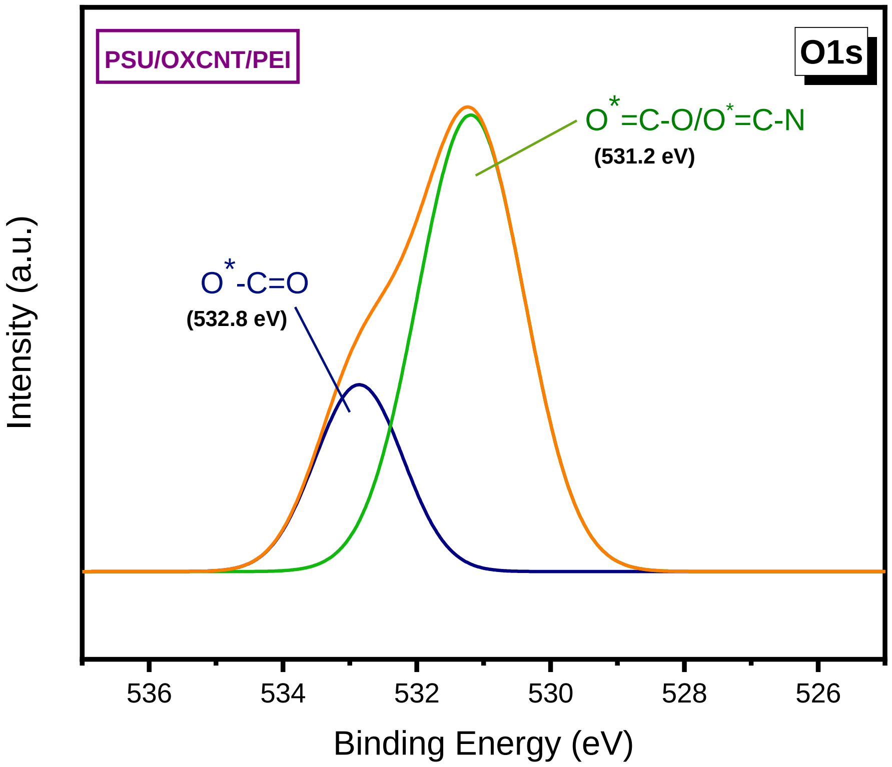


Figure 3.30. O1s XPS spectra of polysulphone/oxidized-MWCNT mixed matrix membrane modified using polyethylenimine (PEI)

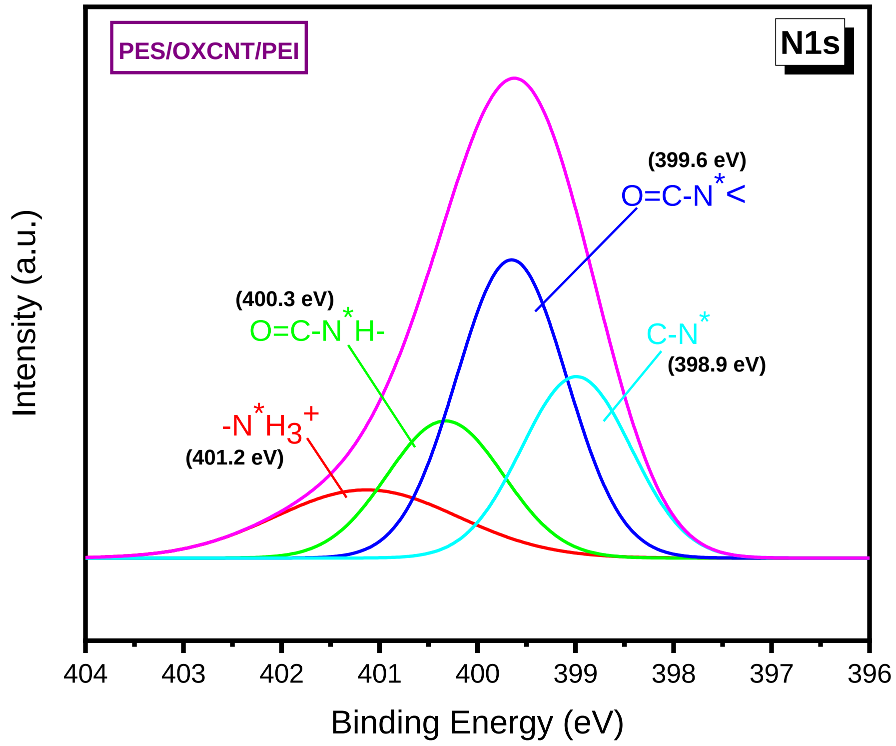


Figure 3.31. N1s XPS spectra of polyether sulphone/oxidized-MWCNT mixed matrix membrane modified using polyethylenimine (PEI)

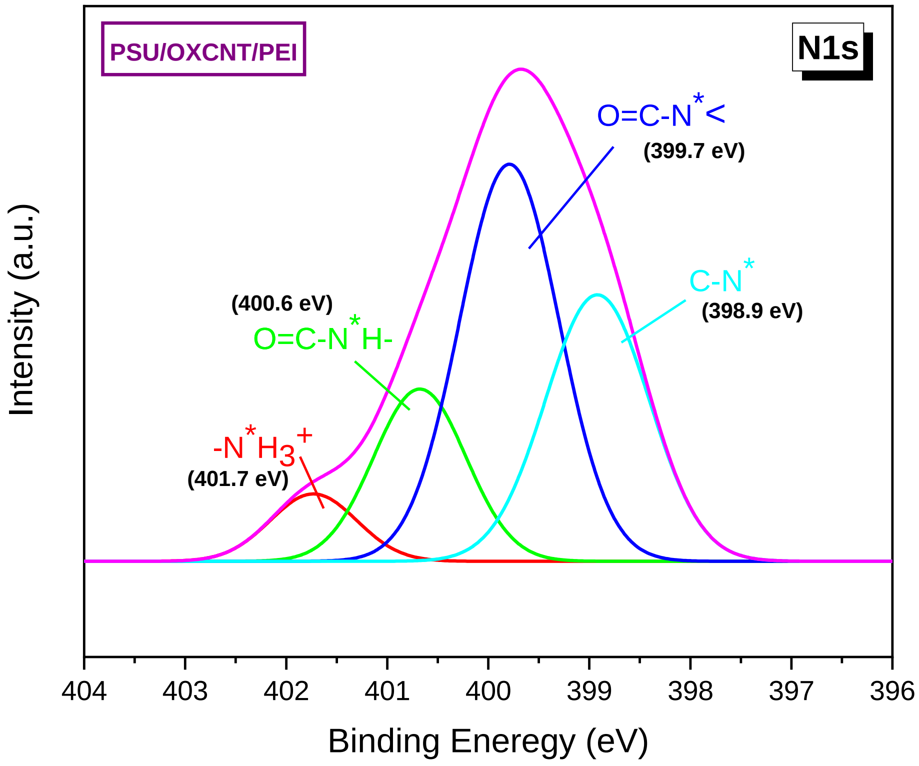


Figure 3.32. N1s XPS spectra of polysulphone/oxidized-MWCNT mixed matrix membrane modified using polyethylenimine (PEI)

3.11.3 Zeta potential

The negative zeta potential of the PSU/Ox-CNT membrane surface was attributed to the presence of carboxylic functional groups, which became more negative as the pH of the solution increased. This was because deprotonation of the carboxylic groups caused the surface to become more negatively charged under alkaline conditions[86]. However, after treatment with polyethylenimine (PEI), more amine groups are introduced onto the membrane surface, leading to a transformation from a negative to a positive zeta potential at lower pH. The positive charge developed on the membrane was caused by protonation of the amine groups under acidic conditions, which altered the electrostatic properties of the membrane. The isoelectric point (IEP) of the membrane also shifted significantly. The IEP of the untreated membrane had an IEP of 3.22; however, after PEI treatment, the IEP shifted to 6.19. This shift was due to the accumulation of positively charged amine groups, which caused IEP to occur at a higher pH level. This result confirms the successful modification of the PSU/Ox-CNT membrane surface with PEI[179,201].

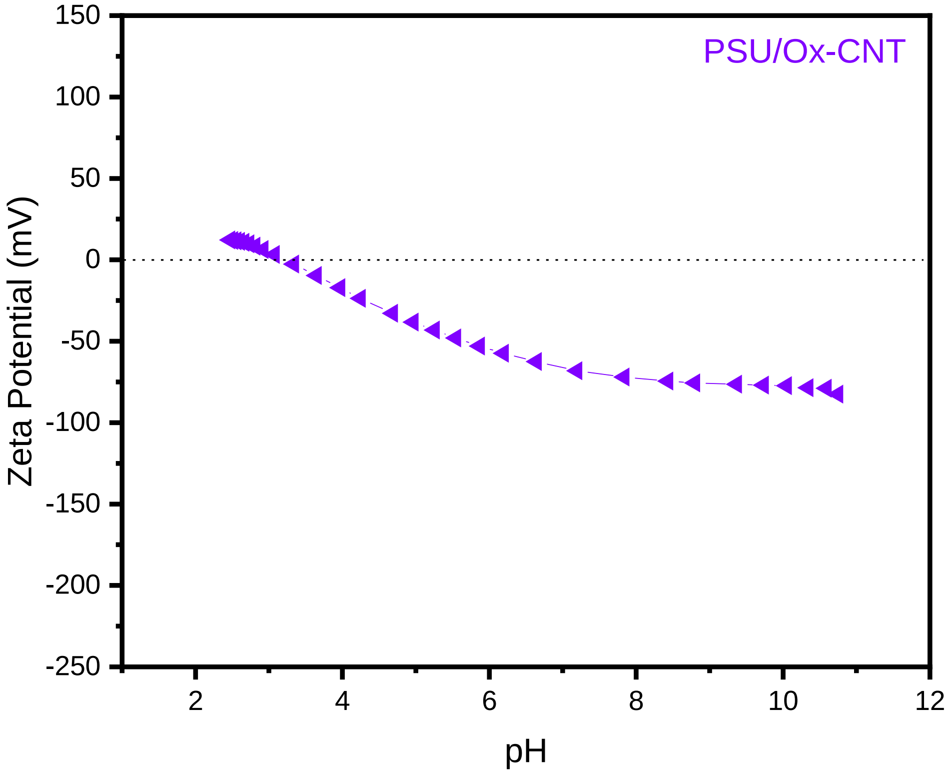


Figure 3.33. Zeta potential values of polysulphone/oxidized-MWCNT mixed matrix membrane

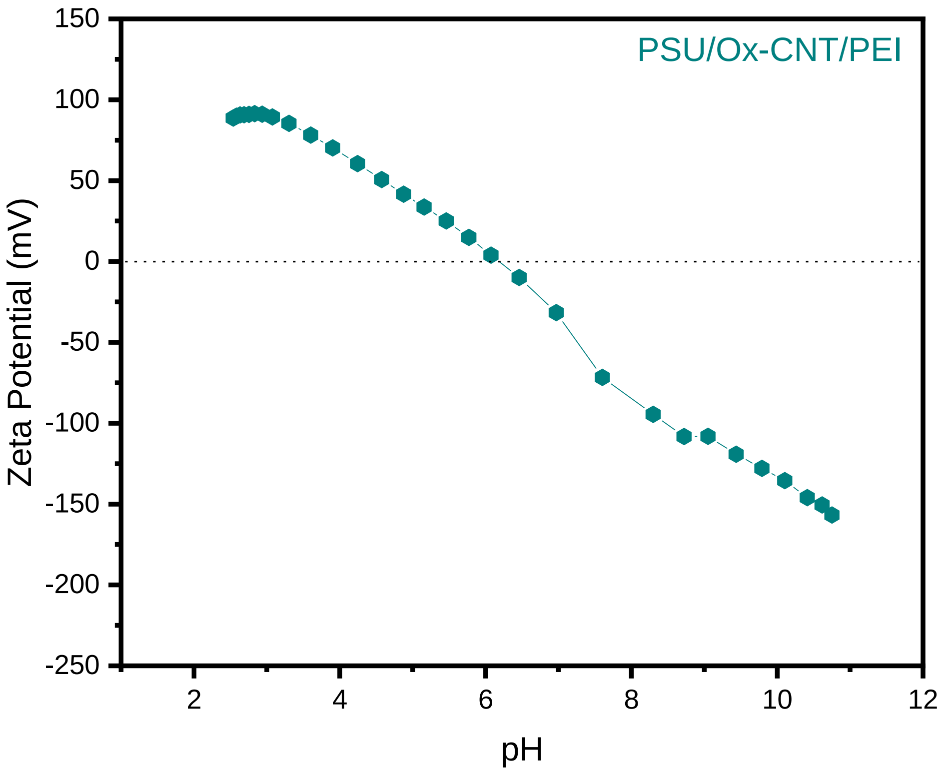


Figure 3.34. Zeta potential values of polysulphone/oxidized-MWCNT mixed matrix membrane modified using polyethylenimine (PEI)