

Article

Sustainable Modification of Polyethersulfone Membrane with Poly(Maleic Anhydride-Co-Glycerol) as Novel Copolymer

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Abstract: This work presented an endeavour to fabricate sustainable and eco-friendly polyether-sulfone (PES) ultrafiltration membranes. A novel and graft copolymer (Poly(Maleic Anhydride-Co-Glycerol)) (PMG) have been synthesized via a facile and rapid route to impart their hydrophilic features onto the final PES membrane. A series of characterization tools, for both nanoadditives and nanocomposite membranes, have been harnessed to confirm their successful fabrication processes. These include Fourier Transform Infrared Spectroscopy (FT-IR), scanning electron microscopy (SEM), Atomic Force Microscopy (AFM), and contact angle measurements (CA). Results disclosed the successful synthesis of PMG nanoparticles that manifested a smooth homogenous surface with an average molecular size of 88.07 nm. The nanocomposite membrane structure has witnessed a gradual development upon each increment in the nanoparticle content ratio along with relatively thicker pore walls. The size and shape of figure-like micropores exhibited critical visible structural changes following the nanoadditive incorporation into the PES polymeric matrix. For the nanocomposite membrane, the SEM imaging indicated that a thicker active layer and less finger-like micropores were formed at higher PMG NP content within the membrane matrix. Hydrophilicity measurements disclosed a reversible correlation with the NP content where the CA angle value was at a minimum at the higher PMG loading content. Compared to the pristine membrane, a considerable enhancement in the performance of the modified membranes was witnessed. The membrane prepared using 2.5 g PMGNPs showcased six times higher pure water flux than neat PES membrane and maintained the highest retention (98%) against BSA protein solution. Additionally, the nanocomposite revealed promising antifouling and self-cleaning characteristics.

Keywords: polyethersulfone; membrane modification; fouling; bovine serum albumin; Poly(Maleic Anhydride-Co-Glycerol)



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1. Introduction

Parallel to the steady growth in urbanization, global population, and industrial activities, the dramatic depletion in freshwater resources has received much concern within the scientific community in the past few decades. This interest is expected to continue for the near and far future at various levels. Although water covers about three-quarters of our planet's total area, access to freshwater resources does not exceed 1%, and the majority of these water resources are salty, frozen, or cannot be utilized without proper treatment [1]. In this context, there is a continuous need for efficient, inexpensive, and sustainable techniques to meet the massive global demand for freshwater [2,3]. Among

the wide range of available physical and chemical treatment techniques, membrane technology has established its status as a prominent separation tool for treating versatile water resources, which has multilateral advantages over conventional separation technologies. Thus, exceptional efforts have been devoted aiming to optimize and engineer novel membranes to overcome the increasingly relevant challenges and opportunities for water treatment and desalination.

Since the first synthetic membrane had been incepted sixty years ago, tremendous attempts were made to end up with desired membrane characteristics in terms of selectivity and permeability. Phase separation, electrospinning, and interfacial polymerization are the most common synthetic polymeric membrane fabrication techniques. Although inorganic materials such as ceramic have been proven to be spectacular membrane materials, regardless of their high fabrication expenses and complexity [4], organic polymers and composites were the preferable and leading fabrication materials researched in the literature. This was ascribed to their cheapness and ease of formation with desired porous structures and selectivity [5]. In this context, with its simplicity and versatility, phase inversion as a direct method has been extensively implemented for membrane fabrication with a wide range of pore size structures, from microfiltration (MF) to reverse osmoses (RO). Although a massive amount of research has been devoted to membrane fabrication in the past few decades, we are still far away from producing a membrane with a stable performance over a long-term operation. Commonly, all synthetic membranes suffer a drop in their water flux due to the so-called membrane fouling. Fouling is considered the predominant issue in the membrane industry that diminishes their performance and should be tackled urgently. Fouling could not only hinder the filtrate quantity but also impact the quality of the product [6]. When this scenario occurs, massive consumable chemicals should be employed to restore the membrane's performance. However, although cleaning chemicals are a necessity here, they could damage the surface structure of the membrane over time, change its selectivity and ultimately constrict the membrane's lifespan [7].

A membrane surface or internal structure modification approach has been suggested to overcome membrane fouling consequences. Simply, membrane modification could be defined as revising a membrane's surface to enhance its active surface layer hydrophilicity. This is believed to diminish the fouling induced by feed components due to the enhanced interactions between the modified hydrophilic surface and the hydrophobic nature of foulants [8]. The incorporation of additives carrying hydrophilic functional groups within the polymeric matrix of the membrane is a common approach to impart this desired hydrophilic nature and reduce the adsorption at the surface and internal pores [9–12]. Compared to the standard pristine membrane, these novel nanocomposite membranes are expected to bestow an enhanced performance in terms of selectivity, permeability, hydrophilicity, hydrophobicity, mechanical, thermal, and chemical resistance characteristics. High-hydrophobic carbon nanomaterials (CNMs) prepared by Aljumali et al., [13] using the chemical vapor deposition technique on nickel-doped powder activated carbon, were implanted with a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) membrane to enhance its performance for desalination application. Results revealed that CNMs have excellent potential for seawater desalination. A novel NaY zeolite modified PES membrane for caesium (^{137}Cs) removal from actual nuclear liquid waste was achieved by Abbas et al. [14]. Results revealed that the best removal efficiency of caesium (99.2%) was obtained by the PES-NaY zeolite membrane prepared using 0.15% NaY. Jiang et al. [15] conducted a study to investigate the influence of bioinspired PDA nanoparticles on the permeability and antifouling characteristics of PVDF membranes. The study showcased greater water flux and antifouling characteristics as indicated by protein separation experiments. This was achieved with long-term consistency for the nanocomposite membrane in the aqueous environment [15].

The importance of a polymeric and ceramic ultrafiltration (UF) membrane lies in its wide use in broad applications such as treating different types of industrial, oil, and nuclear wastes as well as using them in saline water desalination [16–23]. Accordingly, the researchers focused in their study on how to improve the physical properties of this type of membrane. They use different methods to modify the membrane for the purpose of improving its performance and overcoming the phenomenon of fouling, which is one of the main disadvantages in membrane technology. Therefore, the target of this study is to focus on the modification of the membrane by using a new type of nano copolymer as an additive.

For membrane modification purposes, this work is conducted to overcome the conventional nanomaterial challenges through the fabrication of a novel graft copolymer nanomaterial. Herein, novel Poly(Maleic Anhydride-Co-Glycerol) nanoparticles (PMG) with hydrophilic characteristics have been synthesized and employed for nanocomposite membrane fabrication. Following that, these nanoparticles were impregnated within PES membranes at different ratios to optimize the amount of additives to achieve optimum permeation and selectivity performance. In addition, the ability of modified membranes to resist fouling was evaluated by detecting the total, reversible, and irreversible fouling.

2. Experimental Work

2.1. Materials

Medium viscosity Polyethersulfone Ultrason[®] E6020P polymer was donated by Solvay Specialty Polymers, Oudenaarde, Belgium and employed as host membrane material. Dimethyl sulfoxide (DMSO) (85, wt.%) is a highly organic polar aprotic solvent for polymer dissociation. Bovine serum albumin (BSA) was used as a protein foulant model. Maleic anhydride, glycerol, and p-Xylene for PMG nanoparticle preparation were all purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were analytical grades and used without further purification.

2.2. Fabrication of Poly(Maleic Anhydride-Co-Glycerol) Nanoparticle

For PMG nanoparticle preparation, 2.0 moles (196 g) of maleic anhydride and 30 mL of DMSO were magnetically stirred in a 200 mL double-neck round bottom flask. While mixing, the mixture was warmed carefully to 35 °C using a hot plate until clear liquor was achieved. The temperature was automatically controlled with an automatic thermometer equipped to the hot plate. Following that, 1.0 mole (92 g) of glycerol was added to the solution. The solution temperature was raised to 80 °C and then 20 mL of p-Xylene was added to the reaction flask in the form of batches (two drops in each batch). The main reason for adding p-Xylene to the solution was to remove water formed as a by-product of the esterification reaction process during the preparation of the nano copolymer. To withdraw the water formed by the esterification process, the flask was heated for 48 min at 110 °C. Finally, the reaction flask was left to cool down at room temperature and DI was added to the suspension. The suspension was then left to precipitate, filtered, washed with DI water, and left to dry. The procedure is illustrated in Figure 1 below.

2.3. Fabrication of Membranes

All control and PMG-modified UF membranes were prepared via the common non-induced phase separation method. Before casting solution preparation, the PES polymer was dried overnight in an oven to remove the moisture content. For neat PES membrane preparation, PES was gradually added to the DMSO and magnetically stirred at 40 °C overnight to ensure a full dissociation of the polymer. When a homogeneously clear yellowish solution was achieved, the casting solution was left for another night for degassing. Before casting, the glass plate of the casting machine was wiped properly with ethanol to obtain a dust-free surface. The presence of any dust could induce some defects and deteriorate the overall membrane performance. To cast the solution, about 50 g was poured gently on the glass substrate and cast via an automatic film applicator. The glass plate was

then placed in a tap water bath for precipitation. After about one minute, the membrane was detached referring to phase inversion completion. The membrane was rinsed under tap water to eliminate any solvent residuals and placed in DI water for another 48 h. Finally, the membrane was transferred into a 30 wt.% glycerol solution for 48 h to stop the membrane structure from collapsing and cracking. It should be noted here that all membranes were cast with a clearance gap of 200 microns. Additionally, membranes were inspected under light and only good membranes were stored for further characterization.

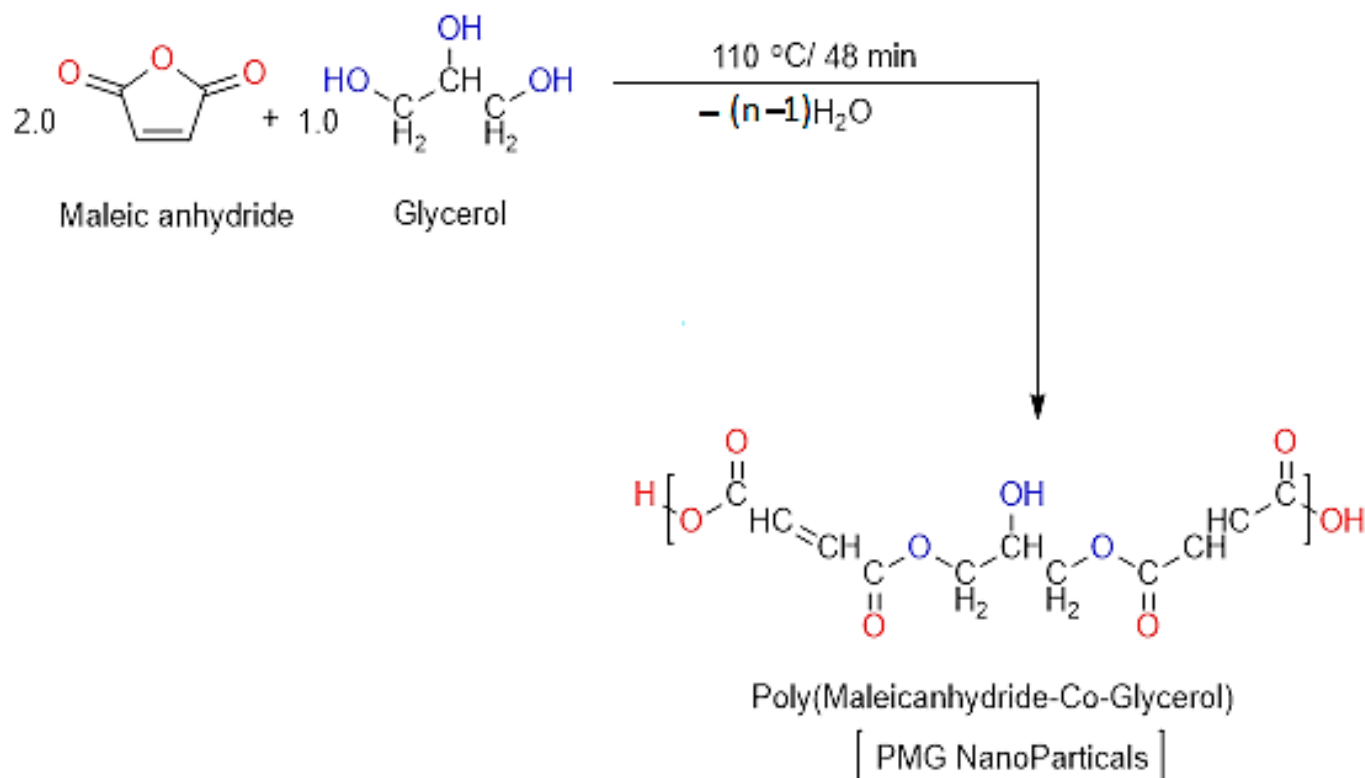


Figure 1. Reaction of synthesized PMG nano copolymer.

For PMG-modified membrane preparation, there was only one additional step. The required amount of PMG nanoparticles was initially added to the DMSO and stirred vigorously for 3 hr before adding the polymer. The composition of all UF membranes is illustrated in Table 1. It is worth mentioning that the addition of more than 2.5 g of Green PMG in the casting solution resulted in a non-homogenous solution.

Table 1. Composition of PMG/PES UF membranes.

Membrane No.	PES (wt.%)	DMSO (wt.%)	PMG (g)
1	15	85	0
2	15	85	0.25
3	15	85	0.50
4	15	85	0.75
5	15	85	1
6	15	85	1.25
7	15	85	1.50
8	15	85	1.75
9	15	85	2
10	15	85	2.25
11	15	85	2.50

2.4. Characterization of the Membranes

The PMG nanoparticle surface and membrane surface topography were inspected using AFM (TT-2 AFM) with a tapping mode in the air with an appropriate silicon tip while the data were analysed with specific software. In addition, the AFM was employed to determine the total rate of the particle sizes of PMG nanoparticles as well as the different proportions of these volumes. AFM was also employed for the characterization of the surface topography 3D image, roughness, and mean pore size of the prepared membranes.

The surface and cross-section morphology of the membranes were visualized via SEM (TESCAN VEGA3). Before cross-section imaging, samples were frozen in liquid nitrogen for a few minutes and directly fractured to avoid damaging the membrane's structure. All the samples were then coated with a thin layer of 5 nm gold using a sputtering machine to make them conductive. Finally, the surface and cross-section samples were placed on an appropriate stainless-steel sample holder ready for imaging.

A UV spectrophotometer (8453 UV-Visible Spectrophotometer, Agilent Technologies) connected to PC software was utilized to detect the BSA concentrations. BSA concentrations in feed and permeate were recorded at a fixed wavelength, and the relationship between the absorbance value and BSA concentration was calculated through a prepared calibration curve.

Wettability measurements of membranes were evaluated via an optical contact angle (CAM200, KSV instrument) using the sessile drop method [24]. The instrument was connected to PC software. A syringe was used to place a 3 μ L deionized water drop on the flat membrane sample. The contact angle between the drop and the flat base was measured via the instrument software. In general, a lower contact angle indicates a greater hydrophilicity value and vice versa.

To confirm the successful synthesis of PMG nanoparticles and their chemical bonding with the PES membrane, an FTIR spectrometer (TENSOR27 IR, Bruker, Billerica, USA) was implemented for this purpose. The measurements were conducted by recording a background spectrum as a reference measurement. Then, the sample was placed on the machine plate and the final spectrum was recorded [25]. The measurements were conducted with transmittance spectra from 400 cm^{-1} to 4000 cm^{-1} .

The permeation/selectivity performance of the control and modified UF membranes was tested in a custom made cross-flow laboratory system. The rig comprises a pump, flowmeter, two pressure gauges, and membrane cell. The cell was constructed from PTFE with an effective internal area of 0.003249 m^2 and has a dimension of 2 cm thickness, 5.7 cm length, and 5.7 cm width. The schematic flow diagram of the filtration rig was illustrated elsewhere [26,27]. Initially, the membranes were compacted using DI water at 2 bars for 30 min, and the pressure was then lowered to an operating pressure of 1 bar. The water flux was then measured according to Equation (1).

$$Jw = \frac{V}{A \cdot t} \quad (1)$$

where Jw is water flux ($\text{L}/\text{m}^2 \cdot \text{h}$), V is permeated water volume (L), t is the measurement period (hr), and A is the effective membrane area (m^2).

The total fouling (FT), reversible fouling (Fr), and irreversible fouling (F_{ir}) have been calculated as shown in the equations below;

$$F_T = F_{\text{rev}} + F_{\text{irrev}} \quad (2)$$

$$F_T (\%) = (J_2/J_0) \times 100 \quad (3)$$

$$F_{\text{rev}} (\%) = ((J_2 - J_1)/J_0) \times 100 \quad (4)$$

$$F_{\text{irrev}} (\%) = ((J_0 - J_2)/J_0) \times 100 \quad (5)$$

where J_0 , J_1 , and J_2 represented the initial water flux of clean membrane, the solute flux of BSA, and water flux of fouled membrane after rinsing, respectively. All measurements are presented as replicates and an average value was considered.

BSA solution retention of the membranes was calculated based on the following equation:

$$R (\%) = (C_p / C_f) \times 100 \quad (6)$$

where $R (\%)$ is the rejection percentage of membranes, C_p is solute concentration in the permeate side, and C_f is solute concentration in the feed side.

3. Results and Discussion

3.1. Characterization of PMG Nanoparticles

FT-IR is a powerful machine utilized to obtain data about various functional groups attached to the sample's surface. The graft copolymer nanoparticle FTIR spectrum is illustrated in Figure 2 below. The characteristic strong broad band appeared at 3338 cm^{-1} and was assigned to the stretching of carboxylic acid ($-\text{OH}$) with stretching (H bond). Additionally, the weak bands observed at about 2953 cm^{-1} and 2887 cm^{-1} were ascribed to the $=\text{C}-\text{H}$ for carboxylic acid and $\text{C}-\text{H}$ aliphatic, respectively. Additionally, the spectrum has manifested a strong band at 1718 cm^{-1} , which is attributed to the stretching band $\text{C}=\text{O}$ of the ester group. The band noticed at about 1014 cm^{-1} was mainly associated with the absorption band of $\text{C}-\text{O}$ [28].

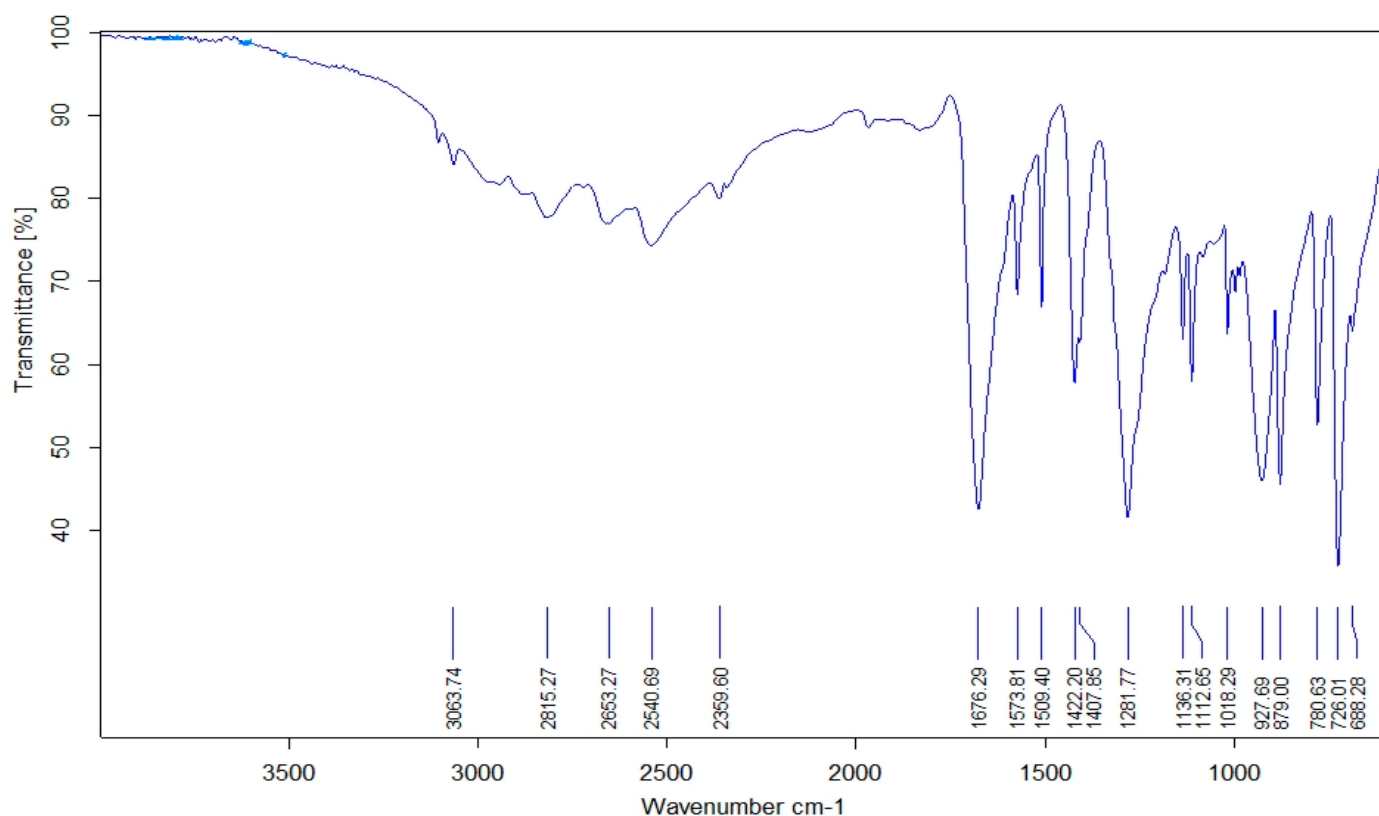


Figure 2. The FT-IR spectrum of PMG nanoparticles.

The ^1H NMR spectrum was obtained to identify the structure of the PMG sample, as illustrated in Figure 3. The singlet signal, at 13.24 ppm, referred to the characteristic of the proton in the carboxylic acid group, while the signal multiples in the region of 7.53–8.10 ppm was ascribed to all protons in the aromatic ring. Additionally, the signals of the four protons of methylene in the polymer structure were located at the 6.27–6.46 ppm region, whereas the multiples at 4.24–4.50 ppm belong to methyl

protons. The triplet signal around 3.44–3.62 ppm was attributed to the aliphatic alcohol proton [29].

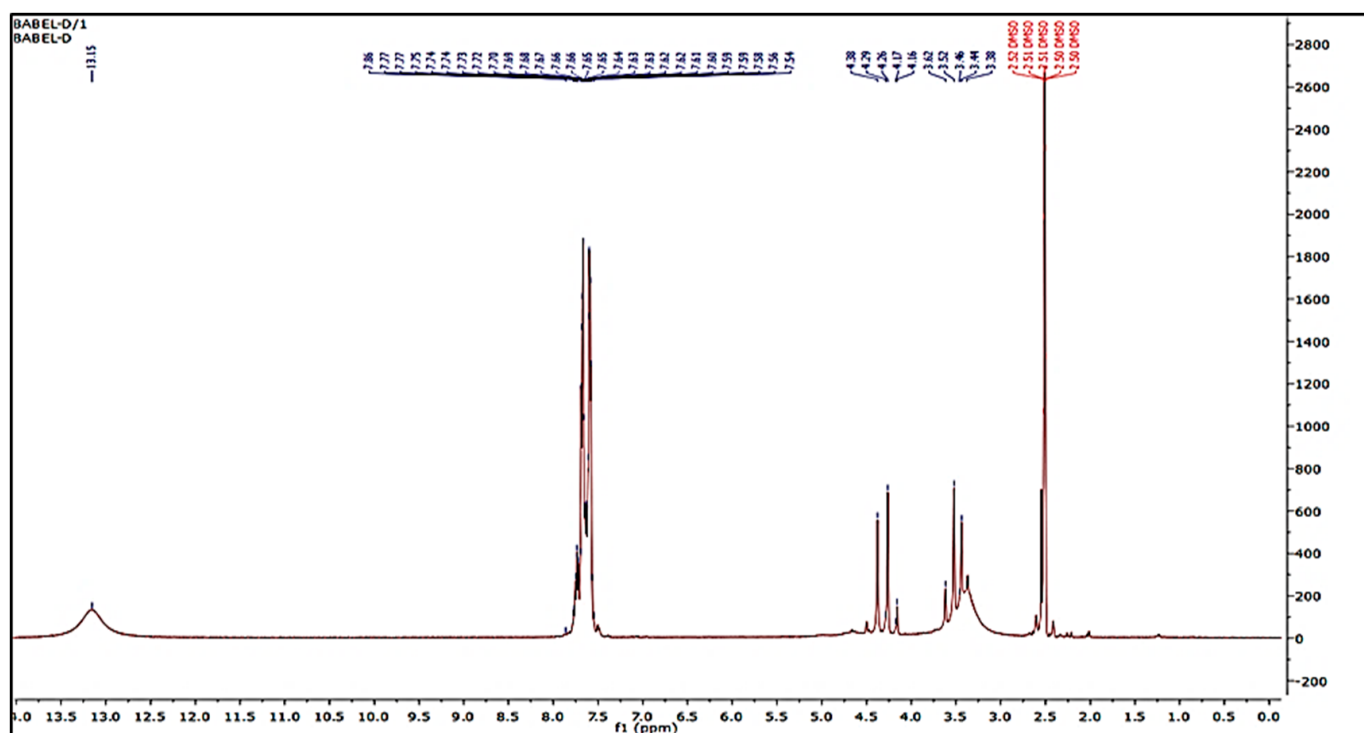


Figure 3. The ^1H NMR spectrum of PMG nanoparticles (f1(ppm): concentration of proton in each peak).

AFM is a well-recognized tool for identifying the surface topography parameters of materials [30–32]. The major surface characteristics of a material surface include determining the average roughness (R_a), root mean surface roughness (R_{ms}), and the average mean height (AV_{mean}). An area of about $1800\text{ nm} \times 1800\text{ nm}$ was scanned via an appropriate tip, and 2D and 3D images were depicted for the sample, as shown in Figure 4A,B. The R_a of the prepared graft copolymer outer surface was determined to be 8.76 nm , while the R_{ms} was about 10.1 nm . This implies that the PMG nanoparticles manifested a smooth homogenous surface. Additionally, the AV_{mean} height has showcased a value of 34.96 nm . The surface of the nano copolymer is homogeneous and smooth, as clearly shown in Figure 4A, where it can be seen that the backbone of the nano copolymer is homogeneous and smooth and the hydroxyl groups hanging from the backbone, which is indicated in white colour. Normally, the value of the homogeneity of the nano copolymer is greater than the value of the backbone of the nano copolymer itself, as clearly shown in Figure 4A [29].

The average mean size of the PMG nanoparticles and their distribution was determined with the AFM as well. Results disclosed that the average molecular size of the PMG nanoparticles was about 88.07 nm with a range of distribution between 55–135 nm (Figure 4C). More information about the accumulative volumes of these nanoparticles is illustrated in Table 2. As can be seen, the smallest nanoparticles were about 55 nm which represented almost 6.25% of the total volume. In the meantime, PMG NPs with 85 nm showcased the highest volume ratio (9.34%). Thereafter, the volume ratios exhibited a gradual decrease to reach 3.1% at 135 nm [33].

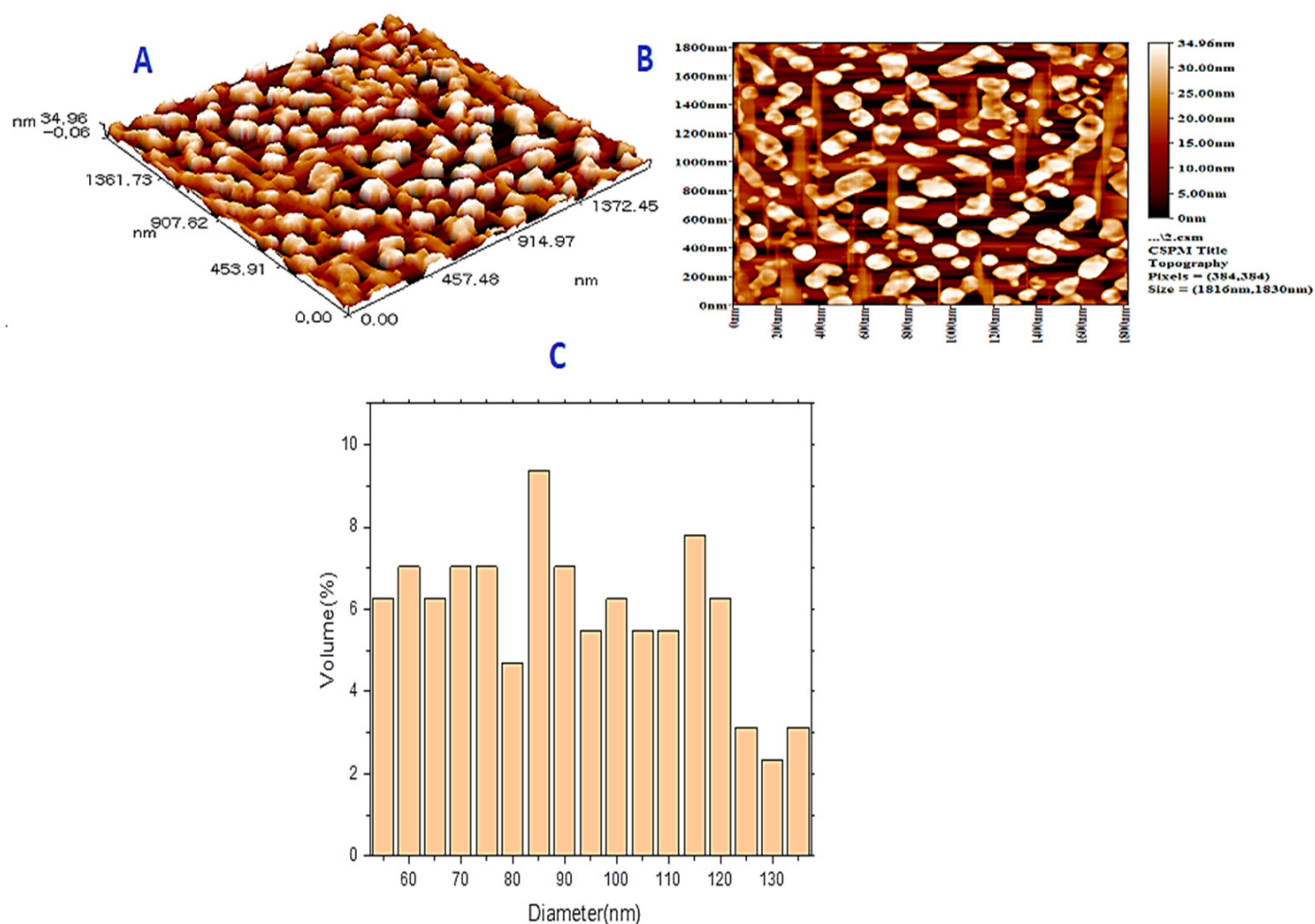


Figure 4. Images of Atomic Force Microscope for the PMG nanoparticles: (A) 3D and (B) 2D images. (C) Granularity cumulative distribution of the PMG NPs.

Table 2. The total rate of the PMG nanoparticles and the disparate proportions of these volumes.

Diameter (nm)	Volume (%)	Cumulation (%)	Diameter (nm)	Volume (%)	Cumulation (%)	Diameter (nm)	Volume (%)	Cumulation (%)
55.00	6.25	6.25	85.00	9.38	47.66	115.00	7.81	85.16
60.00	7.03	13.28	90.00	7.03	54.69	120.00	6.25	91.41
65.00	6.25	19.53	95.00	5.47	60.16	125.00	3.13	94.53
70.00	7.03	26.56	100.00	6.25	66.41	130.00	2.34	96.88
75.00	7.03	33.59	105.00	5.47	71.88	135.00	3.13	100.00
80.00	4.69	38.28	110.00	5.47	77.34			

3.2. Surface Characterization of Membranes

FESEM has been utilized to visualize the impact of PMG content on the surface and cross-sectional morphologies of the PES membrane. As observed in Figure 5 (Left), the neat PES membrane manifested a smooth homogenous surface, which is the intrinsic characteristic of all sulfone-derivative membranes. Apart from that, little aggregates accumulated throughout all the PMG-modified membrane surfaces, especially those prepared via utilizing a high nanoadditive content (Figure 5, Right). This implies that PMG NPs have migrated uniformly to the body of the membrane during the phase inversion process. Undoubtedly, this could bestow exceptional features to the modified nanocomposite membranes depending on the nanoadditive content impregnated. On the other hand, the influence of PMG NPs on the cross-sectional structure of the mem-

branes is depicted in Figure 6. All membrane samples have revealed a distinguished asymmetric structure that encompasses a skin layer propped by a porous structure. A clear thin active layer supported by a tiny figure-like structure was observed for the pristine PES membrane at the upper half cross-section of the membrane (Figure 6A). Noticeably, this structure became wider and manifested a lower number of finger-like pores at the lower half cross-section. Following the PMG NPs impregnation, the nanocomposite membrane structure has witnessed a gradual development upon each increment in the nanoparticle content ratio, along with relatively thicker pore walls. Noticeably, the size and shape of the figure-like micropores exhibited critical visible structural changes following the nanoadditives' incorporation into the PES polymeric matrix. Images revealed a wider and smaller number of finger-like pores at the lower half cross-section. Additionally, a denser active layer was formed, and the wide finger-like pores were extended from the top to the bottom of the nanocomposite membranes (Figure 6B–E). A further amount of nanoadditives within the polymeric matrices have induced additional alterations in the structure of the nanocomposite membranes. The active layer thickness has noticeably increased where a thick dense structure was formed, especially at the greater amount (2.5 g) of nano PMG incorporated into the membrane. In this nanocomposite membrane, the top layer thickness reached around one-third of the entire cross-section. In addition, the figure-like micropores' lengths and their density have considerably declined (Figure 6F–L). Unsurprisingly, these observations were expected since a higher loading content of the copolymer have raised the dope solution viscosity, and ultimately, denser membranes structures could be produced. This is due to the lower mixing-demixing inducing nonsolvent and solvent at the moment of the phase inversion process. These results agreed with preceding investigations reported in the literature [34–36].

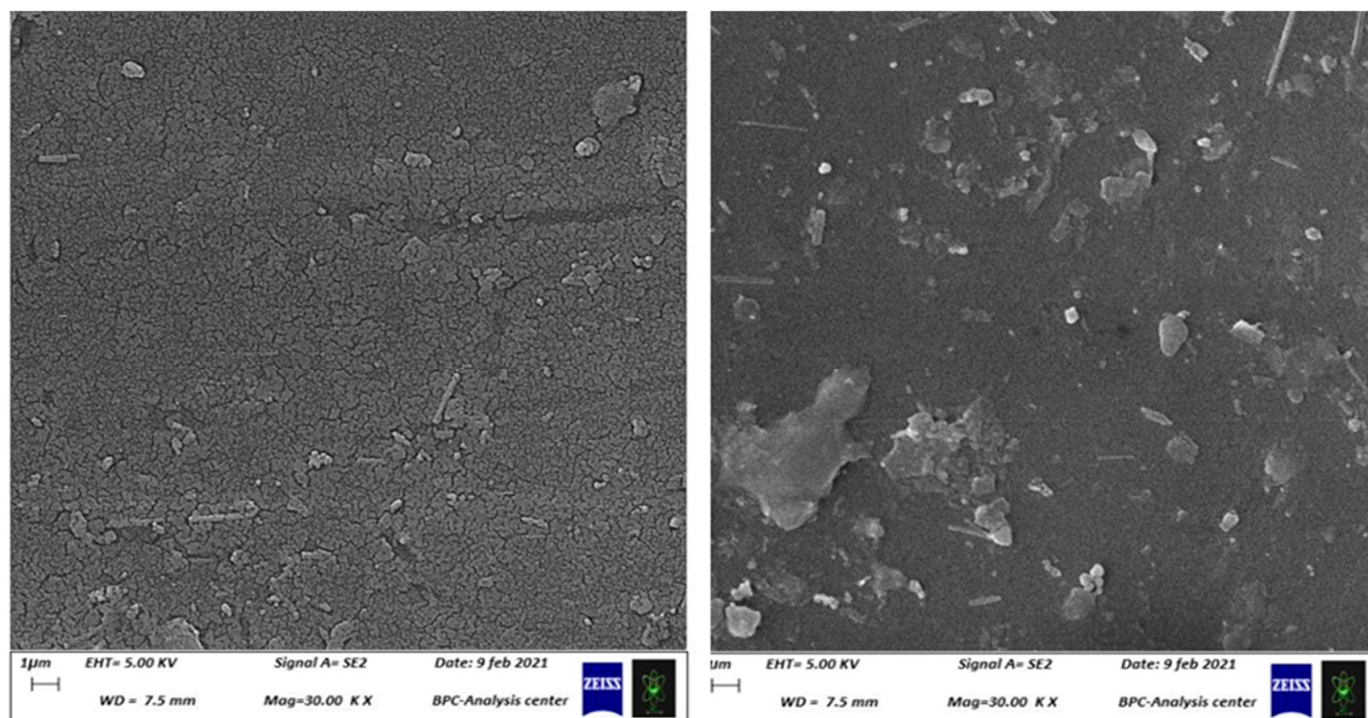


Figure 5. SEM surface images for (Left) pristine and (Right) 2.5 g PMG-modified membranes.

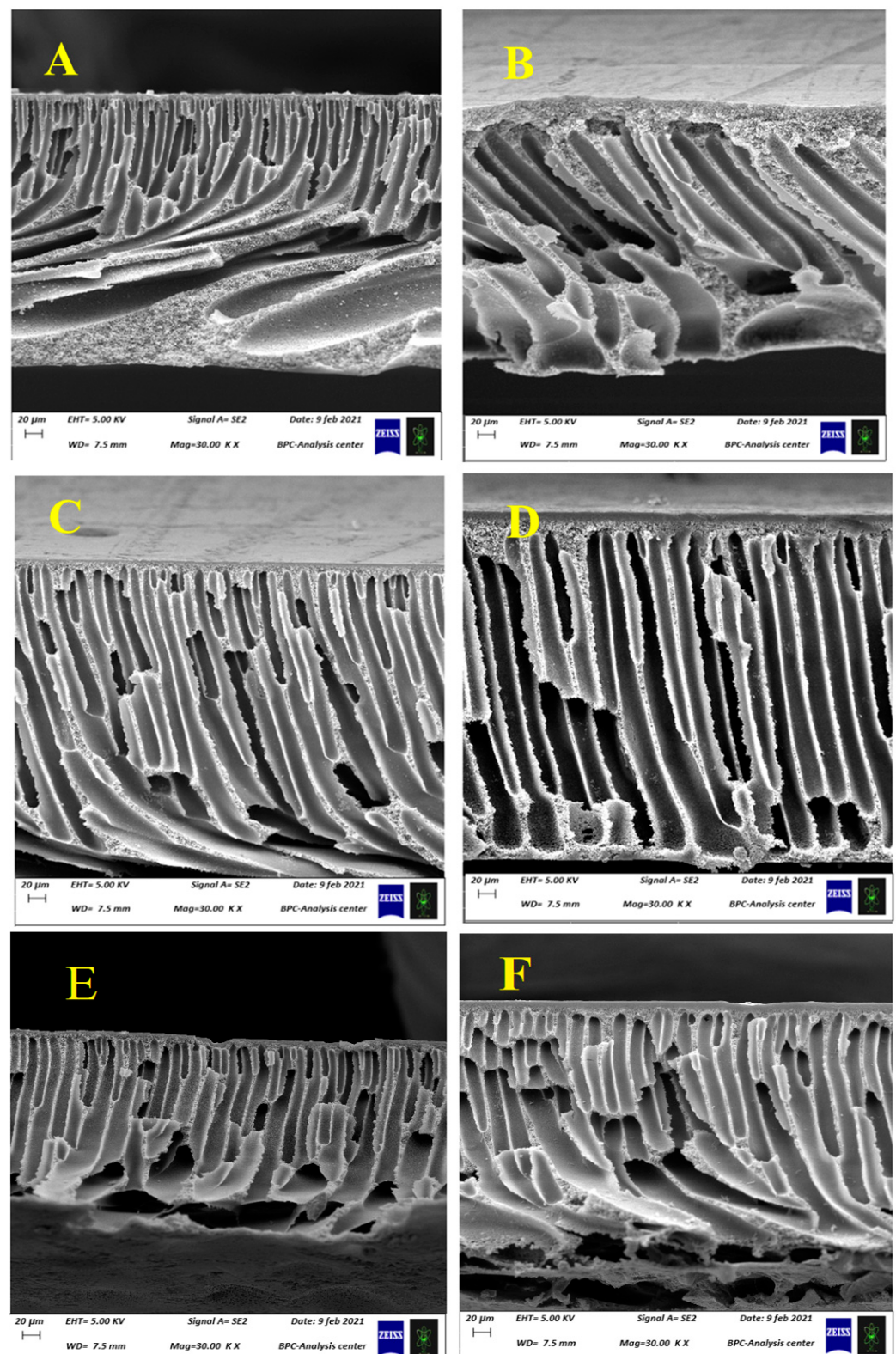


Figure 6. Cont.

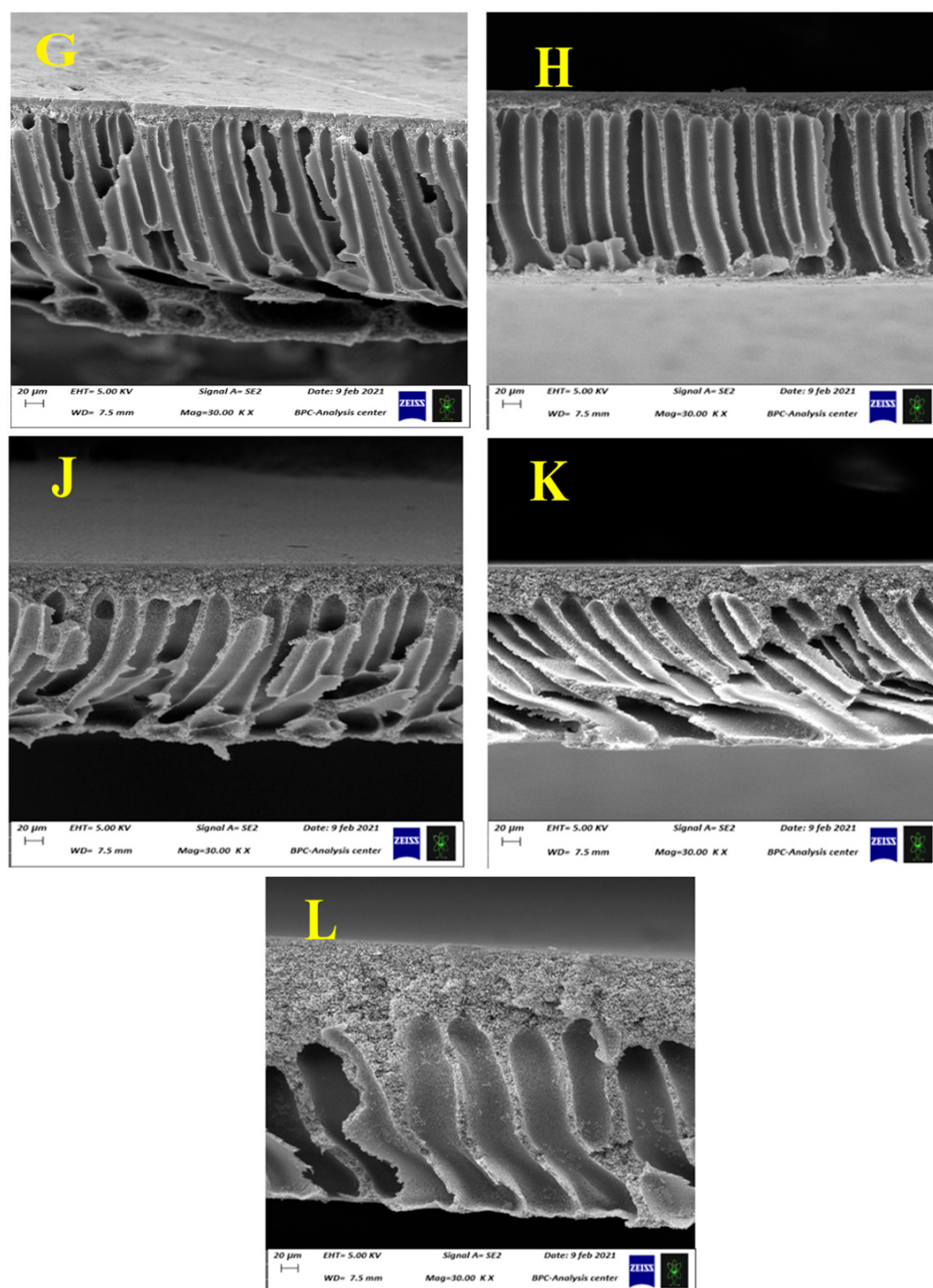


Figure 6. SEM cross-section images for (A) pristine, (B) 0.25 g, (C) 0.5, (D) 0.75 g, (E) 1 g, (F) 1.25 g, (G) 1.5 g, (H) 1.75 g, (J) 2 g, (K) 2.25 g, and (L) 2.5 g PMG-modified membranes.

Surface topography parameters of the pristine and PMG NPs modified membranes have been determined via AFM. The $0.8 \mu\text{m} \times 0.8 \mu\text{m}$ three-dimensional images of the eleven membrane samples are depicted in Figure 7A–L. In the presented images, regions with a dark colour referred to the lowest points, while the regions with a bright colour referred to the peaks. As can be seen in Figure 7A and Table 3, the neat PES membrane revealed the flattest surface compared to other nanocomposite membranes. The arithmetic mean height (Ra), root-mean-square height (Rms), and maximum height (Rz) were found to be 3.55, 6.3, and 24, respectively. Unsurprisingly, these smooth features of the PES membrane were expected since these are the inherent roughness charac-

teristics of the pristine PES membrane surface, as reported in the literature [34–37]. Following the PMG NPs addition, a noteworthy increase in all roughness parameters is witnessed, see Figure 7B–L. Regardless of the amount of nanoadditives employed to synthesize the nanocomposite membrane, all the membrane samples manifested almost comparable values (15–25 nm) for the mean surface heights (Table 3). The R_a value of the nanocomposite membrane prepared using 0.25 g was (15.12 nm) triple that of the control membrane, while it was eightfold when the highest PMG loading content (24.4 nm) was used. These results disclosed that copolymer nanoadditives imparted a significant roughness when impregnated within the membrane matrix. Notably, no obvious relationship was noticed between the roughness parameters versus the increased PMG content in the polymeric matrix. Regardless of the concentration of PMG, the variation in the roughness parameters was trivial. This indicated that the PMG copolymer was homogeneously merged and dispersed within the membrane structure rather than concentrated at the top surface.

In Table 3, the mean pore size showed that increasing the PMG amount with the PES from 0 to 0.25 g increased the mean pore diameter from 57.14 to 67.90 nm, respectively. Further increasing the PMG to 2.5 g highly increased the mean pore diameter of the PES-PMG membrane to 108.28 nm. This phenomenon was visibly shown and emphasized in the morphological structure of the membranes and is discussed extensively in Section 3.2. “Surface characterization of membranes”. Increasing the amount of the PMG in the PES casting solution resulted in an acceleration in the solvent and non-solvent exchange rate during membrane formation, and thus, resulted in a significant tendency to form macrovoids, which increased the membrane mean pore size [38]. Moreover, Table 3 shows the effect of the PMG amount on the porosity of the developed PES-PMG membranes. Increasing the PMG amount in the PES solution from 0 to 0.25 g increased the developed membrane porosity from 70 to 72%, respectively, while further increasing the PMG amount to 2.5 g increased the porosity of the developed PES-PMG membrane to 83%. It is worth mentioning here that the results observed from the AFM and SEM tests proved the porosity results of the developed PES-PMG membrane.

A 500–4000 cm^{-1} total reflection infrared spectra has been taken for the pristine PES and 2.5 g PMG nanocomposite membranes, as shown in Figure 8. For both modified and unmodified PES membrane spectra, the absorption bands observed at 1297 cm^{-1} and 1150 cm^{-1} are the characteristic peaks associated with the PES structure that correspond to asymmetrical and symmetrical vibrations of the sulfone groups, respectively [39]. The two strong peaks at 1011 cm^{-1} and 1240 cm^{-1} are attributed to the stretching vibration of the PES polymer diphenyl C–O–C bond. The benzene rings stretching mode manifested a strong absorption band around the 1480–1580 cm^{-1} region [40]. All aforementioned bands were also seen in the spectrum of PMG-modified nanocomposite membrane. However, additional bands were observed related to the blended copolymer. The characteristic strong broad band appeared at 3338 cm^{-1} was assigned to the stretching of the hydroxyl group (–OH) with stretching (H bond). Additionally, the weak bands observed at about 2953 cm^{-1} and 2887 cm^{-1} were ascribed to the =C–H for carboxylic acid and C–H aliphatic, respectively. Additionally, the spectrum has manifested a strong band at 1718 cm^{-1} , which is attributed to the stretching band C=O of the ester group. The band noticed at about 1014 cm^{-1} was mainly associated with the absorption band of C–O [28].

Additionally, Figure 9 shows the EDX analysis of the PES-PMG membranes at different contents of PMG in casting solution (i.e., 0, 0.25, 1, and 2.5 g of PMG). The constituent elements of both the pristine PES and 2.5 g membranes are depicted in Figure 9. It can be clearly seen that the percentage of C, O, and S significantly decreased with the increase of PMG contents in the casting solution, which confirms the appearance of the effect of PMG. Therefore, the results of this examine confirmed the affinity between the PES membrane and the PMG.

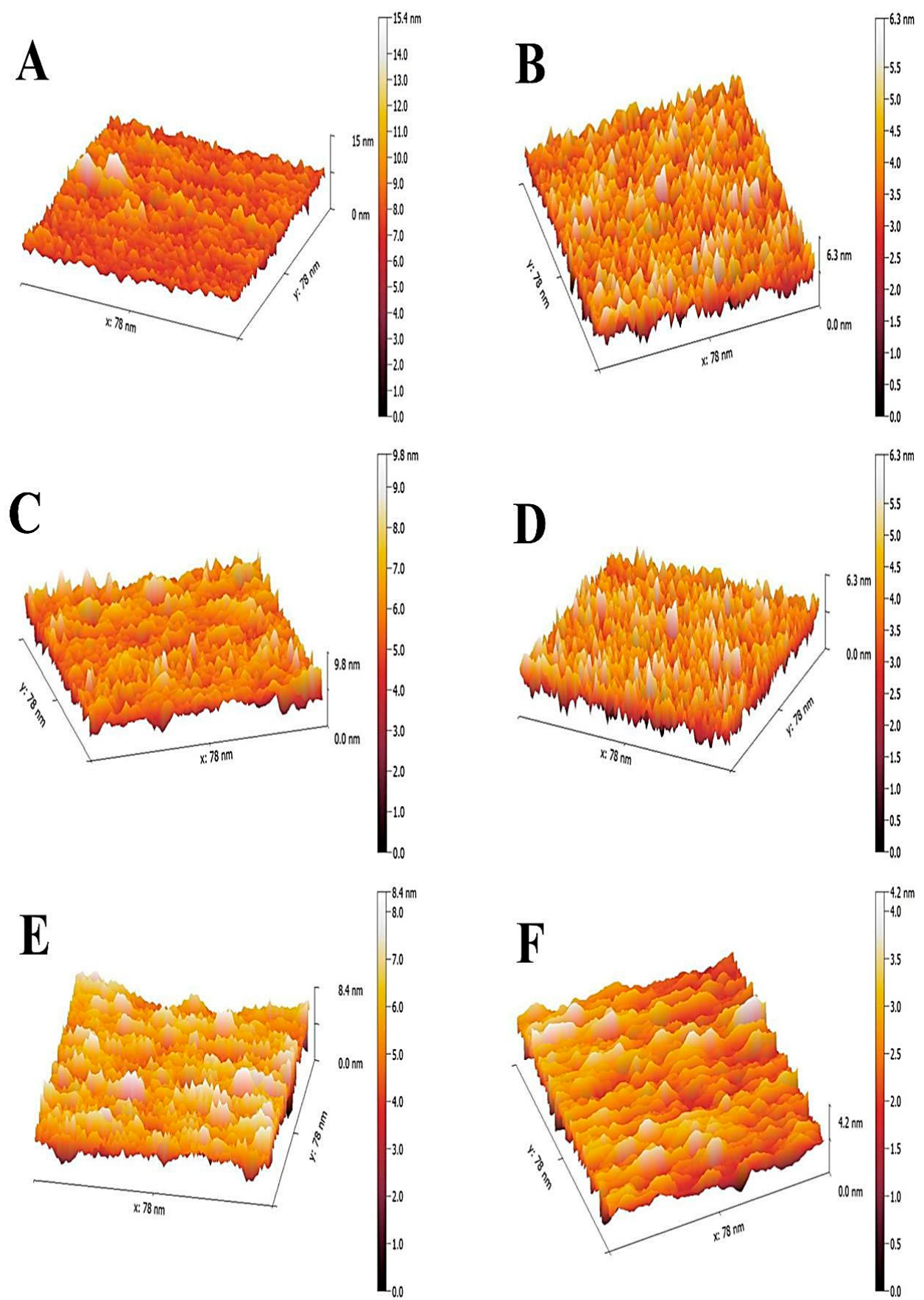


Figure 7. Cont.

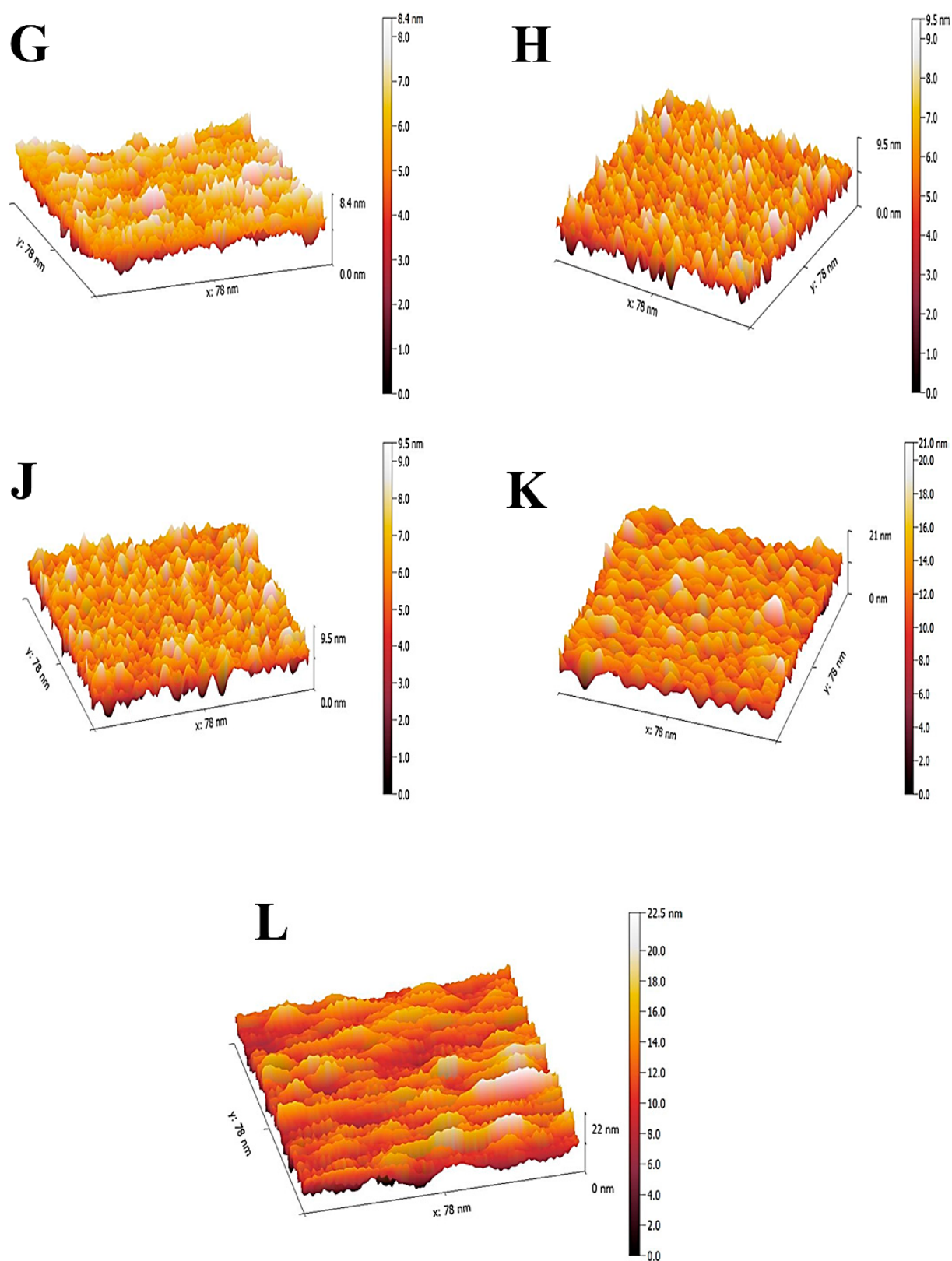
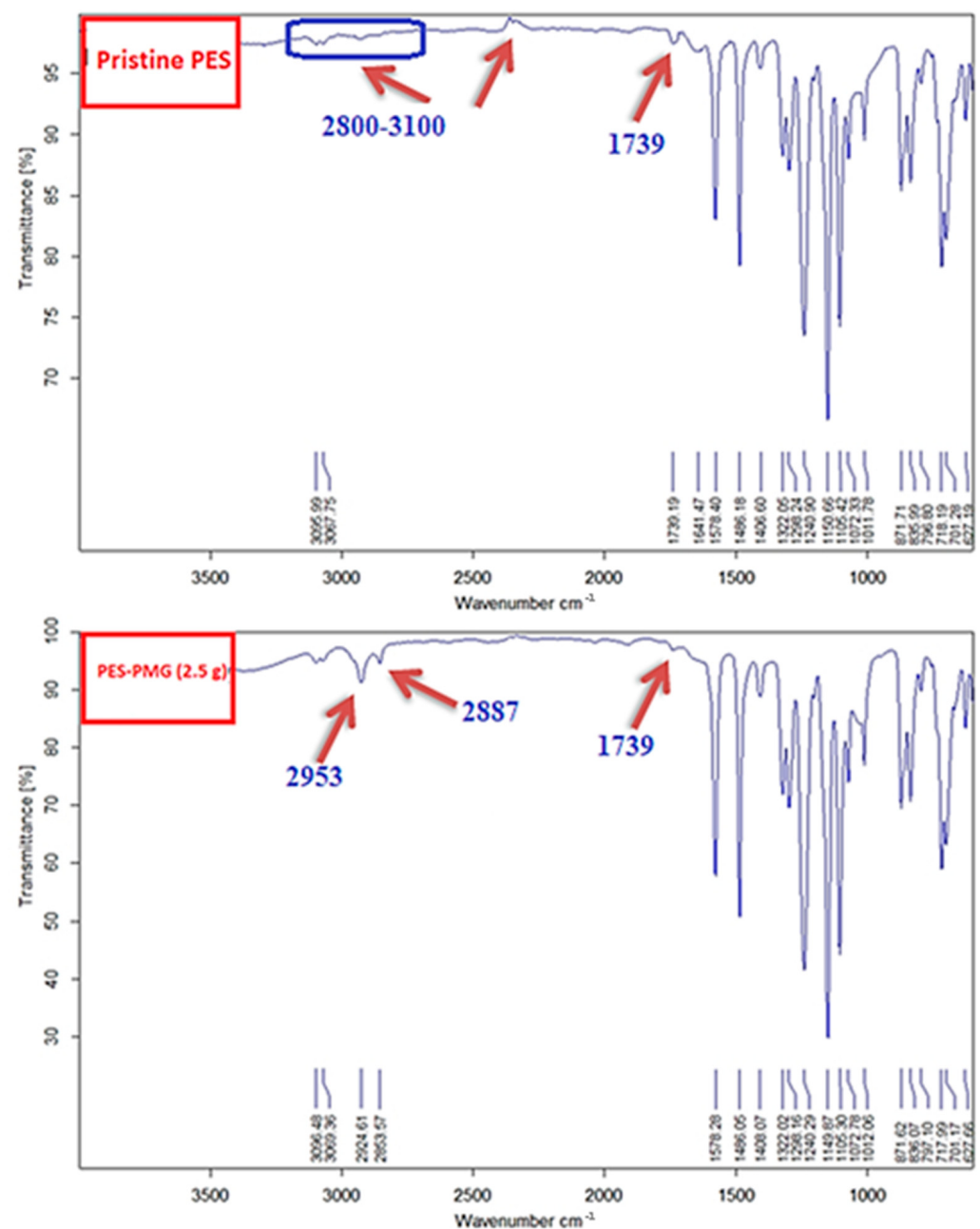


Figure 7. AFM surface topography images for (A) pristine, (B) 0.25 g, (C) 0.5, (D) 0.75 g, (E) 1 g, (F) 1.25 g, (G) 1.5 g, (H) 1.75 g, (J) 2 g, (K) 2.25 g, and (L) 2.5 g PMG-modified membranes.

Table 3. Roughness parameters of the control and PMG-modified membranes.

No.	PMG Content (g)	Ra (nm)	Rms (nm)	Rz (nm)	Porosity (%)	Mean Pore Size (nm)
1	0	3.55	6.3	24	70 ± 1.1	57.14 ± 1.8
2	0.25	15.12	20.18	121.2	72 ± 0.9	67.90 ± 2.1
3	0.5	21.44	23.37	74.5	73 ± 0.84	71.20 ± 1.3
4	0.75	17.22	24.43	96.25	74 ± 1.02	71.34 ± 1.1
5	1	20.90	28.19	138.00	74.7 ± 1.0	78.60 ± 2.3
6	1.25	23.10	26.80	174.2	76 ± 0.98	87.70 ± 1.09
7	1.5	21.15	24.99	138.64	78 ± 0.86	88.30 ± 1.1
8	1.75	24.77	29.9148	150.89	78.4 ± 1.03	88.70 ± 0.8
9	2	18.23	24.80	208.9	79 ± 1.01	90.30 ± 1.05
10	2.25	25.71	31.46	177.2	81 ± 0.98	101.52 ± 3.04
11	2.5	24.4095	31.468	160.15	83 ± 0.82	108.28 ± 1.9

**Figure 8.** FT-IR spectra of pristine and 2.5 g PMG-modified mixed matrix.

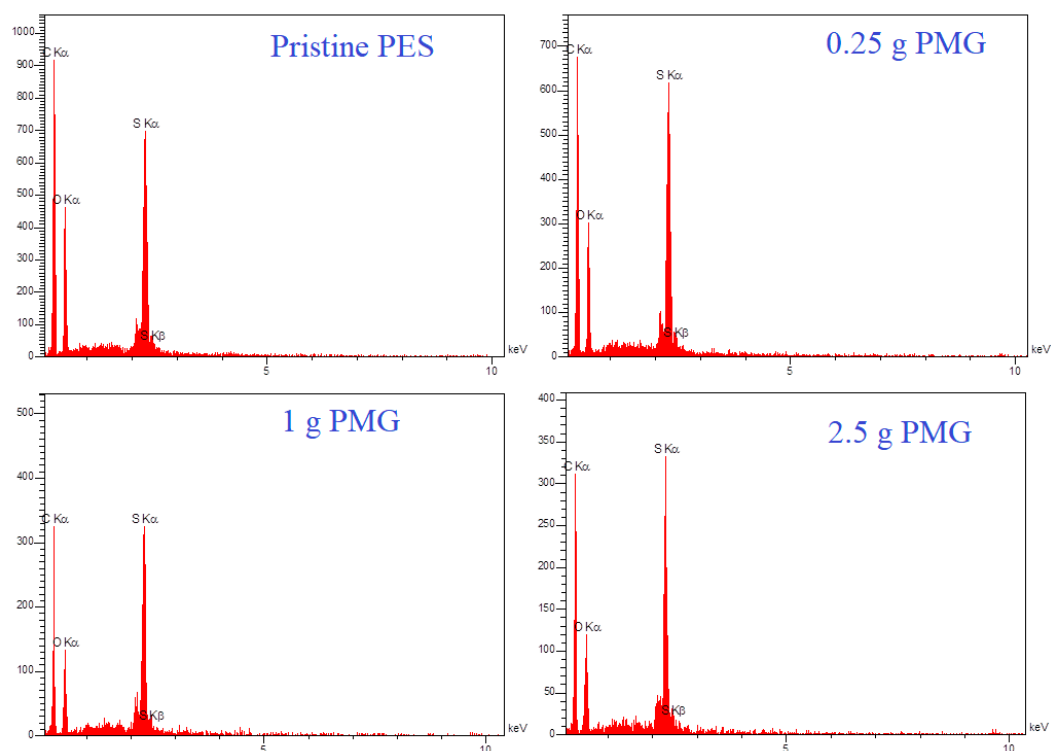


Figure 9. EDX of the membranes prepared form different PMG contents.

Hydrophilicity is a pivotal feature for predicting the permeation and antifouling characteristics of any water treatment membrane. In the current study, contact angle (CA) measurements were conducted utilizing the sessile drop method to assess the influence of PMG nanoadditives on the PES membrane surface hydrophilicity characteristics. Measurements of contact angle for the pristine and PMG-modified membranes are illustrated in Figure 10. The nascent PES membrane showcased about 68° which was within the common range of control PES membranes [34]. This value was the highest recorded contact angle amongst all other nanocomposite membranes. To some extent, an obvious decreasing trend in the contact angle values could be seen in the nanoadditives incorporated in the casting solution. For the mixed matrix membranes synthesized using 0.25 g and up to 1.25 g, PMG recorded contact angles within the fifties (Figure 10). A further development in the nanoadditives induced an additional decline and reached about 41° and 42° for the 2.25 and 2.5 g modified membranes, respectively. Since hydrophilicity has continuously imparted, these results confirmed the hydrophilic nature of PMG NPs which is reflected on the PMG NPs' modified membranes even at the high content.

3.3. Evaluation of Membrane Performance

3.3.1. Pure Water Flux (PWF)

The pure water and solute permeate flux of nanocomposite membranes were compared with that of the pristine membrane. A representative BSA solution as a protein model has been harnessed for this purpose. As is clearly shown in Figures 11 and 12, the pure PES membrane exhibited minimal permeate flux for both pure water and BSA solution, and recorded about 150 and 138 LMH, respectively. Upon the addition of PMG nanoadditives, the modified membranes experienced a surge enhancement in their permeation characteristics. By only adding 0.5 g PMG into the PES polymeric matrix, the pure water flux of the nanocomposite membrane was almost double the pristine membrane flux. With a further amount of the nanoadditives, a continuously increasing trend was observed in the pure water flux measurements. The nanocomposite membrane prepared using 1.75 g PMG NPs has showcased about a fourfold (609.4 LMH)

improvement in the flux magnitude compared to the control membrane. The uppermost pure water flux was reported for the membrane synthesized using a 2.5 g nanoadditive, which was 908 LMH, about six times the pristine membrane flux. Additionally, its BSA solute flux was greater (569 LMH) than all other membranes. This observed increasing behaviour could probably be attributed to the imparted hydrophilicity from the PMG copolymer. Additionally, this resulted from the high increment in the mean diameter of the pores of the developed membrane, which was noticed from the content of PMG in the casting solution. In addition, the higher surface roughness parameters reported for this membrane could be another critical factor since it could endow a higher surface area for performing the filtration.

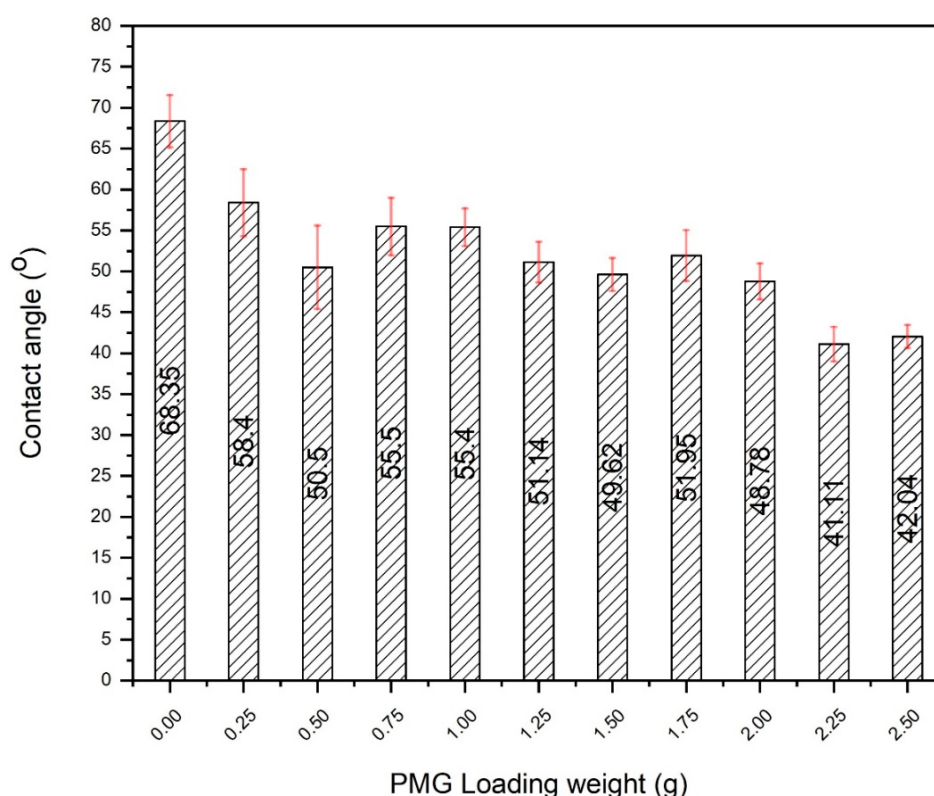


Figure 10. Contact angle measurement of the PMG NPs' modified membranes.

3.3.2. Retention of PMG-Modified Membranes against Protein Solution

A lab-scale cross filtration setup was employed to assess the membrane's rejection efficiency and self-cleaning characteristics over a 60 min filtration time and 1 bar operational pressure. The impact of the copolymer NP content on the separation characteristics of the modified mixed matrix membrane are illustrated in Figure 13 below. Bovine serum albumin (BSA) has been employed as a protein model throughout all the separation performance experiments. As shown, the pristine PES membrane exhibited the lowest BSA retention (69%) potentials amongst other nanocomposite membranes. However, it could be noticed that impregnation of the nano copolymer had significantly influenced the protein retention behaviour of the nanocomposite membranes which recorded 80% to almost complete retention. Increasing the nanoadditive content to 1 g in the membrane induced about a 23.3% enhancement in the rejection of the membrane. Doubling the amount of PMG NPs to 2 g caused further retention (about one-third higher) compared to the neat PES membrane. A higher rejection coefficient (98%) to BSA was maintained by the nanocomposite membrane synthesized using 2.5 g PMG NPs. This proportional correlation between the retention value and the amount of nanoadditive content in the membrane could be attributed to the variation in the pore size of membranes. According to the SEM cross-section observations, membranes prepared with the highest nanoadditive content revealed denser membrane structures and

more likely smaller pore size and pore size distribution. Ultimately, this nanocomposite could perform greater retention since we have excluded the influence of other operation conditions (e.g., pressure, pH, and feed concentration) here in the current work.

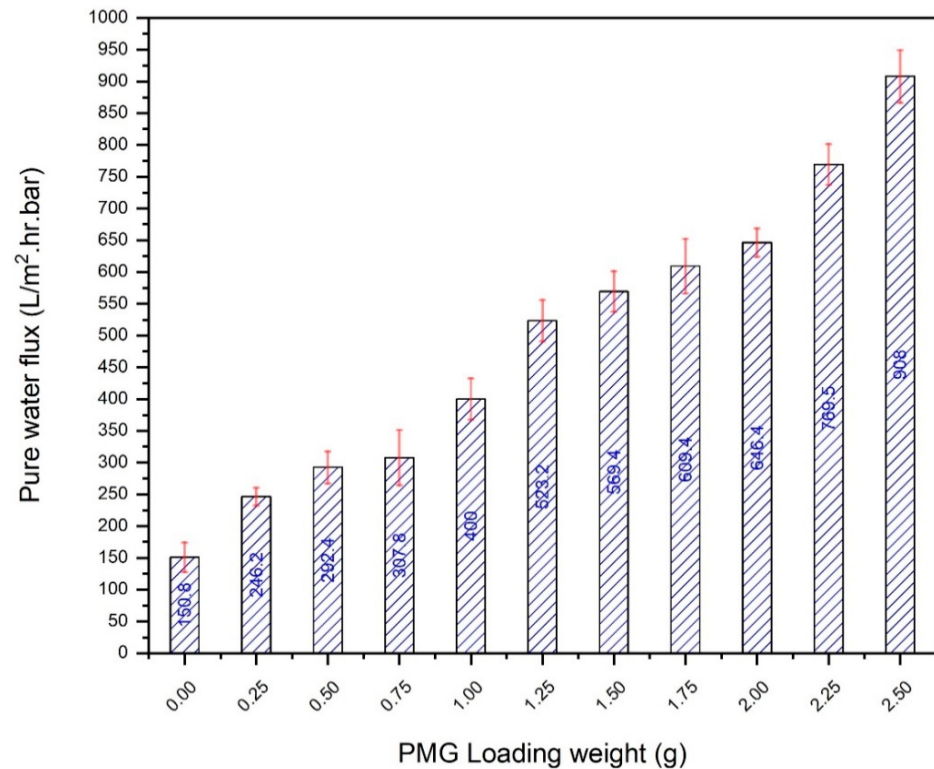


Figure 11. Pure water flux of all pristine and PMG-modified membranes.

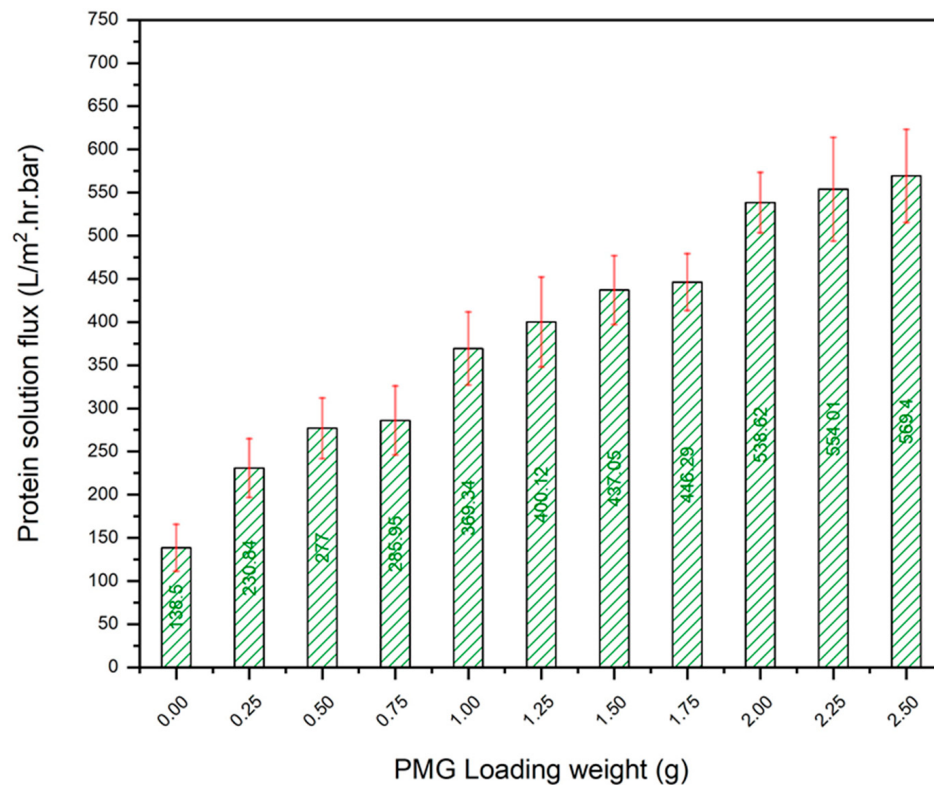


Figure 12. Bovine serum albumin solute flux for PMG-modified nanocomposite membranes.

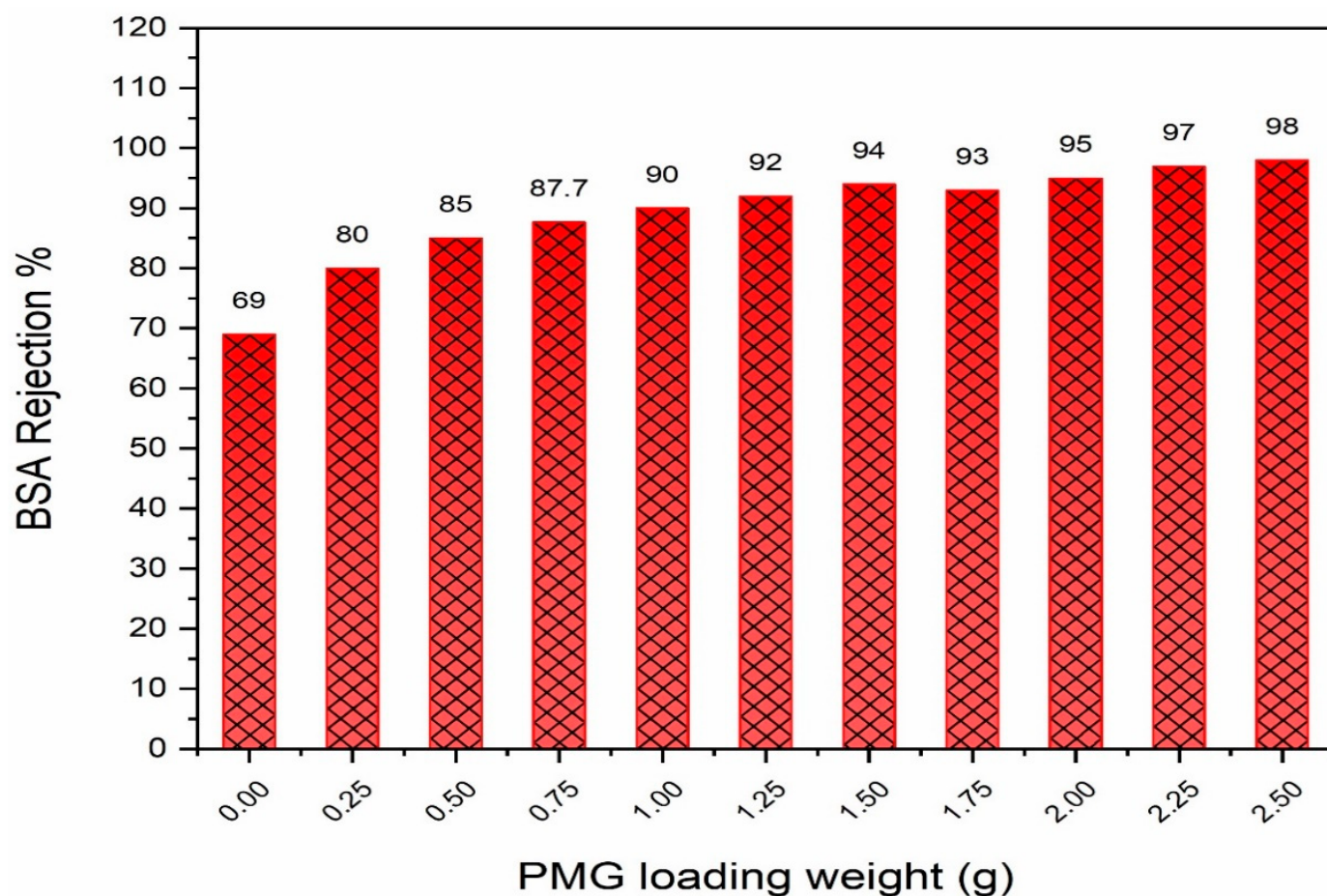


Figure 13. Retention rate of PMG nanocomposite membranes against BSA solution.

3.3.3. Total Fouling and Fouling Mechanisms against BSA Protein Solution

As indicated earlier in the literature review, membrane fouling is directly linked to the permeate flux of that membrane. Deposition or adsorption of solute macromolecules onto the membrane surface or within the inner pores can cause a severe flux decline and diminish the permeate quality [41,42]. The total fouling behaviour of loose UF membranes, as in our case in the current work, can be influenced by many factors (e.g., solution concentration, experimental conditions, and surface characteristics of the membrane) and follow different mechanisms [43]. Figure 14 illustrates the magnitudes of BSA total fouling (F_t), reversible fouling (F_{rev}), and irreversible fouling (F_{irrev}) for pure and modified membranes with various contents of PMG NPs. The PWF of all membranes after backwashing indicated that pristine and nanocomposite membranes prepared with less than 1 g PMG have showcased a relatively slight flux decline compared to the rest of the samples. Their flux decline (J_2) ranged between 5% and 8.1% of the initial flux value (J_0). However, about one-third of the flux was recoverable (F_{rev}). In contrast, nanocomposite membranes prepared with a higher PMG content, especially the ones prepared using 2.25 g and 2.5 g, have disclosed the highest fouling rate which was 28% and 37.2%, respectively. Herein, although the 2.5 g nanocomposite exhibited a high (37.2%) total fouling rate, the majority of flux was irreversible ($F_{irrev} = 31.1\%$). This discrepancy in the fouling behaviour is more likely attributed to the variation in the membrane surface–BSA solute interactions, mean pore size, and pore size distribution [44]. These nanocomposite membranes manifested the highest permeate flux (908 LMH) compared to the others which means higher BSA molecules have been deposited at and/or within the membrane pores. Eventually, this caused complete pore blocking and pore narrowing due to BSA adsorption. Additionally, as the filtration proceeded, BSA–BSA adsorption occurred and built up at the surface of

the membrane forming a thicker deposited BSA layer. These three mechanisms were significant and partially blocked the water from passing through this membrane as enclosed by the higher fouling rate obtained.

The main reasons for the accumulation of foulant on the surface of the membrane are the mechanical retention at the head of the opening pore and the covalent or noncovalent adsorption. The interactions between the foulant and the surface of the membrane mainly depend on the charge, functional groups, hydrophobicity, and physical properties of the foulant and membrane. As the critical concentration of the accumulated foulant at the surface of the membrane is reached, a cake layer starts to shield the membrane. The posterior foulant from the feed solution interacts with the surface of the cake layer instead of the surface of the membrane, and hence, the interaction effect changes from foulant and membrane to foulant-foulant. The covalent complexation is the key mechanism for the cake layer rule, whereas the non-covalent and steric impacts could affect the compactness, porosity, and permeability of the foulant layer. These effects mainly depend on the physical properties of the membrane such as the morphology, hydrophobicity, size, functional groups, and charge of the foulant components. The complexation of the membrane-foulant covalent could be mitigated by minimizing the intensity of carboxyl groups on the surface of the membrane, which is the target of using PMG in this study. Therefore, the results of the EDX test shown in Figure 9 confirmed this phenomenon [45–47].

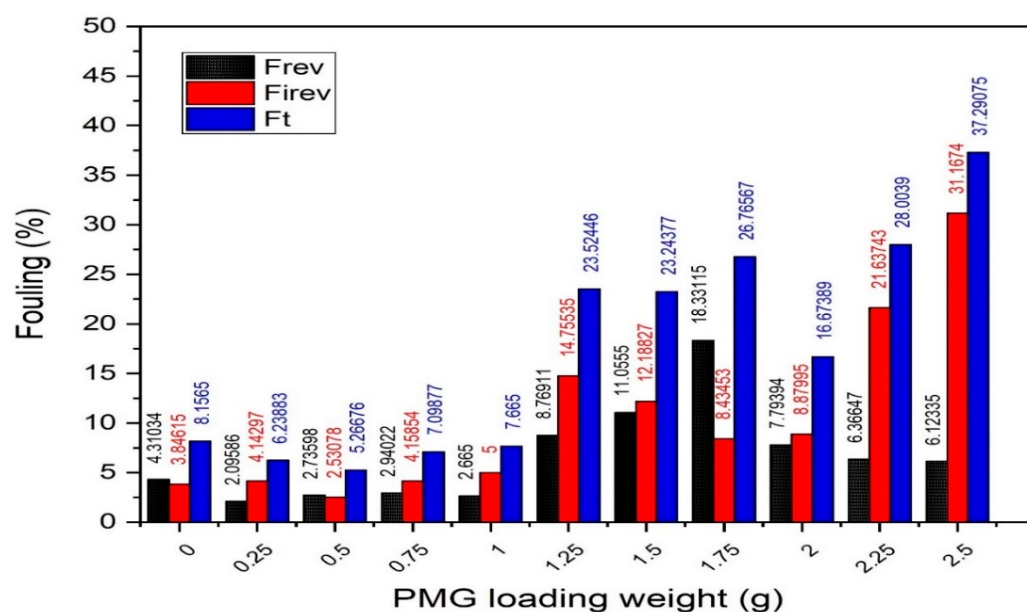


Figure 14. Total fouling, reversible fouling, and irreversible fouling of nanocomposite membranes against BSA protein model.

Table 4 depicts a comparison between the performance of the PES-PMG membranes synthesized by the current study with that of selected studies of synthesized membranes presented in the literature. The significant characteristics of the modified membranes, for example, contact angle, and mean pore diameter are also summarized in Table 4. It can be observed that the membranes synthesized from PES-PMG with 2.5 g of PMG in casting PES solution have an excellent value of water permeance and BSA rejection (%) in comparison with all selected modified membranes from the literature. It can be concluded that the new nano copolymer synthesized by the current work has excellent characteristics for developing the hydrophilic polymer in terms of the physical properties of the membranes.

Table 4. Comparison between the membrane performance fabricated in the current work with some membranes presented in the literature.

Membrane Material	Additives	Mean Pore Diameter (nm)	Contact Angle	R (%)	Water Permeance (L/m ² ·h)	Ref.
PVC (15 wt.%)	MWCNT-g-GO (0.119 wt.%)	259	13.9°	COD: 88.9	254	[9]
PVDF (16 wt.%)	TiO ₂ (<2 wt.%)	47.3	76°	BSA (100)	111.7	[48]
PSf (15)	Janus GO (1%)	-	-	BSA (92)	115	[49]
PVDF (15)	GO (0–2)	-	-	BSA (52)	188.36	[50]
Polyamide 6,6 (20%) and Formic Acid (80%)	Silver-Graphene Oxide (0.8%)	8.3	35.28	BSA (89.8)	-	[51]
* EPVC/PEG; 15:4 wt./wt.%	TiO ₂ (2 wt.%)	25	57.2°	BSA (98)	435	[52]
PVC (15 wt.%)	TiO ₂ : 1.5 gm	77	62.5°	COD (79.7)	116	[53]
Polysulfone (PSF) (16%)	Arabic Gum (3%)	37	40.7°	BSA (80.7)	120	[54]
PES	PMG (2.5 g)	108.28 ± 1.9	42.04	BSA (98)	908	This study

* EPVC: Emulsion poly(vinyl chloride).

4. Conclusions

This work intended to provide a detailed design and synthesis of a novel and sustainable UF nanocomposite membrane for protein separation via the phase separation technique. Additionally, it aimed to enhance the hydrophilic nature of the new membranes. Therefore, novel graft copolymer nanoparticles have been utilized. A wide spectrum (0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 2.25, and 2.5 g) of PMG nanoparticles have been used for the bulk modification of the membranes. The hydrophilic functional groups of carboxylic acid were confirmed by the FTIR strong broad band observed at 3338 cm⁻¹. The AFM power has also been harnessed to calculate the mean particle sizes and their range of distribution. An average molecular size of 88.07 nm and distribution between 55–135 nm has been observed. In this context, all membranes exhibited an asymmetrical structure, as revealed by SEM imaging. With each increment in the PMG content, a thicker selective layer and fewer figure-like micropores were detected by the cross-section images. The active layer thickness has noticeably increased, while a dense porous structure was formed, especially when a greater amount (2.5 g) of nano PMG was incorporated into the casting solution (Ra increased from 3.55 to 24.4 nm). The successful incorporation of nanoadditives has also been confirmed by detecting the PMG novel functional groups on the surface of nanocomposite membranes. The mixed matrix membrane synthesized using 0.25 g has recorded contact angles of 42° compared to only 68° for the pristine PES membrane. This 2.5 g modified membrane has also exhibited the highest PWF (908 LMH) and retention (98%) capability compared to the neat membrane, which showed 150 LMH and 69%, respectively. All nanocomposite membranes exhibited promising antifouling characteristics against BSA protein filtration, indicating the prominent potential to be used for water treatment applications. The future perspective of the presented research is to open the way for researchers to manufacture new nano copolymers with different and excellent physicochemical properties that have the ability to make changes to the morphological structure of the membranes, which would reduce the effect of the fouling phenomenon and enhance the mass production of the membrane as well as improve the removal efficiency of the solutes to be treated.

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