



Research Paper

Heterogeneous Functionalization of Polyethersulfone: A New Approach for pH-Responsive Microfiltration Membranes with Enhanced Antifouling Properties

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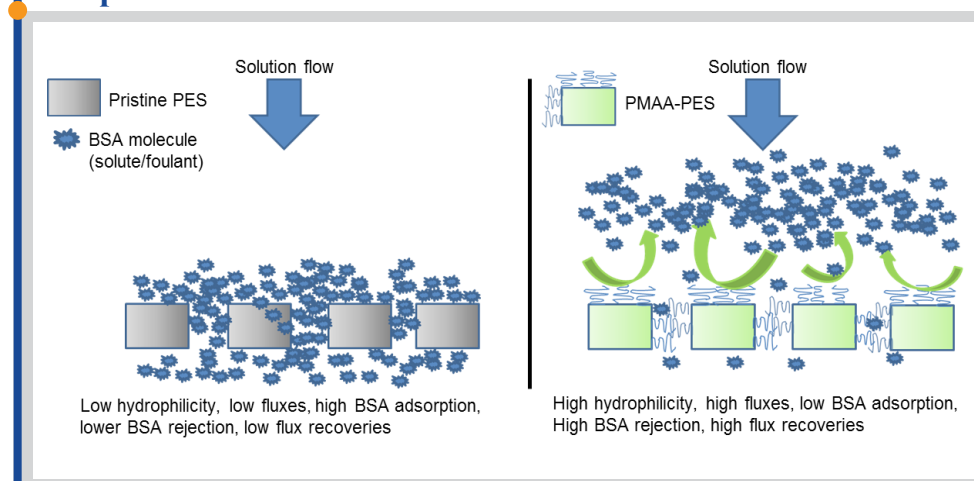
Keywords

BSA rejection
Low-fouling
PES membranes
Bulk modification
Polymer synthesis
Smart polymers

Highlights

- AIBN successfully used as initiator in bulk functionalization of polyethersulfone
- Membranes prepared were hydrophilic, pH-responsive, with high permeability to water
- Membranes with high protein rejection and low-fouling propensity were obtained

Graphical abstract



Abstract

In this work, 2,2'-azo-bis-butyronitrile (AIBN) was exploited as an initiator for the successful bulk heterogeneous functionalization of polyethersulfone (PES) using polymethacrylic acid (PMAA), for the first time. To this end, pH-responsive and exceptionally low fouling membranes of extremely low grafting degrees with low adhesion and high rejection of protein were fabricated. An added advantage of this method is the accomplishment of graft polymerization of methacrylic acid (MAA) in water in the absence of toxic solvents, scavengers or catalysts. Changes to surface functional groups of the PES powder were determined using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy and thereafter validated with X-ray photoelectron spectroscopy (XPS). The phase inversion technique was used to fabricate microfiltration membranes (MFs), which were found to possess up to 40% improved hydrophilicity relative to pristine PES membranes. Protein adsorption was reduced by more than 80% while its rejection and the pure water permeate flux recovery ratio (FR) were 97%, and 86%, respectively. Furthermore, the membrane maintained 90% FR over 10 cycles. The newly fabricated membranes possess enhanced response to pH stimulus.

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1. Introduction

Numerous methods have been used for the graft polymerization onto hydrophobic polymers such as polyethersulfone (PES) to improve membrane surface properties of the resultant membrane. These approaches include, but are not limited to, irradiation, ozone and thermal-induced grafting [1]. In a process termed post-functionalization, the aforementioned methods have however only been applied in polymer functionalization following the completion of the membrane formation step [2]. In the post-functionalization approach, the modification of the membrane takes place on the reactive functional groups located on the surface and pore structure of the membrane. In a process termed post-functionalization, the aforementioned methods

have however only been applied in polymer functionalization following the completion of the membrane formation step [2]. Among others, carboxylic, sulphonyl, amine and amide ligands have been grafted onto hydrophobic membranes such as poly(vinylidene difluoride) (PVDF) and PES in this manner [3-4]. Nonetheless, limitations associated with polymer modification method include an extreme alteration of pore size and pore size distribution, which ultimately affect membrane performance. To this end, pre-modification has recently received plenty of attention [5].

As opposed to post-functionalization, pre-modification or bulk functionalization of polymers enables preparation of reproducible and

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scalable functionalized membranes. Therefore, bulk functionalization is a superior method for the preparation of membranes with improved physicochemical properties [5]. Chemical and irradiation initiation have been used for bulk functionalization of polymers where gamma irradiation was employed for the grafting of *N*-vinyl-2-pyrrolidone groups onto the PVDF powder. The effect of various types of catalysts on the production of the homopolymer and ultimately the graft yields were also investigated [6]. Previously, initiators such as azo-isobis-butryronitrile (AIBN) have been successfully used for the copolymerization or graft polymerization of vinyl (i.e. acrylic) monomers onto polymers such as cellulose, polystyrene, styrene-butadiene; their grafting kinetics has also been studied [7]. Hydrophilic low fouling membranes with enhanced permeation fluxes have also been synthesized via homogenous and heterogeneous pre- and post-modification of similar materials [8]. However, limited data exist on the heterogeneous pre-modification of polymeric powders. One method was reported for the grafting of acrylic acid onto PES powder, and the costly and harmful nature of gamma-ray radiation employed counted against this method [9]. Shi and co-workers (2010) have reported the bulk functionalization of PES with polymethacrylic acid (PMAA) via a thermal initiation method in the presence of benzoyl peroxide (BPO) to produce membranes with enhanced properties [10].

Herein, a novel route for the preparation of pH-responsive PMAA-grafted PES (PMAA-PES) membranes from PES powder is reported. The synthetic approach adopted in this research involved a free radical graft polymerization of MAA using AIBN as a thermal initiator in the absence of any catalysts, inhibitors or toxic solvents. The adoption of the AIBN in this work was motivated by a general lack of the exploitation of this initiator in the literature towards the bulk functionalization of hydrophobic polymers such as PES. To the best of our knowledge, this type of work has not been reported in the current literature. The aim of this work was, therefore, to investigate and interrogate a new synthetic procedure for the thermal-assisted bulk functionalization of PES with MAA using AIBN as an initiator. Relative to membranes prepared from pristine PES, it was envisaged that the grafted powder would enable easy access to membranes with enhanced water uptake, pH response, recyclability, protein rejection, and antifouling properties.

2. Methods

2.1. Materials

PES powder (3100 P, c.a. 1-800 μm radius, 30-55 kDa) was obtained from the Solvay Chemical Company (Belgium). Sodium hydroxide (NaOH) pellets and hydrochloric acid solution (HCl, 36%) were purchased from Merck (Germany). Methacrylic acid (MAA, 99%), ethylene glycol (EG, 99.8%), *N*-methyl-2-pyrrolidone (NMP, 99.9%), 2,2'-azo-isobis-butryronitrile (AIBN, 0.2M), benzoyl peroxide (75%, remainder water), poly(vinyl pyrrolidone) (PVP, 98%) and bovine serum albumin (BSA, 66 kDa, 96%) were obtained from Sigma-Aldrich (South Africa). Unless specified otherwise, all chemicals were of analytical grade and used as received. The water used for all experiments was obtained from the Millipore® system (Japan) at a resistivity of 18.2 M Ωcm .

2.2. Graft polymerization of MAA to PES powder

Heterogeneous graft synthesis was used to modify PES powder via AIBN initiation in water. The graft polymerization (as presented in Figure 1) was carried out in a 100 mL of water/PES powder (4 g) mixture within a 250 mL

three-necked flask in an oil bath set at the reaction temperature (60 and 75°C). After degassing the mixture with nitrogen gas, the polymerization temperature was monitored using a fully automated stirrer heater equipped with a temperature probe (MRHei-Tec, Heidolph Instruments GmbH & Co, Germany) and this allowed enhanced temperature control over systems without temperature probes.

For the AIBN initiation of MAA, 10mL of an aqueous solution of the monomer (0.5-2.0g MAA; crosslinker EG at 5.0 mol% of MAA) was added drop-wise under stirring conditions to the water/PES powder solution and the resulting mixture was allowed to react over a period of 3.5 hours (Figure 1). This reaction allows the initiation of MAA and the resultant formation of MAA radicals, which attack the PES by abstracting the phenyl hydrogen that ultimately leads to the formation of a macro radical that initiates the copolymerization process. For the BPO-initiated polymerization reaction, a grafting method adopted from the literature was followed [10]. Upon completion of the polymerization reaction, the grafted polymeric powder was removed and washed sequentially under vacuum filtration with deionized water, and NaOH (temperature of both solutions was kept at 60°C) to remove the homopolymer, free monomer, and residual initiator.

The degree of grafting (DG) was determined gravimetrically using the following formula.

$$\text{DG}(\%) = [(W_f - W_i)/W_i] \times 100 \quad (1)$$

where W_i is the initial weight of the PES powder, and W_f is the weight of the PES grafted polymer.

2.3. Membrane fabrication

The membranes were prepared via phase inversion using water as the coagulation bath. A mixture of the grafted PES powder, PVP (pore-former), and NMP (solvent) (ratio of 16:8:76w/w%) was heated and stirred at 60°C. Upon complete dissolution process, the resultant solution was degassed under vacuum for an hour prior to casting. Thereafter, the casting solution was spread on top of a clean glass plate with a casting knife adjusted to a height of 200 μm . The glass plate was then immersed in a water coagulation bath, kept at room temperature for 12 hours, and thereafter stored in fresh deionized water.

The designations of the membranes (PES0, PES2.6, PES3.7, and PES5.8) prepared from the pristine and grafted PES powders and their corresponding DG percentage values are listed in Table 1 above.

Table 1
Designations for the membranes prepared in this work corresponding to the DG of the grafted powders.

Membrane	DG (%)
PES0	0
PES2.6	2.6
PES3.7	3.7
PES5.8	5.8

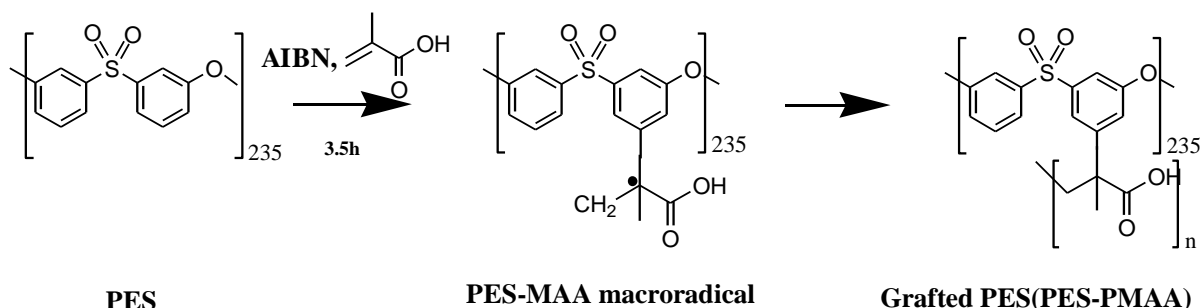


Fig. 1. The schematic representation of the graft polymerization of MAA onto PES powder via AIBN initiation in water.

2.4. Characterization: powders and membranes

Functional group modifications were investigated using ATR-FTIR spectrometry (Spectrum 100, Perkin Elmer Inc., USA) with a working range set between 650 and 2000 cm^{-1} . Prior to analysis, all samples were dried in a desiccator for 24 hours.

Further characterization and chemical composition of the prepared membranes was investigated using XPS (AXIS SUPRA, Kratos Analytical, U.K). Of particular interest to this study was the core C 1s and O 1s, which allows the monitoring of the binding energy (B.E., eV). The peak areas measurement, which was also determined during the determination of the elemental composition, were carried out at the respective working current and pressures of 15mA and 1.8 $\times 10^{-8}$ Torr.

Morphological changes pertaining to surface and cross-sectional structures of the membranes prepared from neat and grafted powders were also investigated. Special preparation of the membranes for cross-sectional analyses was carried out by cutting thin strips of the membranes. This was carried out by dipping them in liquid nitrogen and subsequently fractured to reveal the microstructure. Thereafter, all samples were carbon coated and analyzed using SEM (Vega 3 LMH SEM, Tescan Orsay, Czech Republic). The surface morphology of all the membranes prepared from the pristine and grafted powders was investigated.

To determine the hydrophilicity changes emanating from the grafting process, the optical contact angles (OCA) of the grafted membranes were measured in pure water at various points across the membranes using the OCA 15EC goniometer (Dataphysics Corp., Germany). The membranes were submerged and kept in deionized water prior to analysis.

To determine total membrane porosity and pore size, water uptake or fluid saturation studies were carried out. Before the fluid saturation experiments, the membrane samples were cut into 3.0 \times 3.0 cm^2 square pieces and conditioned for 24 hours in pure water and aqueous solutions of varied pH values, respectively. The water uptake (swelling) of the membranes was determined gravimetrically using equations (2) and (3) [11].

$$M_{\text{water}} = M_{\text{wet}} - M_{\text{dry}} \quad (2)$$

$$\text{Water uptake (\%)} = [(M_{\text{wet}} - M_{\text{dry}})/M_{\text{dry}}] \times 100 \quad (3)$$

where M_{water} depicts the mass of the water absorbed by the membrane. M_{wet} and M_{dry} are masses of the wet and dry membranes respectively.

The determination of the water uptake of the membranes allowed the overall porosity ($\epsilon(\%)$) of the membrane to be calculated using equation 4.

$$\epsilon(\%) = [M_{\text{water}}/\rho A l] \times 100 \quad (4)$$

where ρ is the density of water (0.998 g/cm^3); A is the total area of pores in the membrane in cm^2 (determined via Image J Software, v1.4, NIH.gov); and l is the membrane thickness in cm.

From the porosity data, the mean pore radius, r_m of the membranes was calculated by applying the following Guerout Elford Ferry formula [11]:

$$r_m = [((2.9 - 1.75\epsilon) \times 8\eta l Q)/\epsilon \Delta P] e^{(1/2)} \quad (5)$$

where η is the viscosity of water at 8.9 $\times 10^{-4}$ Pa.s, Q is the permeate volume in m^3s^{-1} , and P is the pressure at 100kPa.

For the determination of the pore radius of the microfiltration membranes, solute transport through the pores was measured to afford this data. The classic formula of the Guerout Elford Ferry equation was specifically chosen for application in this study because of its simplicity. Various other formulae that have been used for determining the mean pore radius include the Pappenheimer-Ussing, Kedem-Katchalsky, and Mikulecky formulae. Whereas the latter ignores water viscosity as a factor in solute transport, the other three formulae are inclusive of this parameter [12].

To determine the pure water permeation and the pH responsiveness of the membranes, dead-end cell filtration experiments were carried out using the HP4750 stirred cell with a diameter of 4.1 cm (Sterlitech Corporation, U.S.A). For these investigations, the membranes were stored overnight in water and solutions of varied pH values and thereafter compacted for 10 minutes at 0.2 MPa before testing. The aqueous solutions of varied pH values were passed through the membrane at 0.1 MPa prior to measurement of the permeated volumes. The same pressure conditions were applied for all experiments and the solutions were stirred at 600 rpm and 20°C.

Membrane performance was assessed by passing 1000ppm BSA solution as a model solute (at pH ranges of 1, 5, 7 and 9) through the membrane. The rejection, R , of BSA, was determined by UV absorption through the use of

equation 6:

$$R\% = [(1 - C_p)/C_f] \times 100 \quad (6)$$

where C_f and C_p are concentrations of the BSA feed and permeate, respectively.

Passing deionized water through the membranes before exposure to the foulant (BSA) provided the initial flux (J_0). After 1 hour's foulant exposure (i.e. after BSA rejection), the membranes were backwashed with 250 mL deionized water. The same experiment was repeated for the washed membranes to give the post-fouling flux (J_1), which was then used to determine the flux recovery ratio ($FR\%$) using the following equation [11]:

$$FR(\%) = (J_1/J_0) \times 100 \quad (7)$$

Additional information on potential membrane fouling was obtained by batch adsorption experiments. The 3.0 \times 3.0 cm square membrane pieces were inserted into a 50mL BSA solution of the same concentration. The containers were agitated in a water bath shaker for 24 hours, keeping the temperature at 20°C. The adsorbed mass, M_{BSA} (μg), was then determined gravimetrically by applying the following equation:

$$M_{\text{BSA}} = M_A - M_B \quad (8)$$

where M_A and M_B are respective the masses of the membranes before and after adsorption.

According to Shi et al. [10], the investigation of the pH reversibility is also important in order to gain information on the pH switching character of the membranes. According to the cited work, permeation fluxes would be anticipated to respond to environmental stimuli due to the pH-stimulated pore gating effects. To carry out these experiments, permeation fluxes were measured by interchangeably passing solutions of pH 1 and 9 over ten (10) cycles through a membrane prepared from the grafted PES.

3. Results and discussion

3.1. Polymerization optimization

Since the use of AIBN as an initiator for the grafting of vinyl carboxylic functional groups onto PES powder has, to the best of our knowledge not been reported, it was therefore deemed necessary to investigate the behavior of this initiator over a range of increasing temperatures and monomer concentrations. Figure 2 illustrates the optimization of the graft parameters in terms of temperature and monomer/initiator concentration. The former is depicted in Figure 2(a). As can be observed, no grafting was recorded at the initial temperature of 60°C. However, increasing the reaction temperatures to 65°C allowed an enhancement in the DG resulting from the augmented formation of radicals which encouraged the graft polymerization. Conversely, further increasing the temperature beyond 65°C did not seem to enhance the DG. This can be due to the promotion of PMAA chain scission reactions at higher temperatures. As such, for the grafting of PMAA onto PES using AIBN, the DG was found to be more controllable at 65°C when compared to higher polymerization temperatures. Similar observations have been reported in literature for the grafting of PMAA chains onto PVDF [5].

Figure 2(b) illustrates the effect of monomer/initiator concentration on DG at the optimized temperature of 65°C. From 5-40m/m% reagent concentration, a linear trend in DG (from 4.5-22.4%) was observed; this demonstrates a positive response of the monomer to the grafting process since sufficient radicals were generated thereby stimulating the polymerization reaction. At 60m/m%, the growth in DG was hindered to the extent that homopolymerization and chain scission were encouraged. Large aggregates of grafted powder also ensued at this point; this suggests structural/rheological damage to the PES, which is quite evident in Figure 3(a-c).

The virgin PES powder (Figure 3(a)) possesses uniform grain sizes of 1-800 μm where large aggregations of extremely hard granules were formed at high monomer/initiator concentrations. No large aggregations were observed for samples with lower DG, and this suggests that excessive concentrations of AIBN can be damaging to the polymer. The third specimen depicted in Figure 3(c) exhibited a lower DG and larger aggregations than that shown in Figure 3(b) thus confirming the observed damage to PES. Furthermore, it was observed that these aggregations start forming immediately upon and after the addition of initiator to the reaction vessel and continued after the introduction of the monomer. This means that at reagent concentration of 40m/m% and higher, the diffusion of the monomer into the PES powder is hindered thus

resulting in a lower DG.

It is also worth noting that high DG levels may also present greater challenges than benefits in the envisaged preparation of membranes; high DG may result in low solubility of casting solutions, which can affect filtration properties as previously reported [10]. This may explain why a decrease in DG was observed. Large aggregates formed when DG levels were excessive and may hinder the diffusion of the initiator and monomer into the PES powder, which allows polymerization of the monomer. Overall, these observations suggest that the AIBN initiator is suitable for low grafting of up to ca. 22%. The low DG that was achieved proves to be useful for the preparation of membranes as envisioned in this work, where high DG has been observed to affect the solubility of the casting solution and thereby compromising membrane performance [5]. To this end, pristine PES powder and grafted PES powders with DG of 2.6, 3.7 and 5.8% were used to prepare the membranes PES0, PES2.6, PES3.7, and PES5.8, respectively. Further characterization and application of these membranes were thereafter undertaken.

3.2. Polymerization response to AIBN initiation

Figure 4 depicts a comparison between the initiator efficacies of AIBN with BPO (as one of the most widely used thermal initiators). It would be useful to utilise AIBN as opposed to the widely used BPO because of the relatively lower temperatures used; this will be important for large scale modification of the polymer. The amount of initiator required to obtain a similar or enhanced result was used as a measure of initiator efficacy. The effect of the specific amounts of the initiator on DG of grafted PES powder was investigated. The DG levels were found to increase with an increase in the amount of the initiator. It has already been demonstrated that high amounts of BPO are necessary for the successful grafting of the MAA [9]. While BPO amounts of 0.0825 mmol or higher were used in [9]. The former is in direct contrast with the lower AIBN amounts (starting at 0.005 mmol) used in the work reported herein. As such, the effect of an increasing amount of the two respective initiators (i.e. AIBN and BPO) on DG was investigated and 0.005 mmol AIBN was found to give a DG of 7.6%. Furthermore, while

0.03 mmol of AIBN resulted in a DG of 22.4%, the same amount of BPO (0.03 mmol) resulted in a DG of less than 1%.

The enhanced DG brought about by the presence of AIBN seems to indicate greater monomer conversion that ultimately leads to the completion of the reaction. This, in turn, suggests that copolymerization was favored over homopolymerization. In contrast, the presence of BPO gave rise to lower DG levels; the poor monomer conversion that is deduced from these results suggests that AIBN is more suitable for this type of grafting. A study involving the use of BPO and AIBN in the initiation of homogeneous copolymerization of MAA and styrene-butadiene rubber has revealed the superior reaction kinetics and graft yields associated with AIBN [13]. Furthermore, an initiation mechanistic pathway reported for the AIBN (i.e. monomer radical formation) proved to be much more efficient than the substrate hydrogen abstraction process associated with BPO.

In this work, a similar initiation mechanistic pathway involving AIBN was observed in the grafting of PES; it appears that AIBN leads to an improvement in the reaction time and DG when compared with studies reported in the literature. The AIBN initiation reaction approach is, therefore, more suitable for reactions that are geared towards the preparation of pH-sensitive and low-fouling microfiltration [5,9]. Similar observations were made for the grafting of PMAA chains and acrylic moieties onto PES, using other bulk or surface modification approaches [10,11]. However, the use of AIBN, which is presented herein, opens further opportunities for the grafting of acrylic and vinylic moieties onto PES. Furthermore, this reaction eliminates the use of toxic organic solvents and catalysts such as dimethylformamide (DMF), acetone, sulfonic acid, and/or Mohr's salt (ammonium ferrous sulfate hydrate) that require extensive removal techniques. To this end, this approach is far more environmentally friendly and less expensive than traditional approaches [5,10,11]. The method reported herein was achieved within a relatively short period of time; DG saturation was reached after only 3.5 hours. Longer reaction periods have been reported for similar work that utilizes BPO [5]. Furthermore, when compared with methods that are currently available in the literature, the method presented herein does not require any overnight swelling of the PES, and no removal of the resultant swelling solvent from the PES is necessary.

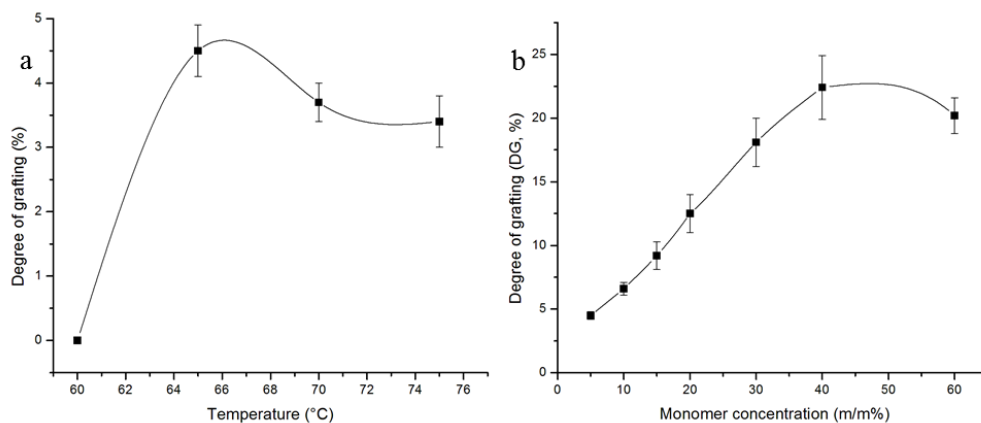


Fig. 2. The response of DG to a) temperature on DG in the presence of AIBN at 5.0% (v/v) monomer concentration; and b) increasing monomer concentration.



Fig. 3. Effect of reagent concentration on polymer powder appearance: a) Pure PES, b) DG= 22.4%, and c) DG= 20.2%. It is imperative to note the aggregations of powder that start forming from b).

Figure 5 shows the FTIR spectra of both the pristine and grafted PES powders, which were prepared using AIBN as an initiator. The absorption bands appearing at 1300 and 1320 cm^{-1} are characteristic of PES. Two additional bands were observed at 1579 and 1486 cm^{-1} in the FTIR spectrum of the grafted PES powder. These bands were attributed to the aromatic chain vibrations and aromatic stretches of the PES, respectively. Upon PMAA grafting, the two aryl bands appearing at 1579 and 1486 cm^{-1} intensified. This indicated the hydrogen abstraction of the aromatic ring followed by subsequent substitution by PMAA side chains. In all the grafted PES powders, the presence of PMAA was established by the appearance of bands at 1725 and 1759 cm^{-1} in the requisite FTIR spectra, which correspond to the stretching vibrations of COO^- groups of PMAA and crosslinking. The wavenumbers of the bands observed in this study correspond to those that have been reported in the literature [8].

Figure 6 shows the XPS core-level C 1s spectra obtained from the analysis of the membranes prepared from pristine and grafted PES powders. The spectra were curve-fitted and deconvoluted by Gaussian sum functions, to give the requisite peak components. In Figure 6(a), the spectrum of PES0 is shown, and the observed peaks at binding energies (B.E.) of 284.5 and 286.1 eV were assigned to the C-C, C-O, and species, respectively. Another peak was observed at 292.1 eV where the phenyl rings of PES are found; the characteristic PES peak was therefore observed for both membranes [14]. In the same region, the adventitious carbon has also been reported in the literature. Adventitious carbon is usually a film of organic material or adsorbed carbon mono or dioxide that forms easily on polymeric surfaces even upon brief atmospheric exposure [15].

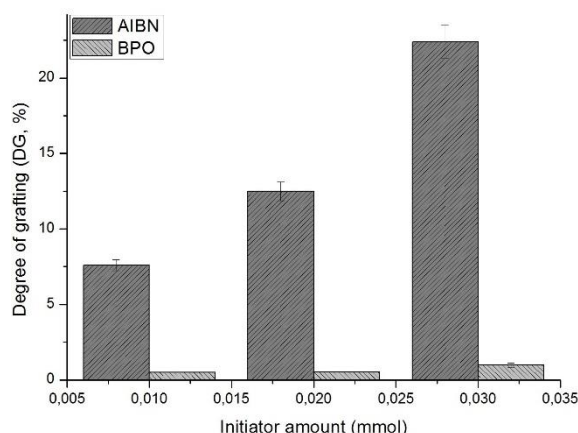


Figure 4. DG vs amount of (a) AIBN and (b) BPO, at equal amounts of the initiator.

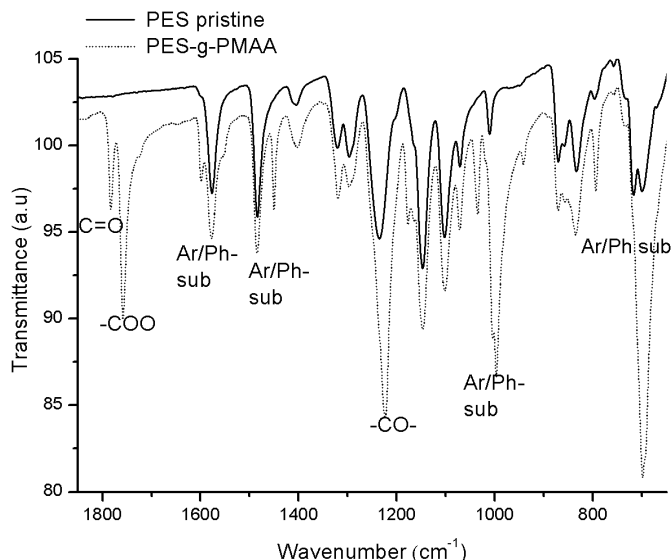


Fig. 5. FTIR spectra of the pristine and grafted PES powders obtained via initiation with AIBN.

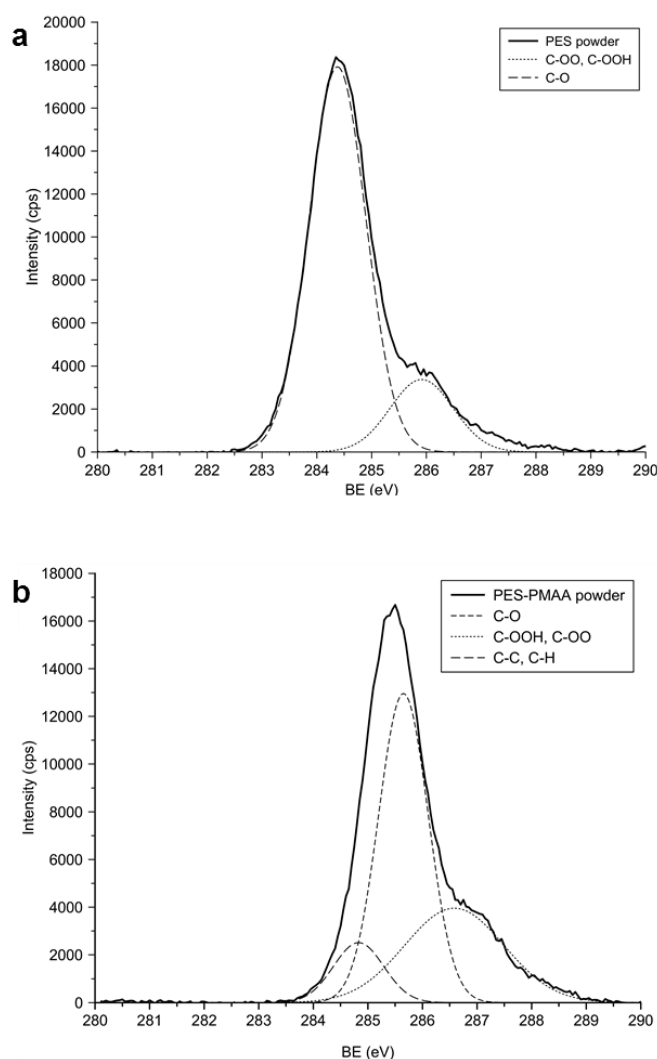


Fig. 6. Deconvoluted core-level C 1s XPS spectra for the membranes, (a) PES0 and (b) PES-PMAA sample with DG=13.6%.

As shown in Table 2, the C-O species comprised 20.3% of PES0. This composition increased to 54.3% after grafting (sample of DG=16.3 was used for analysis). Similar observations have been reported for this irregular upward discrepancy between DG and C-O species coverage. The latter observation can be explained by the upward movement of grafts to the membrane during phase inversion. The C-OH and O=C-OH species were also detected at 286.6 and 287.2, respectively, and this is an indication that the grafts are chemically bound to the PES within the membrane matrix. The composition of these species increased from zero to 33.2%, for the same reasons noted for the heightened detection of C-O species. Meanwhile, the C-C/C-H species decreased from 79.7 to 12.5%, and this was indicative of the grafting occurring via phenyl substitution. Furthermore, the decrease in C-H coverage shows that the surface of the membrane was covered with a dense layer of PMAA and that the C-C/C-H species could only be detected to a minimal level [14].

3.3. Contact angle analysis

The dependence of hydrophilicity on DG for the casted membranes is presented in Figure 7. The natural relative hydrophobic property of PES was deduced from a contact angle of 69° for pristine membrane, PES0. Thus, upon grafting, the hydrophilicity of the membranes increased as evidenced by the contact angle decreasing from 69 to 42°, with increasing DG. This observation, which was ascribed to the increased presence of hydrophilic side chains attached to the PES backbone with increasing DG, demonstrated that the grafting of PES with PMAA yielded a notably hydrophilic composite. As reported in the literature [6,9], hydrophilicity is an important membrane parameter with regards to the resistance of membrane fouling and maintenance of stable and high water permeate fluxes.

3.4. Membrane morphology

Figure 8 shows SEM cross-sectional images of the membranes casted from pristine PES and grafted PES powders. The PES0 membrane in Figure 8(a) shows an asymmetric structure with twisted pore morphology from the skin layer down to the porous sublayer. The porous sublayer occurred as a direct consequence of porogen (PVP) where macrovoids can be observed due to the rapid liquid-liquid demixing and resultant intrusion of coagulant (water) through the surface of the forming membrane. As shown in Figure 8(b), the PMAA-grafted PES powder imparted the formation of long fingerlike pore structure to the asymmetric membrane at low DG of 2.6%. This fingerlike structure was attributed to the presence of PMAA side groups in the membrane matrix, which results in delayed solvent/nonsolvent exchange. A further increase in the DG to 3.7% (Figure 8(c)) resulted in the favored formation of macrovoids in the sub-layer. However, from PES3.7 to PES5.8 no visible changes could be observed due to low increment in DG (Figure 8(d)). The thermodynamic and kinetic factors, nucleation and growth mechanisms, have been used to illustrate the contributions of the skin and support layer to the structures. It can therefore also be seen on the surface of the membranes whereby the randomly spread large pores, which were present before grafting, were reduced in size on PES 5.8 and uniformly spread throughout the membrane. The morphologies of the membranes fabricated in this research conform to those of other researchers [2,9].

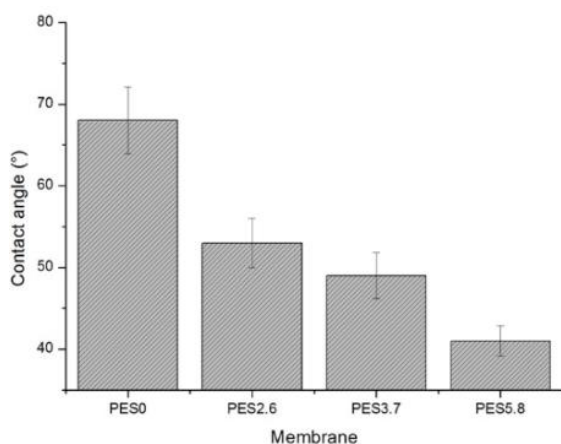


Fig. 7. Pure water contact angle analyses for the casted membranes prepared from powders grafted via AIBN.

Table 2

The surface species composition, binding energies and surface coverage before and after grafting, from XPS data using pristine PES powder PMAA-grafted PES. The grafted PES sample used had a DG=13.6% to exclusively show compositional changes to PES after grafting instead of a sample of low grafting.

Core-level	Pristine PES membrane			PES-PMAA membrane		
	BE (eV)	Peak area (cps)	Composition (%)	BE (eV)	Peak area (cps)	Composition (%)
C 1s	284.5	23342	79.7	284.9	3409	12.5
	286.1	5937	20.3	286.6	14806	54.3
	--	--	--	287.2	9031	33.2

Table 3

Water uptake, porosity and pore radii for the membranes.

Membrane	Water uptake (%)	Porosity (ϵ , %)	Pore radius (μm)
PES0	213.3 \pm 12.1	50.6 \pm 1.8	0.62
PES2.6	374.6 \pm 18.3	85.4 \pm 2.1	0.45
PES3.7	376.2 \pm 14.4	93.2 \pm 2.5	0.41
PES5.8	354.3 \pm 17.7	89.1 \pm 2.0	0.39

The water uptake results of the membranes, which are presented in Table 3, have revealed that PES0 absorbs 213% of water when measured against its dry weight. Upon PMAA grafting of the PES, the absorption capacity of the resultant PE2.6 towards water doubled to 375% relative to its dry weight. The increased water capacity was ascribed to an increased tendency of the PMAA hydrophilic groups to absorb water. Acrylic moieties such as PAA and poly(hydroxyethyl methacrylate) (PHEMA) have a higher affinity for water. Therefore, these moieties increase the swellability of the final modified polymer and thus enhance, as demonstrated in this work, the water uptake of the membranes [2,5,13]. The decreasing pore size was attributed to the increasing availability of the PMAA groups in the due to high crosslinking as the DG increased. As a result, pore formation during phase inversion was limited. The membrane water uptake and porosity results of this study concur with works published by other researchers [11]. Membrane porosity also increased from 50.6 to 93.2% following grafting. The mean pore radii of PES0 to PES5.8 membranes were calculated using the increased porosity values of 93.2%. A significant decrease in the pore size of the membranes prepared from grafted powders (when compared with pristine membranes) can also be ascribed to the amplified availability of PMAA groups. The increased number of PMAA groups allowed enhanced compatibility between non-solvent and solvent and the resultant formation of many but smaller pores (porosity vs pore size). However, for the membranes prepared using the grafted powders, a small disparity in pore size that is consistent with the cross-sectional SEM images presented in Figure 8(e-f) was observed. The decreased pore radii of the grafted membrane were complementary to studies that were previously reported by other researchers [2,10,16].

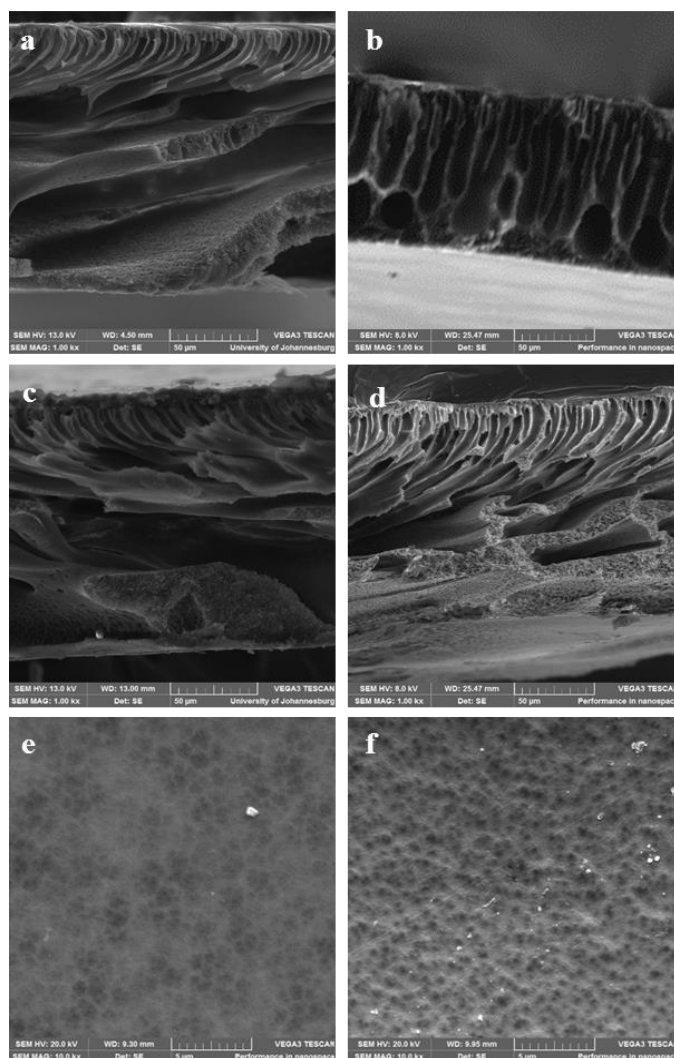


Fig. 8. Cross-sectional SEM images for the membranes prepared from pristine and grafted PES powders: (a) PES0 (pristine), (b) PES2.6 (DG= 2.6%), (c) PES3.7 (DG= 3.7%), (d) PES5.8 (DG= 5.8%), (e) and (f) illustrated the membrane surface for PES0 and PES5.8, respectively. It is worthy to note the differences in pore size and porosity.

3.5. Water permeation fluxes

Figure 9 presents the hydraulic resistance (pure water flux against increasing pressure) of the membranes across different DG values, at pH 7. As expected, the results indicated that the flux through the membrane is dependent on the operating pressure and DG. The PES0 membrane exhibited an increase in fluxes with the increase in operating pressure as increased volumes of water are forced through the membrane. For the membranes prepared using the grafted powders, water fluxes increased with DG; similar results have been reported [5,9]. The increased water fluxes can be attributed to the enhanced porosity of the membranes brought about by increasing membrane grafting. The increased membrane porosity allowed greater volumes of water to diffuse and permeate at any given point in time and pass through the lowly cross-linked PMAA chains within the porous structure, which ultimately led to improved fluxes [10,17].

Figure 10 depicts the water permeability of PES3.7 and its reversibility in response to pH stimuli. The PES3.7 membrane was chosen because preliminary studies on pH-dependent fluxes have revealed this membrane to be the most responsive. No comparative experimental analysis of PES3.7 and PES0 was undertaken in this study due to the latter possessing no pH-sensitive functional groups [5]. According to Figure 10(a), higher fluxes were observed at pH 1 when the PMAA chains are protonated, thus causing an open gating effect within the pores and ultimately allowing the highest amounts of water to permeate through the membrane at any given time. The latter observation was followed by a decrease in fluxes when increasing pH values to 5. The decrease in fluxes is due to the decreased number of protonated side chains; since the isoelectric point of PMAA is 4.8, the side chains stretch and the pores contract in size to impede water permeation. The trend of decreasing fluxes continued from pH 5 all the way to pH9 as has been previously reported by others [16]. The resulting restriction in the flow of water through the asymmetric structure of the membrane occurs, thereby decreasing fluxes. The results of pH reversibility PES3.7 are presented in Figure 10(b).

The pH reversibility phenomena that were observed in this study serve to confirm the smart or switching property of the membranes, whereby such behavior resulted from a response to external stimuli. Sensitivity relating to pH was also found to be stable over ten cycles of interrogation as a direct result of the stimuli sensitive grafts on the PES surface. The ability to switch between low and high fluxes over extended interrogation cycles attested to the stability of the membrane with regards to pH sensitivity [18]. Results reported herein compete with those reported in the literature due to the high fluxes observed at low pH, and the very low fluxes at high pH. This means that these membranes exhibit enhanced response to pH stimuli when compared to other membranes prepared using other methods [9,10,18].

3.6. Protein rejection, adsorption, and low-fouling studies

Protein rejection and adsorption profiles of the membranes are shown in Figure 11. According to Figure 11(a), BSA protein rejection was dependent on two parameters, namely DG and pH. For the former, a rejection of 76% of the initial BSA concentration at neutral pH was reported for PES0. This relatively low rejection rate can be attributed to the presence of large membrane pores as well as the lack of PMAA groups on the surface and

within pores, which repel and minimize the flow of protein. After grafting, an increase in rejection was observed whereby 82, 89, and 92% of the protein was rejected by PES2.6, PES3.7, and PES5.8, respectively. This can be ascribed to the reducing size of the pores and the enhanced repulsion forces existing between PMAA groups and BSA molecules [10,19].

In addition to the observed positive effect of DG on BSA rejection, pH played a further role in this regard. The rejection was enhanced from pH1 to 7 and pH 9. At pH 1, the effect of environmental stimuli can be observed even on PES0 where the rejection was enhanced from 73% to 81%. Given the previously mentioned absence of PMAA grafts in the PES0 membrane, the rejection was now affected by the response of BSA to pH. BSA has been reported to undergo structural conformations at low through high pH. At pH 1, which is lower than its isoelectric point (pH 4.8), the structural conformations of the molecule are such that it undergoes protein folding. Furthermore, pore blockage by the protein can ensue, resulting in the enhanced exclusion of BSA from the membrane pores; hence the reason why a higher rejection has been reported in the literature [20]. The aforementioned protein folding reduces the size of BSA, and some molecules can thus pass through the membrane. At pH levels of 7 and 9, which are higher than the isoelectric point, the conformations favor protein unfolding or denaturation [21]. This protein unfolding can further result in agglomeration of the protein molecules, and hence the rejections were found to increase to 76% and 81% at the respective pH values of 7 and 9. With this knowledge, the rejections were found to increase in membranes PES2.6 to PES5.8.

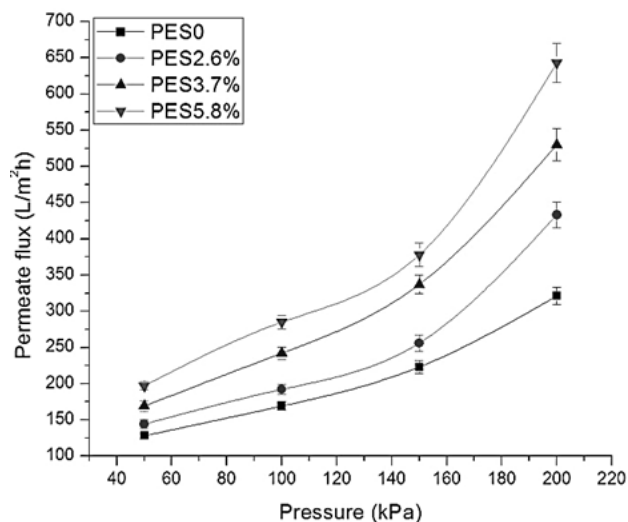


Fig. 9. Hydraulic resistance (pure water flux against increasing pressure) for the membranes prepared from pristine and grafted PES powders.

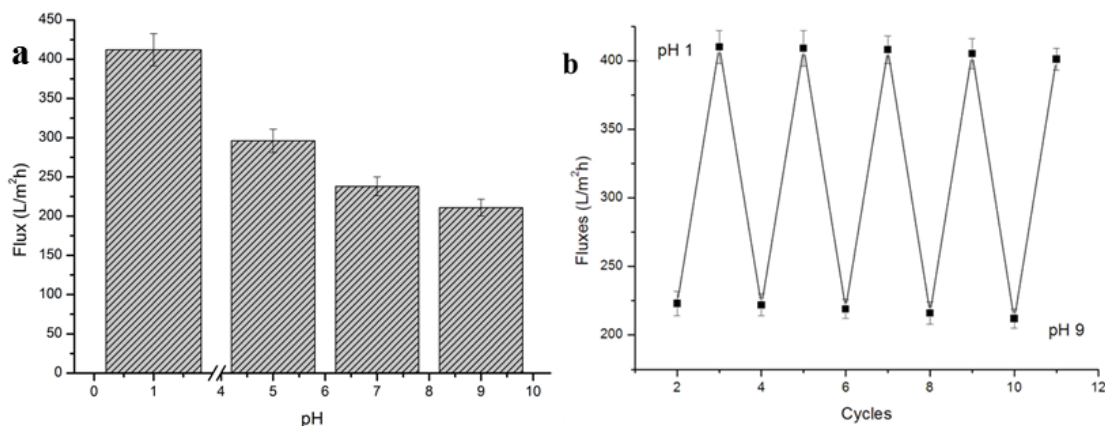


Fig. 10. Water fluxes through the PES3.7 membranes: (a) the pH stimuli-dependent fluxes at pH 1, 5, 7, and 9; and (b) the pH reversibility character at pH 1 and 9. For clarity of the illustrations, only PES3.7 was chosen to explain the observed membrane character from here going forward. The pH points of 1 and 9 were selected to evaluate the acid and basic conditions – a common practice as can be seen in Deng et al. [5].

The rejection increase can be attributed to the presence of pH-sensitive PMAA groups, which shrink at low pH thus increasing pore size. This increase in pore size allows some BSA protein diffusion through the membrane. However, as evidenced by the high rejection of 78% of the former, the protein molecules can pass at a lower degree through PES2.6 than through PES0. This is because both the PMAA side groups and the protein molecules are protonated, thus introducing repulsive electrostatic interactions. Beyond the isoelectric point, the same holds true because the PMAA groups and BSA molecules undergo deprotonation. However, the deprotonation of PMAA groups this time round reduces the membrane pore size. Furthermore, the BSA protein has also been reported to agglomerate to up to 300 nm [22]. This synergy between the pore size reduction and BSA molecular agglomeration further limits the diffusion of BSA molecules through the smaller membrane pores. As a result, enhanced rejections of up to 97% at pH 9, were observed [19,21]. The improved protein rejection observed at pH 9 that is exhibited by the membranes prepared from grafted PES powder indicates that this property is tunable to external stimulus. Additionally, the protein rejection character of the membranes was found to be comparable to the rejection phenomenon presented in the literature for achieving separations that are greater than 96% [10].

Solute rejections are also known to be affected by concentration polarization [12]. It should be noted that the experiments were carried out in a vigorously stirred cell so as to mitigate the effects of concentration polarization. During concentration polarization, some of the solute (i.e. BSA) may accumulate on the membrane surface, thus restricting solute diffusion. This possible occurrence of solute diffusion, together with protein agglomeration can result in an increase in the protein rejection observed in this work; this has been reported for microfiltration membranes prepared by other researchers [22].

The adsorption of BSA by the membranes is illustrated in Figure 11(b). The highest amounts of BSA adsorbed (18.5 and 5.8 $\mu\text{g}/\text{cm}^2$) were recorded at pH levels 1 and 9, respectively. The high adsorption rate can be attributed to the lack of hydrophilic PMAA groups, which assist in minimizing attraction amongst the hydrophobic BSA molecules located on the membrane surface [23]. This lends further credence to the phenomenon of membrane blockage, which was observed for protein rejection. The decreased protein adsorption at pH 9 was attributed to the previously described conformational character of BSA. Lower BSA adsorption was observed for the membranes prepared from grafted PES, in comparison to those prepared from pristine PES. The adsorption of BSA by the pristine membrane at pH 1 was 18.5 $\mu\text{g}/\text{cm}^2$. However, an impeccable decrease of the BSA adsorption (12.0 $\mu\text{g}/\text{cm}^2$, amounting to 32% resistance to protein adherence) was recorded at under similar conditions for the PES membrane. The BSA adsorption tended to improve with pH and the amount of BSA protein adsorbed decreased from 5.8 $\mu\text{g}/\text{cm}^2$ to as low as 1.2 $\mu\text{g}/\text{cm}^2$ at pH 9; this amounted to a reduction of about 80%. The results obtained herein indicate mitigated protein adhesions or fouling material adsorption onto the membrane matrix. Decreased foulant adherence properties of the membrane material are important for the preparation of low-fouling membranes for envisaged water treatment applications. The 1.2 $\mu\text{g}/\text{cm}^2$ protein adsorption observed in this work is lower than the minimum of about 3.8 $\mu\text{g}/\text{cm}^2$ reported in other works where much higher grafting was even required [16,17]. Furthermore, these results seem to suggest that extensive grafting is not required for the fabrication of PES microfiltration membranes with low protein adsorption and high protein rejection properties. The membranes prepared from PMAA-PES powders of

low grafting exhibited BSA rejection levels similar to those accessed through high grafting and were reported in the literature [5,9,10]. The low grafting requirements coupled with low BSA protein rejection capabilities augurs well (both in terms of initiator and MAA) for the membrane separation efficiency of these membranes, which can be fabricated using fewer amounts of raw material. The synthetic method for accessing these membranes and the applications thereof promises to be very cost-effective when compared with similar membrane reported in other works.

Figure 12 illustrates the flux recovery ratio (FR%) in pure water (after backwashing). The flux recovery ratio is a very important membrane property for the fabricated membranes. It was observed that both normal batch mode washing and front-washing methods resulted in lower FR% than backwashing. For this reason, this study reports on the latter. The ability to backwash with only water suggests the ease with which the membrane can be cleaned as a result of the low protein adsorption. This eliminates the need for harsh chemicals and long washes times, which lowers maintenance costs. After this backwashing, a FR% of 50 \pm 2% for the PES0 was recorded. These results indicate that fairly high levels of fouling had occurred. However, FR% of 73 \pm 4% was recorded for PES2.6, and this FR% increased with DG to 86 \pm 3% for PES3.7. This enhancement in FR% can be attributed to the increasing presence of the hydrophilic PMAA with DG. This, in turn, results in increased fouling resistance and improves flux recoveries due to the decreased adsorption protein adsorption onto the membrane matrix, and thus increased antifouling behavior. Furthermore, the membranes become easier to wash when PMAA groups are present within the matrix [23,24]. The FR% for PES5.8 was found to be 84 \pm 2%, which was within the error for membrane PES3.7. Overall, the antifouling property was enhanced for the membranes prepared from the grafted PES powder relative to the pristine membrane. The cycling periods of the membranes were also investigated with a view to determining their stability following repeated use and fouling exposure. The enhanced antifouling propensity of PMAA-PES membranes means that these membranes can be expected to possess increased longevity and robustness; that is they are easy to clean and are thus cost-effective in terms of power consumption and cleaning requirements. The demonstrated ability to clean the used membranes with deionized water further corroborates the anti-fouling and thereby cost-effective nature of these membranes. It suffices to say that very few works have reported on this ability in literature [11, 16].

The cycling period of the membranes was also investigated in order to determine their stability during repeated BSA fouling exposure. The FR% of PES0 after the first two cycles was only about 54%. The FR% of the PES3.7 increased steadily, and by the tenth cycle, it had reached 86%. The remarkable enhancement in membrane stability associated with PES3.7 can be attributed to the presence of hydrophilic and antifouling PMAA groups within the membrane matrix [11]. Consequently, by the tenth cycle PES3.7 had lost only 2% of its original FR of 86%. Yet again, the effect of presence of the antifouling PMAA grafts assists in the long term the cyclability and lifespan of the membrane as compared to PES0 which does not possess hydrophilic functional groups. The ability of hydrophilic moieties to minimize fouling and maintain high FR% has previously been reported [16]. The membranes in this work possess enhanced FR% as compared to those reported in the literature where DG of greater magnitudes was required for the achievement of the same result. The high cyclability of the membrane also indicated greater stability of the membrane in terms of long term use. These results indicate that the modification method is feasible and it leads to enhanced membrane properties [5,9,25,26].

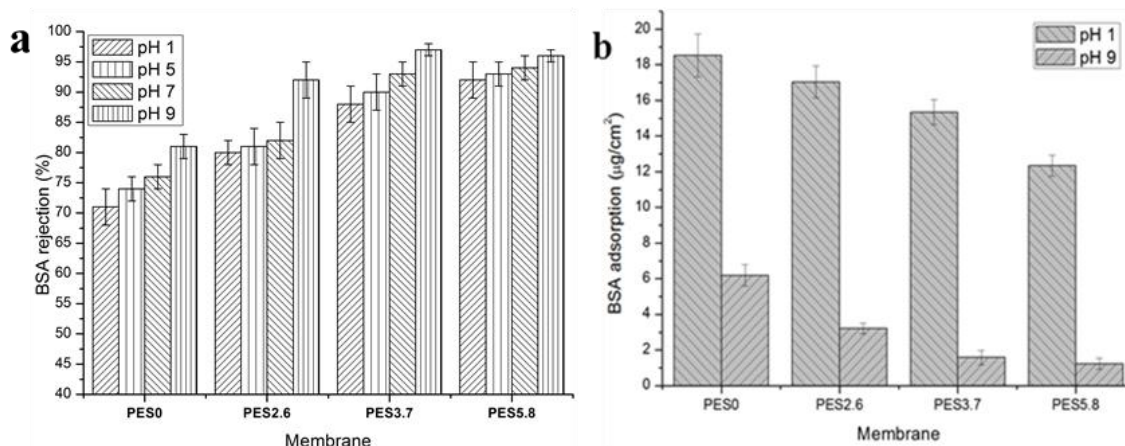


Fig. 11. Membrane properties in terms of (a) Protein rejection at pH 1, 5, 7, and 9; and (b) protein adhesion properties of the membranes.

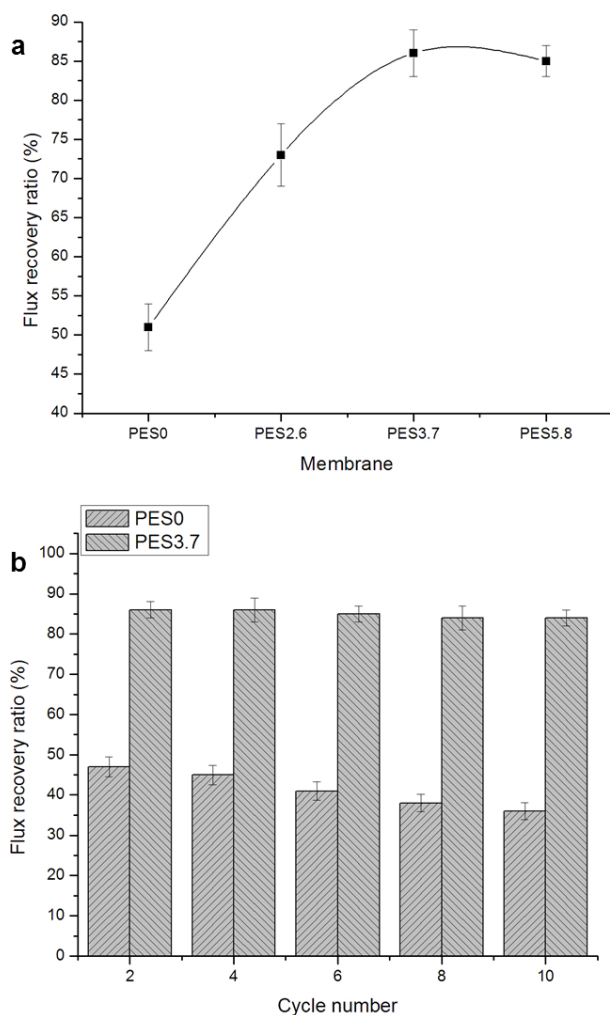


Fig. 12. Flux recovery ratio (FR%), as a measure of fouling propensity for the membranes.

In summary, as shown in Table 4, the several membranes have been prepared using different approaches highlight the extent of modification that is required for the achievement of specific important properties of the synthesized membranes. A comparative analysis of the current work and already published methods was undertaken with a view to highlighting the benefits of the synthetic method presented herein. For instance, in the study by Nady et al. [23], several modification steps were carried out and a high DG of 75.9% was required to obtain an FR of 95.4%. Additionally, in the current work, attempts were made to present membranes that possess much lower protein adsorption of 1.8 compared to the 3.5 – 4.0 $\mu\text{g}\cdot\text{cm}^{-2}$ that was achieved by Qin et al. [16]. The modification presented in this work is simple and it requires lower reaction times, no catalysts, and solvents to achieve commendable FR. This indicates that the membrane reported herein has great potential for use in processes where antifouling properties are very critical.

4. Conclusions

In this work, the heterogeneous AIBN-initiated functionalization of PES powder with MAA is reported for the first time. As such, this work constitutes a significant contribution to scientific literature. The membranes prepared from the grafted PES powder were compared with those prepared from pristine PES and were found to possess amplified hydrophilicity, water uptake, and protein rejection properties. Furthermore, the membranes were found to possess envisaged low protein adhesion and fouling properties. These properties were achieved at lower temperatures and with extremely low grafting of hydrophilic side groups such as PMAA than reported in literature. The success of this greener synthetic method augurs well for the production of membranes in a cost-effective manner. As evidenced by the maintenance of high fluxes after 10 cycles of fouling exposure, the properties imparted on the membranes through the modification process are essential for membrane durability, stability, and longevity. This means the membranes prepared in this work have great potential practicability in water treatment due to ease of cleaning and lower replacement costs. Potential water treatment applications of these membranes include protein filtration and treatment of water contaminated with bacteria and other biological matter. Other potential applications outside the scope of water treatment include dialysis and plasmapheresis.

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Table 4

Overall comparison of the literature to the values as found in this work.

Membrane/s prepared from	Method	Notes	Highest DG for best result (%)	Lowest protein adsorption ($\mu\text{g}\cdot\text{cm}^{-2}$)	FR%	Ref.
PVDF and PES modified with AA and Protein A	Thermal, plasma, surface coating	Sequential steps of modification	N/A	0.09 ($\text{mg}\cdot\text{ml}^{-1}$)	N/A	[3]
PVDF with AA MAA	γ -irradiation	Exposure to radiation; high DG required	29.6; 21.3	N/A	~85 and ~92	[5]
PES with MAA	γ -irradiation	Exposure to radiation	20	N/A	N/A	[9]
PES, with polyvinylacrylate (PVA), polyethylene glycol (PEG), and chitosan	UV, UV/ozone interfacial polymerization (IP)	High BSA adsorption	N/A	18.6	N/A	[14]
PES with AA and HEMA	AIBN-initiated solution polymerization	Long reactions	N/A	3.5; 4.0	55-110	[16]
PES with feluric acid	Enzyme-catalyzed grafting	excessive modification required	75.9	2.1	95.4	[23]
Polystyrene (PS)/PES, PAA	Atomic replacement radical polymerization	Long reactions, solvents, product cleaning	N/A	N/A	N/A	[26]
PES with MAA	AIBN-initiated heterogeneous grafting	Inexpensive processes, no added catalysts, solvents, ease of cleaning	3.7	1.8	86%	This study

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