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Fouling-resistant brush-like oligomers of poly(3-aminophenol)

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ABSTRACT

Membrane fouling can be considered the major obstacle in the application of membranes in different separation processes. This drawback can be minimized (or avoided) by cutting off the interaction between the foulant itself and the membrane's surface. For that, membrane surface modification has been presented as an effective tool to improve the membrane's performance. In the current paper, laccase-catalyzed bio-grafting of 3-aminophenol (3-AP) onto poly(ethersulfone) (PES) membranes is presented. This modification was carried out at room temperature and in aqueous medium using green catalyst; thus, the process can be safely labelled "green surface modification". The modified PES membranes were evaluated based on their performance and bulk properties. The effects of modifications on the membranes' performance, the flux reduction, and the protein repellence were assessed. Also, the flux reduction due to (irreversible) protein adsorption was determined. The change in the color of the modified membranes was also correlated to the amount of the added modifier per unit membrane area (the grafting yield). Both blank and modified membranes were characterized using TGA, DSC, XRD, FTIR-ATR, ^{1}H-NMR, SEM as well as mechanical strength testing. Moreover, the shape and structure of the modified layer(s) grafted on the spin-coated PES layer on silicon dioxide slides were investigated using other analytical techniques that include the static water contact angle, scanning probe microscope (SPM), and Raman spectroscopy. This green modification slightly improved both the membranes' performance and the membranes' bulk properties. The water flux of the modified membranes increased up to 35% relative to the blank (unmodified) membrane, and the protein adsorption was reduced up to 90%. In addition, a very slight change in the membranes' strength was observed. The formed layer(s) most likely contain both free amine groups and hydroxyl groups that are present as brush-like oligomers of 3-AP grafted on the membrane surface.

Keywords: Poly(ethersulfone) membrane; Antifouling surface; 3-aminophenol; Biocatalysis; Brush-like oligomers; Green surface modification

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1. Introduction

Green chemistry has been targeted as a short, direct route to a sustainable environment. Recently, enzymes have been utilized to address many of the challenges of applying green chemistry in industry. Enzymes are biological catalysts that work by lowering the activation energy required for a reaction, thus dramatically increasing the rate of the reaction. Enzymes differ from ordinary chemical catalysts in several aspects, such as their mild reaction conditions and high reaction specificity [1,2]. Laccase [EC 1.10.3.2], a blue multi-copper oxidase [3], has attracted considerable attention as a green catalyst in a wide variety of processes, such as delignification and pulp bleaching [4], organic synthesis [5], bioremediation processes [6], and surface modification [7]. Laccase-catalyzed modifications are reactions that are accompanied by a reduction of molecular oxygen to water as the only by-product of the catalytic cycle of laccases. Laccases have a wide substrate range that can be further extended by the use of laccase-mediators that make laccase an ideal candidate for the development of green chemistry [8–10].

The different isomers of aminophenol are interesting materials because they carry two groups (–NH_2 and –OH) that can be oxidized mainly by electrochemistry [11,12]. In the electrochemical polymerization of aminophenols, the relative position of these two groups is important because the produced oligomers or polymers are completely different [13–15]. The electrochemical polymerization of ortho-aminophenol (2-AP, *O*-aminophenol) has been proposed to have either a ladder polymer structure by phenozaxine units [16,17], or linear dimers of 2,2′-dihydroxyazobenzene that are produced in neutral or alkaline medium [18]. The spectra of the enzymatic polymerization of 2-AP [0.1 M of phosphate buffer solution with a pH of 5.55 containing 25 $\mu g \cdot ml^{-1}$ of laccase and 10 mM of 2-AP] were identified as free of the 2,2′-dihydroxyazobenzenel [19]. The enzymatic polymerization leads to the formation of round polymeric microstructures composed of 3-aminophenoxazone [19,20]. The electrochemical oxidation of 4-aminophenol (4-AP, *p*-aminophenol) on different electrode materials was identified as 4-benzoquinone [21–25]. Moreover, the polymerized 4-AP suppresses the growth of different bacteria, such as *Staphylococcus aureus* (gram-positive) and *Escherichia coli* (gram-negative) [21]. The enzymatic-catalyzed polymerization of 4-AP on/onto poly(ethersulfone) (PES) membranes has been reported to improve the protein repellence of the modified membranes [26].

The chemical oxidation of 3-aminophenol (3-AP, meta-aminophenol) in aqueous sodium hydroxide medium using persulfates oxidizer was done at room temperature (30°C), and a nanocomposite of the produced poly(3-AP) and silver nanoparticles was prepared and doped by hydrochloric acid to be used in ammonia vapor sensing [27]. In addition, poly(3-AP) was prepared using potassium dichromate oxidizer [28,29], and in the presence of sodium dodecyl sulphate (SDS) as an emulsifier [28], the chemical polymerization of 3-AP in acidic medium (HCl) with ammonium peroxydisulphates oxidizing agent has been reported [30]. The chemical and electrochemical polymerization of 3-AP takes place via C–O and/or C–N coupling [30,31]. The electrochemical polymerization of 3-AP in aqueous solution on SnO_2 electrodes indicated that only the amino group was oxidized while the hydroxyl group remained unchanged [32]. Moreover, the oxidation of the 3-AP on a platinum electrode in acid medium has yielded a polymeric product that may have a cross linked or a linear structure analogous to polyphenol [13], as shown in Fig. 1.

Surface modification of the membranes aimed to minimize the adsorption or adhesion of the substances from the flowing fluid on the membranes' surface, or in more specific terms minimize the membrane fouling (i.e., minimize the accumulation of substances on the membranes' surface and/or within their pores, which results in deterioration of the membranes' performance) [33]. Among

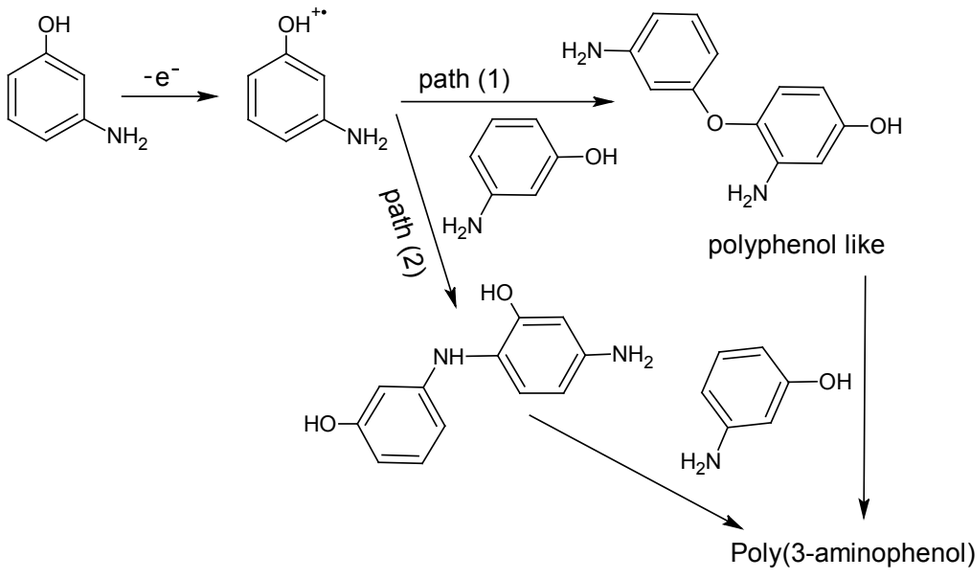

Fig. 1. Proposed structure of polymerization of 3-aminophenol (3-AP) [13].

the currently investigated surface modification techniques (such as coating, blending, composite, chemical, and grafting), the surface grafting of a brush-like hydrophilic polymer layer has been highlighted as an effective approach to minimize membrane fouling and consequently improve the membranes' performance. The antifouling mechanism in this modification approach depends on both the steric hindrance and the osmotic effect of the hydrated brush-like polymer layer [34,35]. Recently, the enzyme-catalyzed modification of PES membranes [36–40] used laccase from *Trametes versicolor* as a bio-catalyst to create reactive radicals that can covalently bind to each other (polymerization) and/or onto the PES membrane (bio-grafting), mainly via their phenolic groups [33,37]. In addition, PES membranes have been modified using 4-aminophenol [26] and 2-aminophenol [41].

In the current research, a 3-AP has been used as a modifier (substrate for laccase or a monomer for polymerization), and the modified PES membranes were evaluated based on their productivity (flux) and their ability to reject protein (protein repellence). This substrate of laccase (i.e., the modifier or the monomer) was chosen because it carries an amino group that could induce unique properties in the PES membranes under eco-friendly conditions. The modification conditions were varied and were studied as a function of the gravimetrically determined grafting yield. The following modification conditions were used: concentration of the 3-AP modifier (5 and 15 mM), modification time (15, 30, 60, and 120 min), and modification temperature (25 and 40°C). The membrane color change was measured and was related to the grafting yield. Both blank and modified membranes were characterized using many techniques that include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), x-ray diffraction (XRD), Fourier transform infrared spectroscopy–attenuated total reflection (FTIR-ATR), nuclear magnetic resonance (^{1}H-NMR), scanning electron microscope (SEM), and tensile strength. Moreover, the shape and the structure of the formed modification layer(s) were investigated using aspin-coated PES layer on silicon dioxide slides as well as different analytic techniques (that include the static water contact angle, scanning probe microscopy (SPM), and Raman spectroscopy). The combination of these data allows an outlook on the laccase-catalyzed modification of PES membranes using 3-AP modifier.

2. Experiment

2.1. Chemicals

3-aminophenol(3-AP, 99.8%), dichloromethane (DCM, 99.9%), sodium acetate (anhydrous, 99%), acetic acid (99%), and catechol (98%) were obtained from Sigma-Aldrich. Flat sheets of commercial PES membrane's circles were purchased from Sterlitech (symmetric, 0.2 µm pore size, 47 mm diameter, USA). PES polymer was obtained from BASF (Germany). Prime grade silicon wafers with a 2.5 nm native oxide layer were purchased from wafer Net Inc (USA). Laccase from *Trametes versicolor* (> 0.5 U·mg^{-1}) was obtained from Fluka. All chemicals were used without extra purification. Distilled water was used to prepare fresh solution before each experiment.

2.2. Laccase activity

The laccase activity was determined with catechol, as was done in previous published work [36]. The oxidation of catechol was monitored by the increase in absorbance at 400 nm (ε = 26,000 M^{-1}·cm^{-1}) [42] during a 20-min reaction time.

2.3. Preparation of the spin-coated PES layers on silicon dioxide strips

The spin-coated PES on a silicon wafer was used for SEM and SPM imaging and for measuring the static water contact angle. The wafers were cut into strips of 1 × 1 cm^2 (for SEM and SPM imaging) and 1 × 3 cm^2 (for static water contact angle measurements). The strips were sonicated in ethanol for 15 min, washed with water and ethanol, and dried in a stream of nitrogen. Subsequently, the strips were given a plasma treatment (PDC-32G, Harrick ata high RF level) for 10 min. Then, immediately after plasma cleaning and removing any dust using a flow of nitrogen, the strips were used to prepare the spin-coated PES layers by spin coating 0.5% w/w PES solution in DCM for 30 sec at 2500 rpm. Then, the PES-coated strips were dried at 300°C for 60 min.

2.4. Modification of PES membranes and spin-coated PES layers

The membranes were immersed in 0.1 M sodium acetate buffer (40 ml) containing different concentrations of 3-AP and enzyme laccase. Oxygen was supplied as a component of the air source as well as for gentle continuous mixing to ensure a homogenous modification medium. After a specific modification time (15, 30, 60, or 120 min), the membranes were removed from the modification medium and washed by a strong spray of flushing water; then, they were dipped three times in freshly boiled (> 95°C) deionized water. The modified membranes were dried in glass dishes placed in desiccators supplied with self-indicating blue silica gel for 48 h before evaluation. The spin-coated PES layers were modified using the same method while keeping the ratio between the used volume of the reaction solution and the surface area of the immersed spin-coated PES layer constant.

2.5. Total color change of membranes

The color of the modified membranes, relative to the blank membrane, was determined with an X-Rite (SP62 Sphere Spectrophotometer, CIE L*a*b*, and ΔE* at D 65/10°, while a compare mode of operation was used). The differences in color values—ΔL* (lightness), Δa* (red-green axes), Δb* (yellow-blue axes), and ΔE* (the total change in the membrane color)—were measured using an 8 mm aperture size diameter. Three different readings were taken from each sample, and the average value was calculated. Each membrane was washed by a spray flushing of distilled water three times, followed by immersion in deionized water and decantation three times (the absorption of the washing solution was measured by the spectrophotometer, and it was zero). Then, the membranes were washed by filtration using at least 150 ml of deionized water and dried

for 48 h before measuring the total color change of the membrane relative to the blank membrane.

2.6. Laccase, 3-aminophenol (3-AP), and poly(3-aminophenol) adsorption test

The blank membrane sample was incubated in sodium acetate buffer (40 ml of 0.1 M adjusted at a pH of 5.5, 24°C ± 1°C) containing 0.5 U·ml^{-1} enzyme in the absence of 3-AP, for 2 h. The amount of the adsorbed enzyme was calculated from the weight difference. The same test was performed with the 3-AP solution (without laccase). In another experiment, the reaction of 3-AP and laccase was carried out without the PES membrane for 2 h. The laccase was inactivated by adding 1 M NaOH (0.5 ml) while stirring for 10 min. After re-adjusting the pH to 5.5 with concentrated HCl, the PES membrane was immersed for 2 h in this solution. The membrane was then washed by strong flushing followed by dipping in freshly boiled (>95ºC) deionized water (three times), and then the membrane was dried and the total color change and the adsorbed homopolymers were determined.

2.7. Water flux

A dead-end stirred filtration cell (Millipore, Model 8050, active transport area 13.4 cm^2) was used to measure the pure water flux of blank (unmodified) and modified membranes at a constant trans-membrane pressure of 1 bar at 24 ºC ± 1ºC and 200 rpm. The pure water flux was calculated using Eq. (1):

$$J_w = \frac{Q}{\Delta t \cdot A} \quad (1)$$

Where J_w = water flux (m^3·m^{-2}·s^{-1}), Q is the volume of permeate collected (m^3), Δt is the sampling time (s), and A is the membrane area (m^2).

2.8. Gravimetric-added modifier (grafting yield)

The amount of the poly(3-AP) added onto the membrane surface was calculated from the difference in the weight of the membrane, before and after the modification process relative to the membrane unit area. Before modification, all the membranes were kept for 48 h in glass-covered dishes in desiccators supplied with self-indicating blue silica gel to remove any moisture. To remove any enclosed or loosely bound material, the weight of the membrane after modification was measured after washing the membrane by filtration with at least 150 ml of deionized water.

2.9. Protein adsorption

Bovine serum albumin (BSA) was used as a model compound to evaluate the protein adsorption on the blank and the modified membranes, as described in previous research [37,38]. BSA (1 g·l^{-1}) solution at a pH of 7 was prepared using (0.1 M) sodium acetate buffer. The membranes were immersed in BSA solution (50 ml) and gently shaken (200 rpm) at 25°C for 24 h. The BSA concentration in the solution was measured using a UV-Vis spectrophotometer (280 nm), and the adsorbed amount was calculated from the difference between the initial and residual BSA amounts.

2.10. Scanning electron microscope (SEM) imaging

Blank and modified membranes as well as spin-coated layers were imaged using a JeolJsm 6360 LA scanning electron microscope (SEM, Japan). The surface of the blank and the modified membranes was cut using a very sharp shaving blade. All imaged surfaces were coated with Au before imaging. A voltage of 10–20 KV and a resolution of 1280 × 960 pixels were used.

2.11. Scanning probe microscope (SPM) imaging

Blank and modified spin-coated PES layers were prepared on square strips (1 × 1 cm^2) and were imaged using a scanning probe microscope (SPM, Shimadzu, Japan). The non-contact mode was used to image a 5 × 5 μm sample surface area.

2.12. Raman and infrared spectroscopy analysis

Raman spectroscopy analysis was done using blank and modified spin-coated PES layers on silicon dioxide slides (1 × 1 cm^2). A Bruker SENTERRA Raman microscope was used, and a laser beam at 532 nm a with power of 10 mW was applied (wide range).

Fourier transform infrared spectra were recorded in "reflectance mode" for the membrane surface throughout the range of 4600–350 cm^{-1} on a Perkin Elmer GX spectrophotometer.

2.13. Static water contact angle measurements

The static water contact angle of both blank and modified spin-coated PES layers on silicon dioxide slides was measured using a Krüss DSA 100 apparatus. Drops of demineralized water were deposited on three different spots of each spin-coated PES layer, and the contact angle was calculated from six different measurements taken on two independently modified slides.

2.14. Nuclear magnetic resonance (NMR)

A membrane was modified (15mM 3-AP, 0.5 U·ml^{-1} laccase, 0.1 M sodium acetate buffer, at a pH of 5.5, 25°C, 24 h modification time) and was dried for 72 h in a desiccator. Then, the half membrane was laid on the porcelain sieve and the dichloromethane was poured over the membrane surface. The poured dichloromethane dissolved most of the PES and went through the pores of the sieve and left a thin modified layer attached to the PES molecules. Subsequently, the left modified layer was re-solidified by adding the distilled water. After drying the re-solidified layer for extra 48 h, the dried layer was completely dissolved in DMSO-d_6 for analysis on aJEOL nuclear magnetic resonance (^{1}H-NMR) Spectrometer resonating at 400 MHz, equipped with an inverse broadband gradient probe.

2.15. Differential scanning calorimetery (DSC) testing

The glass transition temperature (T_g) was measured with differential scanning calorimetry (DSC, NETZSCH, DSC-200PC) at a heating rate of 10°C/min. The T_g was defined as the onset temperature of the change in heat capacity during the heating cycle.

2.16. Thermal gravimetric analysis (TGA)

TGA of the blank and the modified membranes was carried out using a Thermal Gravimetric Analyzer (Shimadzu TGA –50, Japan). The samples were scanned over a temperature range of 20°C –800°C at a temperature gradient of 10°C/min under nitrogen flow.

2.17. X-ray diffraction (XRD) testing

X-ray diffraction patterns for membranes were obtained by a Shimadzu XRD-7000 X-ray diffractometer using a CuKα radiation source operating at 40 kV and 30 mA. The samples were analyzed without further preparation.

2.18. Mechanical properties testing

Samples of membrane were cut in a dumbbell-like shape. The total length of each sample was 37 mm, the gauge length of the samples was about 16 mm; the width was 13 mm at the top and 7.2 mm (narrowest) at the middle of the sample, to force a fracture in the middle of the sample. Tensile testing of the films was performed with the Texture Analyzer T2 (United Kingdom), at a constant crosshead speed of 6 mm·min^{-1} until breaking. Stress–strain curves were calculated from load–elongation curves measured for 2 samples from each film.

3. Results and discussion

As illustrated in the experimental part, PES membranes were modified using 3-aminophenol (3-AP) using laccase biocatalyst. The grafting of 3-AP (the monomer and the enzyme substrate) onto the membrane surface and the homopolymers' formation in solution are competitive reactions [36,37]. A coloration of the membrane was observed with different modification conditions. Therefore, the qualitative color change of each modified membrane relative to the color of the blank membrane (i.e., a compare mode of operation of X-Rite was used to determine the total change of the membrane color upon modification relative to the blank white membrane) was determined using an SP62 Sphere Spectrophotometer, which was used for the color determination of flat plastics. The obtained change in membrane color was measured and was related to the amount of added modifier (i.e., grafting yield was calculated from the difference in the weight of the membrane before and after the modification process relative to the membrane unit area), as illustrated in Fig. 2. Varied modification conditions were used as mentioned in the experimental part. The laccase concentration was 0.5 U·ml^{-1}, and a reaction pH of 5.5 was obtained using 0.1 M sodium acetate buffer.

As shown in Fig. 2, the color change of the membranes increased as the grafting yield increased. As observed, there are three sets of different color changes at the same grafting yield (17.3, 28.8, and 34.6 μg·cm^{-2}), which may be an indication for formation of layers that have very similar shape/structure at these modification conditions. The regression constant is sufficient for considering a direct relationship between the color change of the membrane and the grafting yield (i.e., R^2 = 0.96 for modification using 5 mM 3-AP at 25°C and 15 mM 3-AP at 40°C), which proposed a direct increase of the number of oligomers on the membrane surface (an increase in the grafting density) with increases in the color change of the membranes [43]. Most likely, the grafting contains brush-like oligomers, as in the case of using 4-hydroxybenzoic acid modifier in previous work [36]; this is confirmed by the SPM images in the following section.

On the other hand, the blank tests determined the extent of the homopolymer adsorption onto the membrane surface and the possibility of carrying out the reaction in the absence of the enzyme. Both the gravimetric grafting yield and the total membrane color change were determined in the two cases. The immersion of the membrane in monomer without enzyme for 2 h at 25°C and at a pH of 5.5 using 15 mM 3-AP that was dissolved in 0.1 M sodium acetate buffer resulted in no grafting yield (under detection limits of the balance) and a 0.5 total membrane color change (ΔE*). Adding the enzyme (0.5 U·ml^{-1}) in the conditions in which the membrane was immersed resulted in a 35.2 μg·cm^{-2} grafting yield and a 23.32 change in the membrane color (ΔE*). In addition, using the same reaction condition, but without immersing the membrane inside the reaction medium for 2 h, only the homopolymer reaction was formed. Then, the reaction was stopped using 1 M sodium hydroxide (to inactivate the enzyme). Then, the pH of the formed homopolymer solution was re-adjusted to 5.5 using concen-

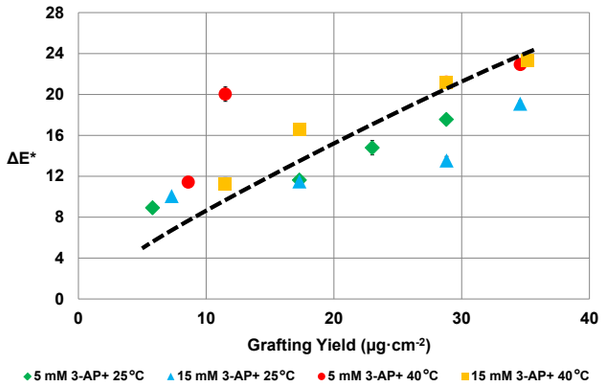

Fig. 2. The color change of membranes (ΔE*) with different grafting yields of 3-aminophenol (3-AP); the reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase. Different conditions were studied as follows: 5 mM 3-AP at 25°C (green diamond), 15 mM 3-AP at 25°C (blue triangle), 5 mM 3-AP at 40°C (red circle), and 15 mM 3-AP at 40°C (orange square) modified for 15, 30, 60, and 120 min modification times. The grafting yield increased as the modification time increased. The dashed black line is a guide for the overall trend.

trated hydrochloric acid. After that, an unmodified membrane was immersed for 2 h inside this reaction medium. After washing the immersed membrane, as described in the experimental section, the grafting yield and the change in the membrane color were determined. In this case, the determined added materials (the grafting yield) can be attributed only to the adsorption of pre-formed poly(3-AP). The adsorbed homopolymer amount and the change of the membrane color (ΔE*), were 5.7 μg·cm^{-2} and 5.5, respectively. Thus, the adsorbed homopolymersmay contribute to the determined grafting yield (35.2 μg·cm^{-2}), by about 15% of the modified membrane in the case of using the same reaction conditions. Much lower homopolymer adsorption is expected when using a lower concentration of 3-AP or carrying out the modification for less time. However, the amount of the adsorbed homopolymers may be increased when carrying out the modification reaction at a warm reaction temperature; 40°C. In addition, the adsorption of the enzyme on the membrane surface was determined as 2.7 μg·cm^{-2} without coloration of the membrane, and consequently the effective adsorbed amount of the homopolymers may be lower than 5.7 μg·cm^{-2}.

The color change of the membrane (ΔE*) can be used as an indicator of the extent of the grafting process using 3-AP modifier, as previously done in a similar work using 4-hydroxybenzoic acid modifier [37], whereas ΔE* cannot be used as an indicator in the case of using 4-aminophenol modifier [26] or gallic acid modifier [36]. This is because the main products of the enzyme-catalyzed polymerization of 4-aminophenol (4-AP) and gallic acid modifiers are quinones [21,26,37,38] that predominate the modification process (i.e., quinones adsorption is the main reaction process). For that, the direct relationship between the grafting yield and the total color change is present only when the grafting process on/onto the membrane surface is the dominant reaction in the modification process (i.e., the adsorption ratio of the homopolymers, which are formed in the reaction medium, on/onto the membrane surface is minimum), and those moieties are likely in the shape of brush-like oligomers.

There was an increase in the clean water flux of most modified membranes of up to 35% relative to the blank membranes, as shown in Fig. 3. Only one point was recorded at a 2% reduction in flux and can be considered within the error limits. This may be attributed to the formation of a homogenous layer without plugging the pores of the used membrane (0.2 μm pore size), as shown in the SEM images in the following section. In addition, this increase in the flux can be attributed to the addition of (free) polar groups (amines and hydroxyls) onto the membrane surface, especially at a low grafting yield, which facilitates the transportation of the water molecules. On the other hand, many more grafted oligomers (at a high grafting yield) may lead to a possible reaction of the polar groups with each other, which decreases the available free polar groups for bonding the water molecules [35,44]. However, the modified membranes (or surfaces) can still be described as more hydrophilic membranes relative to the unmodified membranes, as confirmed by the static water contact angle measurements presented in Fig. 4.

To illustrate the effect of the formed poly(3-AP) modifying layer on the surface hydrophilicity, the static water

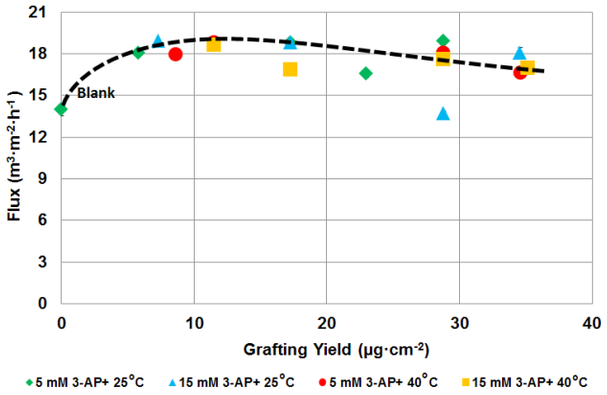

Fig. 3. Flux change of membranes with different grafting yields of 3-aminophenol (3-AP); the reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase. Different conditions were studied as follows: 5 mM 3-AP at 25°C (green diamond), 15 mM 3-AP at 25°C (blue triangle), 5 mM 3-AP at 40°C (red circle), and 15 mM 3-AP at 40°C (orange square) modified for 15, 30, 60, and 120 min modification times. The grafting yield increased as the modification time increased. The dashed black line is a guide for the overall trend.

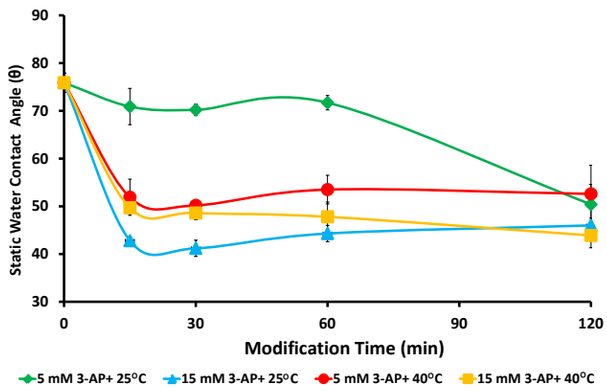

Fig. 4. Static water contact angle as a function of the modification time. The reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase. Different conditions were studied as follows: 5 mM 3-AP at 25°C (green diamond), 15 mM 3-AP at 25°C (blue triangle), 5 mM 3-AP at 40°C (red circle), and 15 mM 3-AP at 40°C (orange square) modified for 15, 30, 60, and 120 min.

contact angles were determined and shown in Fig. 4. As observed, the static water contact angle on the unmodified pure PES layer (around 76°) was reduced with modification. This reduction was significant for the first interval of modification (30 min) and then declined gradually, although still the measured static water contact angle on all the modified surfaces are lower than the static water contact angle on the unmodified surface. Using a low concentration of the 3-AP modifier grafted at room temperature (25°C) resulted in a stepwise reduction in the static water contact angle with modification time, and this may be attributed to a 3-AP concentration that is low for an effective reaction. For that,

using a high concentration of 3-AP produced more hydrophilic surfaces at a shorter modification time (ex. 15 and 30 min) especially at 25°C reaction temperature.

The static water contact angle on the modified spin-coated PES layers (surfaces) using 15 mM 3-AP at 25°C was reduced up to 44% (maximum reduction in the static water contact angle in this study) relative to the unmodified spin-coated PES layer. However, the modified spin-coated PES layer that showed the lowest static water contact angle did not show the best reduction of (irreversible) protein adsorption on the membranes' surface, as shown in Fig. 5. This observation proposes that at a short modification time, the density of the grown oligomers is not sufficient to keep the protein molecules away from the membranes' surface [38,44] although a reduction in the contact angle was observed.

The adsorbed amount of BSA (shown in Fig. 5) decreased exponentially with modification. As observed, the highest reduction in protein adsorption was 90% at a high grafting yield (35.16 μg·cm^{-2}). In addition, the modified membranes that carry the same amount of the grafted poly(3-AP) showed almost the same reduction in protein adsorption as well as the same flux change due to the modification, as shown in Fig. 3.

This is considered a sign of the formation of modified layers of the same structure/shape on the membranes that took place at different modification conditions. Moreover, increasing the grafting yield resulted in a reduction in the irreversible protein adsorption, although a slight increase in the static water contact angle was observed relative to the determined static water contact angle on spin-coated PES layers with a low grafting yield. Apparently, the structure and the density of the grafted layer is dependent only on the reaction time.

The blank membranes showed a flux reduction due to the irreversible BSA adsorption that reached 16%, whereas the modified membranes always showed higher residual fluxes (< 5% flux reduction; shown in Fig. 6).

Comparing these results to the original flux of the unmodified membrane, the total flux loss (due to modification in addition to irreversible BSA adsorption) of the modified membranes is much lower (three times) than the flux loss of the blank membranes due to the irreversible BSA adsorption. As shown in Fig. 6, some points showed no change in the flux due to irreversible BSA adsorption, suggesting that almost all the adsorbed protein is reversible and can easily be washed out by washing solution.

SEM was used to image both the blank (Fig. 7A) and the modified PES membranes (Fig.7B). The modified PES membranes did not show the homopolymer lumps that were observed in the previous study when using 4-hydroxybenzoic acid modifier [37]. This is because the reaction of 3-AP was carried out homogeneously on the entire membrane surface at the same time as well as the used low concentration of the modifier which resulted in a reduction in the amount of the formed homopolymers inside the reaction medium that leads to reduce its adsorption on the membrane surface (i.e., using 28.8 mM of 4-hyrdoxybenzoic acid resulted in an increase of the possibility of homopolymer lumps formation on the membranes' surface). Some very tiny lumps have appeared at higher temperatures and under conditions at which the homopolymers are most likely to be formed (higher substrate concentrations with long modification times).

To illustrate the shape of the formed layer on the membrane, a very thin layer of PES was spin-coated on a silicon dioxide substrate and was imaged by SEM, as shown in Fig.7C and 7D. We can easily notice poly(3-AP) oligomers or polymers grown perpendicularly on the spin-coated PES layer, which can be labeled as a brush-like surface, as shown by SPM in Fig. 8. As illustrated in the SPM images, the highest profile (i.e., z-direction) of the surface has changed from 302 nm for the pure spin-coated PES blank layer (surface) to 371 nm with modification for 15 min and then to 435

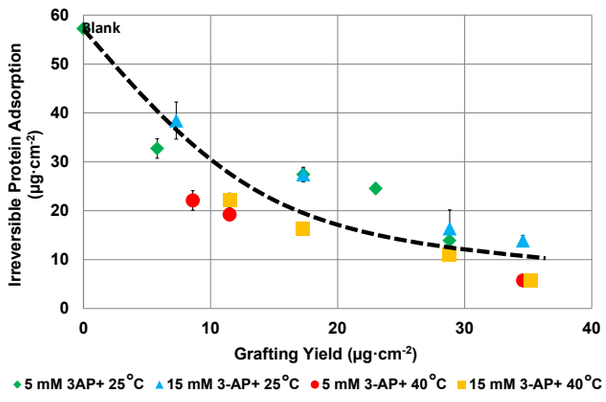

Fig. 5. Protein adsorption of membrane change with different grafting yields of 3-aminophenol (3-AP); the reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase. Different conditions were studied as follows: 5 mM 3-AP at 25°C (green diamond), 15 mM 3-AP at 25°C (blue triangle), 5 mM 3-AP at 40°C (red circle), and 15 mM 3-AP at 40°C (orange square) modified for 15, 30, 60, and 120 min. The grafting yield increased as the modification time increased. The dashed black line is a guide for the overall trend.

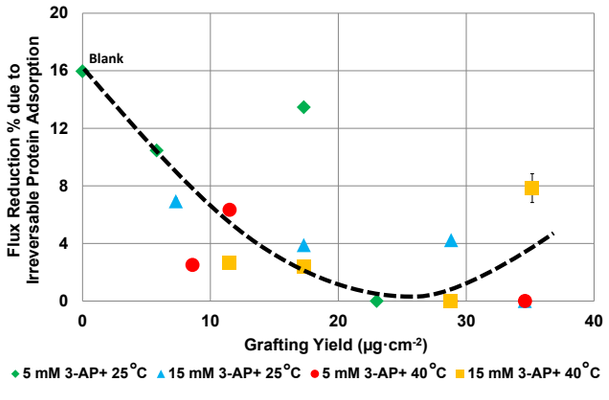

Fig. 6. Flux reduction % of membrane due to the irreversible adsorption of protein with different grafting yields of 3-aminophenol (3-AP); the reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase. Different conditions were studied as follows: 5 mM 3-AP at 25°C (green diamond), 15 mM 3-AP at 25°C (blue triangle), 5 mM 3-AP at 40°C (red circle), and 15 mM 3-AP at 40°C (orange square) modified for 15, 30, 60, and 120 min. The grafting yield increased as the modification time increased. The dashed black line is a guide for the overall trend.

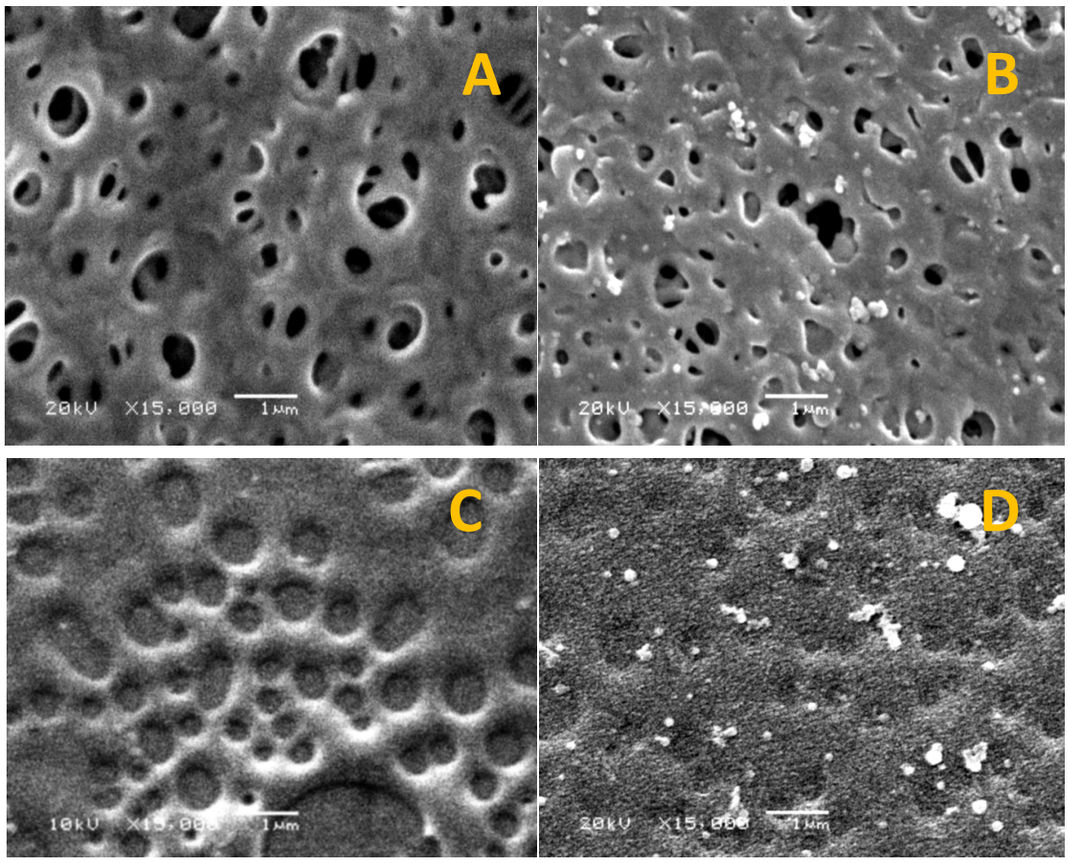

Fig. 7. SEM (A)–(D) images for blank and modified PES membranes. (A) and (C) show SEM images of a blank PES membrane and spin-coated PES layer, respectively. (B) and (D) show SEM images of a modified PES membrane and a modified spin-coated PES layer, respectively. The modification condition is 15 mM 3-aminophenol (3-AP), 0.5 U·ml^{-1} laccase, a pH of 5.5 using 0.1 M sodium acetate buffer, a 2 h modification time, and 25°C. SEM images are at 15000× magnification, and the scale bar is 1 µm.

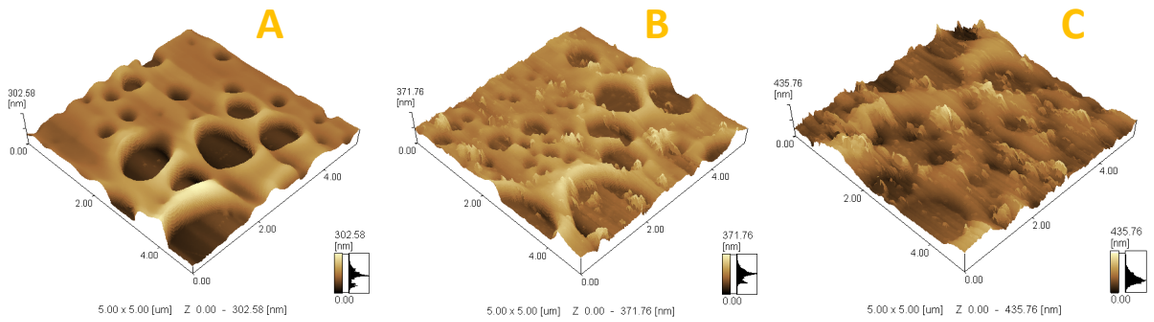

Fig. 8. SPM images (5 × 5 µm) of blank (A) and modified spin-coated PES layers (B) & (C), respectively. The modifications for 15 min (B) and 120 min (C) have been prepared using 15 mM 3-aminophenol (3-AP), 0.5 U·ml^{-1} laccase, at a pH of 5.5 using 0.1 M sodium acetate buffer, and 25°C.

nm with modification for 120 min. Moreover, the reaction seemed fast in the beginning of the modification process and then it decreased. This observation shows that the accumulation of grafting in the first 15 min was much higher than the following 105 min.

The effect of modification on the bulk properties of the membrane should be considered for the different applications of the modified membranes, for that the bulk properties of the blank and the modified membranes were examined using different analytical techniques such as TGA, DSC, and XRD. The results for TGA analysis are shown in Fig. 9. For blank PES membranes, the effect that was seen between 400°C–600°C corresponded to the sulfur dioxide cleavage and the ether bond cleavage. At higher

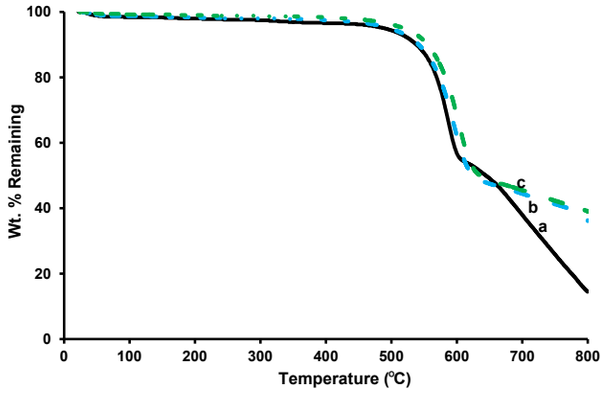

Fig. 9. TGA analysis of PES membranes. Blank membranes (a), black solid line) and modified PES membranes (b), green dashed line) and (c), blue dashed line) using 5 mM and 15 mM 3-aminophenol (3-AP), respectively. The reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, 0.5 U·ml^{-1} laccase, a 120 min modification time, and at 25°C.

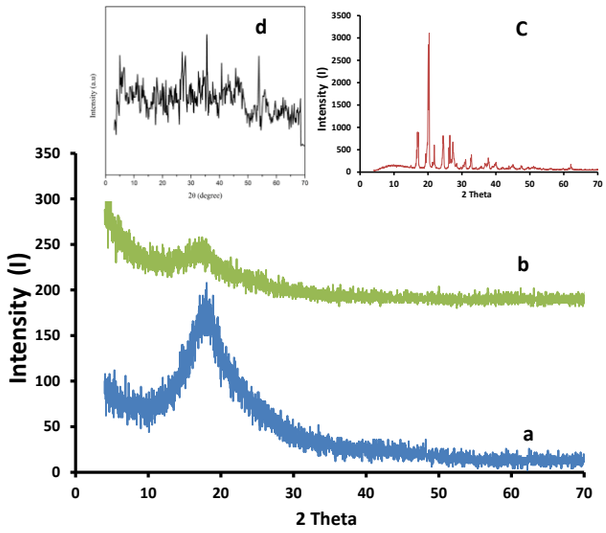

Fig. 10. XRD analysis of (a) a blank membrane, (b) a modified membrane, (c) 3-aminophenol (3-AP) monomer, and (d) poly(3-aminophenol) from ref. [45]. The membrane modified using 15 mM 3-AP for a 15 min modification time, 0.5 U·ml^{-1} enzyme, 25°C, a pH of 5.5, and 0.1 M sodium acetate buffer.

temperatures, the backbone (benzene ring) decomposes. When comparing the modified to the blank membranes, the temperature at which the first significant weight loss occurred was increased by about 60°C upon modification. In addition, the rate of decomposition of the backbone of the modified membranes is somehow slower than that rate of the blank membrane. As noted at 800°C, the remaining wt% is about 38 of the modified membrane, whereas only 15 wt% remained of the blank membrane. These TGA results confirm the enhanced thermal stability of the modified membranes. Furthermore, the DSC analysis not shown revealed that the glass transition temperature of the blank PES membranes was 226°C, and it decreased very slightly upon modification to 224°C.

XRD analyses of the blank membrane (Fig. 10a), the modified membrane (Fig. 10b), and the 3-AP modifier (Fig.10c) were compared to the XRD of poly(3-AP) (Fig. 10d) that has been taken from reference [45]. The blank PES membrane has a characteristic peak at 2θ = 18.04°, while the modifier 3-AP has multiple characteristic peaks (includes 17.1°, 20.4°, 21.8°, 24.4°, 26.4°, 27.3°, and 32.8°). However, poly(3-AP) has five broad peaks (at around 5.07°, 27.02°, 35.54°, 40.8°, and 53.8°). These broad peaks have been used as indicators for the crystalline domains in the amorphous structure of poly(3-AP) [45]. The modified membrane shows weak extra peaks compared to the blank membrane, in line the signals of amorphous poly(3-AP). This effect of adding poly(3-AP) may contribute to the increase of the flux of the modified membranes.

The effect of the modification on the tensile strength of the membranes was evaluated and was illustrated in Fig. 11. A slight decrease in the tensile strength of the blank membranes was detected. However, the modified membranes at a high grafting yield showed recovery the membrane's strength relative to the blank membrane.

The key issue is to determine the presence of free amine groups (that have an antifouling effect) on the modified surfaces. For that, Raman analysis (Fig. 12) of both blank and modified spin-coated PES layers was done.

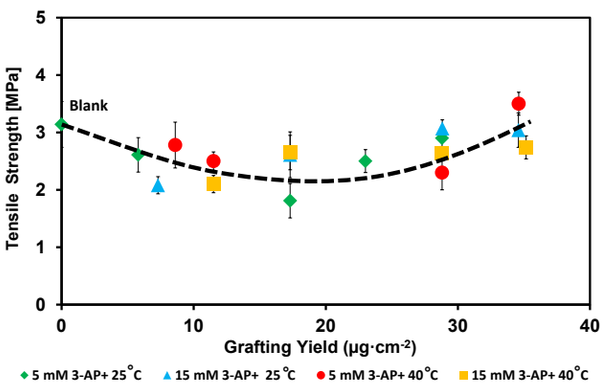

Fig. 11. Effect of the grafting yield of 3-aminophenol (3-AP) on the tensile strength of the blank PES membrane. The reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase. Different conditions were studied as follows: 5 mM 3-AP at 25°C (green diamond), 15 mM 3-AP at 25°C (blue triangle), 5 mM 3-AP at 40°C (red circle), and 15 mM 3-AP at 40°C (orange square) modified for 15, 30, 60, and 120 min. The grafting yield increased as the modification time increased. The dashed black line is a guide for the overall trend.

Raman spectra of both the blank and the modified spin-coated PES layers showed a peak at 530 cm^{-1}, which is attributed to the Si-O-Si and was related to the silicon dioxide support layer on the silicon slides. The peaks at 950 and 980 cm^{-1} are attributed to the C–O–C stretching. The peak at 1600 cm^{-1} can be attributed to a quinoid or the C=N stretching vibrations. The peak at 1345 cm^{-1} can be assigned to the C–N. This confirms the presence of the amine groups on the membranes' surface. Fig. 13 showed

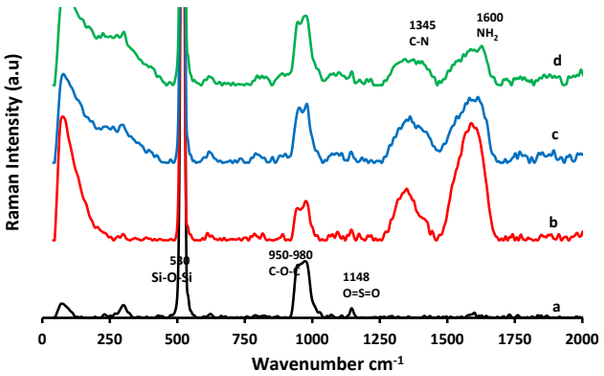

Fig. 12. Raman spectra of the blank (a) and modified (b)–(c) spin-coated PES layers on the silicon dioxide support surface; (b) and (c) modified PES layers using 15 mM 3-AP at 15 min and 60 min modification times, respectively; and (d) modified PES layer using 5 mM 3-AP at a 15 min modification time. The reference modification condition is a pH of 5.5 using 0.1 M sodium acetate buffer, and 0.5 U·ml^{-1} laccase at 25ºC.

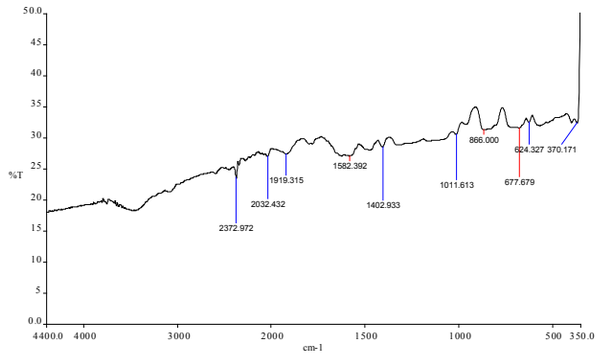

Fig. 13. FTIR-ATR spectra of PES membranes modified for 120 min using 15 mM 3-AP, 0.5 U·ml^{-1} laccase, a pH of 5.5 (0.1 M sodium acetate buffer), and at 25ºC.

identical characteristic absorbances in the infrared region of the modified membranes.

The NMR integration results of the analyzed peaks as well as the broad OH and NH bands of the FTIR-ATR spectra shown in Fig. 13 did not favor a particular structure of the modified PES membranes.

4. Overall outlook

In this study, the effect of the grafting yield (i.e., grafting density) of the brush-like oligomers on the interaction between the modified surfaces and water molecules and between the modified surfaces and foulant molecules (such as proteins) has been determined from the obtained results. At low-density/short-grafted oligomers, the water molecules can mix with the grafted oligomer chains and interact with the PES surface, and the foulant particles and their aggregates can easily reach the PES surface and be adsorbed on it, as shown in Fig. 14A. Here the van der Waals interactions are the main proposed physical force [43]. At a moderate density of swollen oligomer chains, the repulsive forces (hydrophilic and hydrophobic interactions) may be proposed as the dominant force. Good wetting of the grafted oligomers will reduce the static water contact angle. In this case, although the contact angle is significantly reduced, the foulant molecules have the ability to penetrate the brush-like oligomers to the PES surface and the adsorption still can take place, as shown in Fig. 14B. At a high grafting density, entropic forces may act as the dominant force with poor miscibility of water and foulant particles within the dense bush-like oligomers, as shown in Fig.14C [37,43].This high-density grafting (i.e., high grafting yield) resulted in the best reduction in the foulants' adsorption, although nonsignificant change in the static water contact angle was determined. Clearly, the foulants can penetrate into the modified surface at short/low or

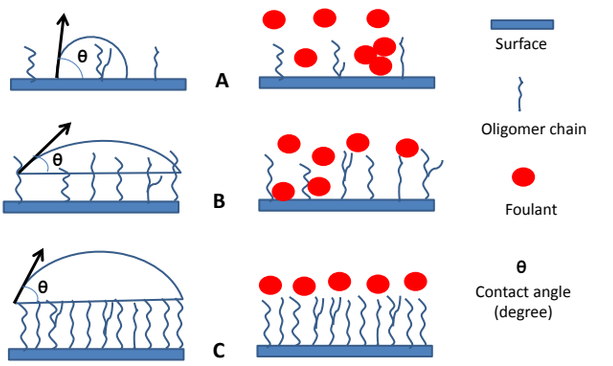

Fig. 14. Water and foulant interacting with brush-like 3-AP oligomers: (A) short/low-density oligomer chains and the surface is not wetable by water, and the foulants and its aggregates can be easily reached into the surface; (B) Good wetting with moderate grafting density surface with the foulant can penetrate into the modified surface; and (C) Branched high-density brush-like oligomers with poor miscibility with oligomer chains resulted in good foulant repellence. Modified from reference [43].

moderate density oligomer chains, whereas the branched high grafting density oligomer chains shield the membrane and protect it from foulant adsorption [46].

Adsorption is a very complex phenomenon. Different forces (e.g., the van der Waals interactions, hydrogen bonding, hydrophobic interactions, π-π stacking) contribute to the interaction between the foulant and the surface of membranes [46]. For example, the proteins may be initially adsorbed due to hydrophilic interactions, but their irreversible adsorption is caused by hydrophobic interactions [47]. In addition, the change in the enthalpy, the entropy, and the Gibbs energy of the separation system may cause the adsorption of foulants [47,48]. For example, the dehydration of the surface or the protein molecules will cause a large entropy gain and reduced Gibbs energy [46–49]; this will lead to more protein adsorption. On the other hand, the steric hindrance and the osmotic effect of this hydrated grafted oligomer chain on the surface contribute to the fouling repellence, as confirmed by the obtained results in

this study. The observed protein repellence of the modified surfaces is attributed to the existence of the protein behind a water barrier (i.e., hydration layer) that keeps the proteins at a distance from the membranes. Moreover, the strength and thickness of this hydration layer have effectively reduced the probability of the proteins' adsorption on the surfaces covered by other polymer brushes [50]. In addition, the protein structure, protein stability and concentration, pH, and ionic strength of the reaction medium cannot be neglected as additional effective parameters that cause the undesirable fouling phenomenon [51].

5. Conclusions

PES membranes were successfully modified with 3-AP using the enzyme laccase under very mild conditions. The change in the membrane color has been proportional to the amount of grafted 3-AP. The water flux of almost all modified membranes has increased by 35%. The modified membranes showed a significant reduction in the protein adsorption up to 90%. The analysis of the formed poly(3-AP) indicated the successful addition of free amine side groups on the grafted brush-like chains. This modification slightly improved the bulk properties of the original blank membrane. The modification of the PES surface with 3-AP is a successful innovative surface functionalization for PES and the analogue materials.

Acknowledgments

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