Fabrication of electro spun nylon6.12/chitosan @PES nanofibrous UF membrane towards dyes rejection from synthetic wastewater

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Abstract

Nanofibrous ultrafilter of nylon6.12/chitosan@Poly ether sulfone (N6.12/CS@PES) membrane were fabricated by chitosan casted PES membrane and coated with nylon6.12 thin layer using electrospinning technique for dye rejection. The membranes were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD). The capacity of the membrane to reject both cationic and anionic dyes was evaluated for basic blue dye41 and alizarin red dye, respectively, with regard to solution parameters (pH, Zeta potential, pressure, dye concentration and different electrolyte) through filtration system. In addition, the influence of parameters on dye rejection, as well as their potential interactions, has been investigated. An enhanced hydrophilicity and anti-fouling property was observed for the composite membrane as compared to pristine PES ultrafiltration membranes. The results show that the rejection of dyes increase with the decreases of operating pressure. At optimum condition of PH = 7, and pressure = 10 bar and concentration = 220 mg/L, the rejection ratio improves from 75.3 to 99.5% and 71 to 82% for basic blue dye41 and alizarin red dye, respectively. Dye rejection is not changed after 7 cycles and not change separation efficiency of dyes. The mechanical and electrical properties were investigated for PES and N6.12/CS@PES composite membrane. The results showed that the N6.12/CS@PES composite membrane exhibited the highest mechanical properties and the highest dielectric constant especially at low frequencies with low dielectric loss. This study demonstrated that the developed nanofibrous composite membrane were successfully characterized and proved to be a good rejection for dyes from aqueous solutions.

Keywords Chitosan · Composite membrane · Electrospinning · Rejection dyes · PES · Nylon 6.12 · Ultrafiltration
Introduction

Wastewater is polluted by synthetic dyes that are not biodegradable, carcinogenic, and may contaminate freshwater. Typical treatment procedures are generally insufficiently effective for economic and technological reasons. Various dye rejection techniques have been implemented [1], which, due to their superior performance, and inexpensive separation efficiency and the lack of additional chemical agents in these systems, the membrane separating processes have demonstrated promising alternatives to the conventional processes. This reduces chemical consumption during the dyeing process to a minimum and reduces energy consumption [3, 4]. Given global environmental problems and the high water demand requirements, membrane technology development and wastewater treatment research are rapidly expanding [1].

The hydrophilicity of membranes and their porous structure are significant in the membrane separation process, particularly with ultrafiltration membranes. An effective porous membrane must have high permeability, good hydrophilicity, and excellent chemical resistance to the feed solution [2]. There has been considerable interest in natural or synthetic polymeric materials used as membrane materials. Variety of trade polymer membranes, such as polyimide 6, polyimide 66, polyvinylidene-diflouride, polysulfone, polyethersulfone, and polypropylene, have good chemical, mechanical and thermal stability [6]. They also have good chemical, mechanical and thermal stability [3, 4]. The polyethersulfone (PES) has outstanding mechanical and thermal properties and is commonly used as a promising material in waste treatment applications [9]. The greatest disadvantage of the PES-based membrane is the sulfonile group connecting the two phenylene rings that cause hydrophobicity, low permeation, and antifouling properties [5]. Thus, hydrophilic membrane improvement is important in the science and technology of membrane during wastewater treatment [6]. Several chemical and physical modifications were studied to improve the hydrophilic properties of membranes of PES (e.g. mixing, casting, painting, grafting, and surface treatment of membranes with various organic or inorganic hydrophilic additives) [16]. The final goal of membrane modification using hydrophilic agents is to integrate hydrophilic material into the membrane surface and pores to enhance membrane selectivity and minimize fouling [6]. Several studies on membrane modifying with chitosan have been published in order to generate strong antifouling hydrophilic membranes. The use of a hydrophilic polyamide layer is another approach to improving the anti-fouling properties and surface properties of membranes. Polyamide offers various functional groups that can serve as binding sites, for example, amines, carboxylic acid, and an acylchloride unreacted group [7, 8]. Hydrophilic polymers with polyamides and amines have been stated to enhance the hydrophilic structure and selective characteristics of polymer membranes. Chitosan, a derivative of chitin deacetylate (a crustacean shell product), is the second most prevalent natural fiber after cellulose, a linear polymer with a greater weight. Chitosan is also a natural renewable resource with desired qualities such as bio-friendly, biodegradability, biocompatibility, non-toxicity, and the ability to absorb and kill bacteria [9]. A wide range of amino and hydroxyl functional groups in chitosan chains are employed as coordination sites that can act as polluted binding sites.
improving both the hydrophilic characteristics and the perm selectivity of the membrane. Chitosan can alter the hydrophobicity of the membrane and react with the most negatively charged polymers because it is a cationic polysaccharide [10]. Metals and dyes can also be removed from chitosan and chitin to clean water since the metals and dyes can be adsorbed into the working groups of cationic amine on chitosan. It also can be positively charged and electrostatic forces extract dye in an acid environment. The results revealed that increasing chitosan’s molecular weight (MW) from 80,100 to 308,300 lowers its color adsorption capability. A thin surface layer enhances the hydrophilicity and thus increases the permeation property of the membrane. Casting an acidic Chitosan solution on a Polysulfone support surface has been studied in the literature [11–13], and using a Nylon6.12/chitosan electrospun blend to create composite membranes for water purification applications [14–17]. Nylon 6.12 is a synthetic polymer that is biocompatible, biodegradable and has excellent mechanical, thermal, chemical, and physical properties [18]. Chitosan/nylon blend has many of the advantages of combining the benefits of Nylon6.12 with biodegradability, high hydrophilicity, and antifungal and antibacterial properties of chitosan [17]. As a result, nanofibrous electrospun membranes with larger surface areas and pore sizes are preferable for dye extraction from wastewater.

In this context, the goal of this study was to create a chitosan casted PES membrane that was coated with a nylon layer using an electrospinning technique for dye treatment as the functional polymer to provide hydroxyl groups and additional amine groups to make it adsorptive for the flat sheet N6.12 membrane. Formic acid was used to prepare the casting solution as the solvent for N6.12 and CS, and water was used as a coagulant. During dye rejection, the efficiency of synthetic N6.12/CS@ PES composite UF membranes is observed in response to solution pH, zeta potential, pressure, dye concentration, and electrolyte concentration. The dynamic and static mechanical properties and electrical properties of synthesized composite membranes were also investigated.

**Experimental**

**Materials and chemicals**

The materials used in this study are Polyethersulfone (PES, Ultrason E6020P, 51 kDa) was obtained from BASF Co. Ltd., Germany, Nylon 6.12 (N6.12, C18H38N2O4, Mw 346.5 g/mol) was obtained from Sigma-Aldrich Co. (USA) and chitosan (CS, high molecular weight > 1000 kDa) was obtained from PT Bio-tech Surindo (Cirebon, Indonesia). Formic acid (FA), N-Methylpyrrolidone (NMP), acetic acid and Dichloromethane (DCM) were used as solvent from Merck. Tween 80 used as non-ionic surfactant was obtained from PT BratacoChemika (Cikarang, Indonesia). Sodium chloride (NaCl), Calcium chloride (CaCl2) and n-hexane (anhydrous, 95%) were purchased from Merck Millipore, Australia). Distilled water was obtained from the distillation of laboratory water (Lab glass Aqua III).Blue-basicdye41 (C20H26N4O6S2) and Alizarin red dye (C14H8O7S) were produced by
Sigma-Aldrich Pty. Ltd., NSW, Australia). All materials were used without any purification as they were obtained.

**Composite membrane synthesis**

Membrane preparation stages as shown in Fig. 1 involved the following.

**Membrane composite support (Chi@PES) preparation**

The first step, to prepared Chitosan Tween 80 (CT) solution, 4 gm of Chitosan was dissolved in 100 ml of 2% acetic acid and then Tween 80 solution was added. The second step, preparation of homogenous PES-CT solution, PES (13%) was dissolved in N-Methylpyrrolidone (NMP) at 70 °C, then 0–7.5% CT solution was added and stirred. In the third stage, the PES-CT solution was cast at a thickness of about 200 μm. Finally, the membrane was solidified and washed for an hour in water in a coagulation bath (36 °C). Before drying, the prepared membranes were cleaned and soaked for a day.

**Electrospinning of thin layer nylon 6.12**

To prepare an electrospinning solution for nylon 6.12, formic acid (FA) is a well-known solvent. The FA has a low vapor pressure, and dissolved Nylon 6.12 is

![Fig. 1 Process flow diagram of the synthesis of N6.12/CS@PES composite membrane](image)
difficult to spin, according to our early research. Combining DCM, a low boiling point, and a cheap solvent with FA improved the rate of solvent evaporation in this research. The optimal ratio of FA and DCM solvents was found to be 8:2 to permit fiber dragging while maintaining appropriate adhesion between the electrospun nonwoven mid-layer and the PET backing layer were mixed overnight at room temperature with a 10% homogenous solution of FA and DCM in a co-solvent blend. To prepare a nanofibrous mat, a volume of 2.5 mL was electrospun into the composted supporting layer under a 25 kV potential field. Using a method outlined in our earlier study, these experiments were carried out under room temperatures and humidity [19]. Under the spinning parameters, nylon 6.12 can be readily spun and generated a fiber of excellent quality with few defects and beads.

Membrane batch adsorption experiments

To make the stock dye solution, dissolve 0.22 g of dye in 1L of distilled water. 0.1 M HCl or 0.1 M NaOH solutions were used to adjust the pH of the experiment solutions. To obtain the required concentration range, the experimental solutions were prepared by diluting the stock dye solution with deionized water. Using a UV–visible spectrophotometer, the dye concentration was measured. The absorbance-concentration profile was obtained by plotting a calibration curve between absorbance and dye solution concentration. Changes in solution pH, Zeta potential, pressure, dye concentration, and electrolyte were used to perform batch adsorption experiments. In each experiment, a specified weighted adsorbent was mixed with 50 mL of desired dye concentration in a 250 mL conical flask and shaken at a constant temperature.

Performance evaluation

Membrane-solute interactions were evaluated using adsorption fouling, whereas membrane-solute–solute interactions were evaluated using ultrafiltration fouling and a dead end cell. Polarization of pressured concentration occurred in the test cell due to the magnet agitating system across a membrane. A N2 high pressure tank is utilized as a pressure source. The feeds are for a 2.5 l feed solution, and the stirred cells have a capacity of 0.5 l. A magnetic agitator freely moves around the membrane’s surface [20]. The UV absorbance of the dyes was determined at a wavelength of 270 nm. The following equation was used to calculate the apparent color rejection ($R$): 

$$R\% = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

(1)

where $C_p$ and $C_f$ are the dye concentrations of the permeate and feed of the dye solution, respectively.
Effect of PES/chitosan membrane ratio

By dissolving the desired quantity of PES beads (15 wt%) in Dimethyl Sulfoxide on a magnetic stirrer at room temperature (26 °C on the day), polymeric solutions were generated. After the PES granules had completely dissolved, different amounts of chitosan particles (0, 0.5, 1, and 1.5 wt%) were added. The casting solutions were stirred for 24 h to create a homogenous gel. The dope solution was cast on a glass plate using a casting knife with a thickness of 250 m. The entire glass was submerged in a deionized water bath at room temperature for 20 min. after the gel was applied. The glass plate was detached from the membrane sheet. To allow the solvent to completely desorb from the membrane, the sheets were immersed in deionized water for 24 h. To remove any remaining water or solvent, the membranes were dried in a 75 °C oven. The thickness of the membranes was measured using a digital micrometer.

Characterization of membrane

Scanning electron microscopy (SEM, Hitachi S-4800) with a 10 kV accelerating voltage was used to examine the surface morphology and diameter of the N6.12/CS@PES nanofibrous composite membrane. The X-ray diffraction (XRD) patterns of all samples were analyzed with (Philips 1830) diffractometer using the CuKα radiation (λ = 1.5418 Å) was used at a rating of 40 kV and 40 mA and from 4 to 80° (2θ). The functional groups were detected using a Fourier-transform-infrared (FT-IR) spectroscopy model spectrum one (Perkin Elmer, USA) in the wave number range of 400–4000 cm⁻¹. The concentration of dyes in the solution was measured using a Thermo Scientific AQ 7000 UV/Vis spectrophotometer. The concentration of mixed salts NaCl, CaCl₂ and NaOH contained in dye solutions was analyzed by ion chromatography ( Dionex ICS-2000 System, USA). Solution pH was measured with a pH meter (ZDJ-4A, Shanghai Precision Scientific Instrument Co. Ltd.).

A Hioki 3532–50 LCR Hitester was used to evaluate dielectric characteristics in the frequency range of 50 Hz to 5 MHz. A Triton Instruments was used to perform dynamic mechanical analysis (DMA) throughout a temperature range of 25 to 150 °C at a scanning rate of 5 °C/min in the tension mode at a frequency of 1 Hz. To investigate Young modulus, static tension properties were carried out using Triton Instruments with preload force 0.01 N, load rate 0.2 N/min and to maximum force 2 N.

Results and discussion

Scanning electron microscopy (SEM)

Figure 2 showed SEM pictures of the surface of the electrospun nylon fiber. Relativeness was raw on the surfaces, no flammable retardant was shown on the fiber.
There were almost no troughs or fiber flaws in the broad view of the cross section. Because fiber is more aggregated, the agglomeration of fiber aggravates, the cover performance for the membrane is better. The fibers are also more likely to aggregate. The area within the shell of the bundles of fibers is loosening. The good distribution of fibers will prevent the shell damages and fiber bundles will be dragged away; certain materials that are refractory are also pulled out, since they connect fiber bundles with shell, so that bundles can improve the coating strength but the reinforced effect will decrease. The strength of the hull falls dramatically when the negative influence is greater than the positive one. This fabric of nylon 6.12 fibers is a strong structured coating on the entire membrane-reinforced polymer and a high-quality filtering surface for dyes with the ability to be physically adsorbed on the surface.

Figures 3 and 4 demonstrate the N6.12/PES and N6.12/CS cross-sectional SEM images, respectively. Very few surface pores are seen in ultrafiltration membranes and there is a typical asymmetric configuration for both membranes that have a top layer and a support layer. The nylon layer formed over the hydrophobic PES membrane (N6.12/PES) and the hydrophilic chitosan (N6.12/CS@ PES) combination PES membrane has different surface morphology. Similar observations were reported by Ghosh and Hoek, whereby the membrane’s roughness character decreased with the addition of hydrophilic chitosan, possibly due to the formation of chitosan complexes with N6.12 structure and the filling of empty nylon layer spaces [21].
FT-IR spectroscopy

FT-IR spectra of PES, nylon6.12, chitosan, and electrospun nanofibers of N6.12/CS@ PES composite membrane are shown in Fig. 5 to gain information on changes in the surface chemistry of PES membrane after casting with chitosan and coating with nylon. The PES spectrum observed characteristic absorption peaks at 1492 cm⁻¹ and 1391 cm⁻¹ corresponds to benzene ring and C=C stretching vibration, respectively, an aromatic ether band at around 1132 cm⁻¹ and a sulphone groups observed at bands around 905 cm⁻¹, 991 cm⁻¹ and 1036 cm⁻¹ [22]. The corresponding bands in the nylon 6.12 spectra are at 3561 cm⁻¹ (H-bonded N–H stretch vibration), 1744 cm⁻¹ (amide I, C–O stretch), and 1621 cm⁻¹ (amide II, C–N stretch and CO–N–H bend) [23]. In chitosan spectrum, the absorption bands at around

![Fig. 4 SEM of nylon layer generated over hydrophobic PES membrane which combined with hydrophilic chitosan (N6.12/CS@ PES)](image)

![Fig. 5 FT-IR spectra of PES, N6.12, CS and N6.12/CS@ PES composite membrane](image)
3178, 2758 and 2112 cm\(^{-1}\) are characteristic of stretching vibrations of the –OH, –CH\(_2\), and –CH\(_3\) groups, respectively. The broadband at 3208 cm\(^{-1}\) owing to O–H and amine N–H stretching of chitosan. There were additional peaks at 1550 cm\(^{-1}\), which were identified as amide II bands, in addition to the peak at 1621 cm\(^{-1}\), which was attributed to amide I. C–O bending, which is characteristic of saccharide structure, has a peak about 1.013 cm\(^{-1}\) [24]. The peak of 1566 cm\(^{-1}\) (amide II) which is also observed for the composite which is attributed to the amino groups of blend nanofibers [15]. This confirmed a uniform blending of component in composite membrane.

In the spectra of N6.12/CS@PES composite membrane indicated that the sulphone groups bands of pure PES are shifted to higher wavenumbers. Further, amide I, C–O stretch (1744 cm\(^{-1}\)) and amide II, C–N stretch and CO–N–H bend (1621 cm\(^{-1}\)) of N6.12 are shifted to \(\approx 2100\) cm\(^{-1}\) and \(\approx 1900\) cm\(^{-1}\), respectively. This shifting in in the stretching frequencies of N6.12/CS@PES composite membranes indicates the hydrogen bond generated between the amide group of N6.12 and –C–O group of PES [25]. Also, in the spectra of N6.12/CS@PES composite membrane, the absorption peak of pure CS at \(\approx 1200\) cm\(^{-1}\) disappeared. This result suggested the formation of hydrogen bond between CS and PES [26]. Moreover, the broad bands appeared at 3208 cm\(^{-1}\) for the CS and at 3561 cm\(^{-1}\) and \(\approx 3100\) cm\(^{-1}\) for N6.12 are shifted and became extremely week indicating a complex interaction between PES, CS and N6.12. This can be attributed to redistribution in the hydroxyl group association arrangement because of the different geometry induced by increased crosslinking bonds [27].

**XRD analysis**

Figure 6 shows the X-ray diffraction (XRD) spectra of pristine PES and composite membranes. As can be shown, the pure PES polymer shows a relatively sharp peak at \(2\Theta=13.42^\circ\) which is known as amorphous halo and represents amorphous structure of polymer, is similar to the reported peak for pure PES due to the amorphous structure [28]. The second peak (hump) of amorphous polymers at \(20\) around 40° in the XRD diagram. For composite, the amorphous nature of the PES remains intact although its amorphous peak slightly shifts to higher values at \(2\Theta=18.82^\circ\). The sharp peaks correspond to crystalline domain and diffused peaks for amorphous regions of polymer samples. This implies amorphous membrane enhancement, which increases the intensity of the crystalline peak of composites.

**Coating layer thickness**

There are two causes for changing the measured permeability according to membrane thickness. The first is the presence of frontier layers or interface resistors. The other is the fluctuation of the membrane permeability, like the laminated film composites with several layers of permeability [29]. Both polymer’s thick membranes were manufactured by casting solution and dye permeability was controlled with the use of GTR-11A/31A devices [30]. To study the effect of the
thickness of the nylon layer on the membrane surface, it was studied by changing the concentration of the nylon in the solution from 1 to 5% in the solution, which in turn affected the thickness of the upper layer in the membrane as shown in Fig. 7. We note that with the increase in the concentration of nylon, the thickness of the upper layer increases, but not to a large degree that matches the concentration used, and this indicates the ability of the polymer to shrink and form a compressed surface with small holes compared to large concentrations of it [31].

![XRD spectra of PES and N6.12/CS@ PES composite membrane](image1)

Fig. 6 XRD spectra of PES and N6.12/CS@ PES composite membrane

![Average thickness of nylon 6.12 layer as a function of nylon solution concentration (1–5%) of prepared membranes](image2)

Fig. 7 Average thickness of nylon 6.12 layer as a function of nylon solution concentration (1–5%) of prepared membranes
The permeate flow of membranes and the pressure of pure water are both evaluated (Figs. 8 and 9). When the pressure was increased from 10 to 40 bar, all four membranes showed a linear increase in volumetric water flow. Reverse osmosis membranes with smaller holes than traditional membranes are usually constructed with nylon polyamide materials, resulting in decreased water flow. The effective density of the membrane and pores has an impact on the solvent permeability across the membrane [32]. The PA layer attributed to the lower permeability of the water, but increasing the chitosan content enhanced the flow from 10 l/m²h to 57 l/m²h, 70 l/m²h, and 89 l/m²h to PES, PES/1 wt percent, and PES/1.5% wt percent/chitosan, respectively. The relationship between the amine group of chitosan and the active PA-layer might be explained by the formation of a thin layer on the membrane surround. Membrane water molecule sorption was improved by adding more chitosan.

**Performance evaluation of the membranes for dye treatment**

The permeate flow of membranes and the pressure of pure water are both evaluated (Figs. 8 and 9). When the pressure was increased from 10 to 40 bar, all four membranes showed a linear increase in volumetric water flow. Reverse osmosis membranes with smaller holes than traditional membranes are usually constructed with nylon polyamide materials, resulting in decreased water flow. The effective density of the membrane and pores has an impact on the solvent permeability across the membrane [32]. The PA layer attributed to the lower permeability of the water, but increasing the chitosan content enhanced the flow from 10 l/m²h to 57 l/m²h, 70 l/m²h, and 89 l/m²h to PES, PES/1 wt percent, and PES/1.5% wt percent/chitosan, respectively. The relationship between the amine group of chitosan and the active PA-layer might be explained by the formation of a thin layer on the membrane surround. Membrane water molecule sorption was improved by adding more chitosan.
amine groups that couldn’t interact with unreacted groups. This behavior resulted in increased membrane flow depending on the PES/chitosan combination. Similar observations were reported in the literature [31].

As represented in Fig. 9, PES/PA and PES/PA combined with chitosan biopolymer membranes are rejected. Despite that chitosan had a more linear effect on membrane permeability in the PES/PA combination, dye rejection was not detected. This was not the case, though. Until the chitosan level reached 1 Wt%, all membranes increased their rejection of all selected pollutants. Dye was observed with a maximum rejection of 90.3% at this loading. Either the extra chitosan was little or it caused a deterioration. The electrostatic viscous effect is observed when an electrolyte flows through charged surface pores[32]. The AMD was positively charged at pH 3.2, indicating that the membrane was charged as a consequence of amine group protonation. Low pH causes an increase in the osmotic pressure at the membrane’s surface. The thread is held in place by the interaction between the positively charged membranes and the repulsive electrostatic force applied between the teeth and the membrane surface. The addition of chitosan enhanced the porosity and water flow of the membranes due to the improved hydrophilic nature of the membranes, as demonstrated in Figs. 8 and 9. When compared to the PES/PA, the chitosan/PA (PE/0.5 wt%), PES/0.75 wt%, and chitosan/PA (PE/1 wt%) all showed a significant increase in dye rejection (PES). This occurred as a result of the addition of additional functional amine groups that resist or attract coloration when protonated [33].

Zeta potential

The zeta potential of the membranes is defined over a wide pH range (2.5–12), as shown in Fig. 10. For each pH value, the zeta potential was measured four times. The correlation coefficient was more than 0.9 in both situations. The isoelectric point for PES, PES/N6.12, and N6.12/CS@PES membranes was discovered at

![Fig. 10 Zeta potential of PES, N6.12,CS and N6.12/CS@ PES composite membrane](image-url)
Acidic pH values; for PES at pH < 5, for PES/N6.12 at pH < 4.5 and for N6.12/CH@PES at pH < 4. At basic pH values of >10.5, the zeta potentials of most membranes become more negative when pH increases and functional groups deprotonate, according to several studies [34].

**Factors effect of rate rejection of dyes**

**Different electrolytes and dyes concentration**

Figure 11a, b show the rate of rejection of dye of blank membrane and composite membrane. Show the rate of rejection of basic blue dye with CaCl$_2$ > NaCl > NaOH due to the high magneticity of Ca$^{+2}$ which will increase the positive charge on the surface of membrane lead to increase the repulsion force between dye and surface of membrane. The rate of rejection of alizarin red with NaOH > NaCl > CaCl$_2$, where alizarine red is anionic dye will made chelation of Ca$^{+2}$ and attracted to the positively charged membrane. When compared to PES membrane, N6.12/CS@PES membrane exhibited a considerable rejection increase. This was ascribed to an increase in amine functional groups, which when protonated repel cations and attract anions. In order to evaluate the effect of increasing ionic group content on the dye filtration performance of N6.12/CS@ PES composite membranes, 220 ppm of Basic blue dye 41 (R1) and Alizarin red dyes, respectively, were filtrated. A dead-end stirred cell was used under operating pressures of 15 bars with a solution pH of 8. Figure 12a, b show the concentrations of dyes used are (220, 150, 75 and 30) ppm. The rate of rejection increased has been observed from 220 to 150 ppm while it is almost stable from 150 to 30 ppm, where rejection will increase till some pores will blocked thus it will be constant after that.

![Fig. 11](image)  
Rejection (%) of different electrolytes using **a** PES membrane **b** N6.12/CS@ PES composite membrane
The pH effect

The charge density is influenced by the functional groups on the membrane surface, the chemical membrane structure caused by functional group dissociation, and the migration of charged solutes from a solution to the membrane surface [34, 35]. Nylon layer is coated onto the chitosan/PES membrane to generate carboxylic, amide, alcoholic, and amine functional groups in the N6.12/CS@ PES composite membrane. The amine groups in the membrane matrix will be supplied by Chitosan combined into PES granules. Partial polyamide hydrolysis leads to ammonium and carboxylic groups during membrane rejections. Figure 13a, b carboxyl groups (–COOH) at the low-pH (acidic medium) are unrelated and amine groups are protonated into quaternary groups of amines, and the membrane becomes positive and so the rejection rates of simple blue dye were raised to pH = 6, due to the

![Fig. 12](image1.png)

**Fig. 12** Rejection (%) of different dyes using a PES membrane b N6.12/CS@ PES composite membrane

![Fig. 13](image2.png)

**Fig. 13** Effect of pH on the rejection of Basic blue dye 41 (R1) and Alizarin red (R2) in a PES membrane and b N6.12/CS@ PES composite membrane
repulsion forces between cationic dye and membrane surface. But alizarin red dye (anionic dye) will attract with surface membrane thus rate of rejection will decrease till pH = 6, at high pH (basic medium). Membranes become negatively charged as carboxyl groups are separated, thus the rate of rejection of basic blue dye will almost stable from pH 6 to 11 after that it will decrease due to attraction force between cationic dye and surface membrane but the rate of rejection of alizarin red dye (anionic dye) will be stable after pH = 6 till decrease more at pH = 13. The optimum pH value will be at pH = 7 due to the surface membrane will be positively and negatively charged.

Effect of pressure

The produced membrane sheets were evaluated for mechanical strength under various applied pressures, as shown in Fig. 14a, b. The permeation tests were performed at room temperature with a maximum operating pressure of 35 bar and a feed solution capacity of 20 L. In blank membrane by increasing of pressure with cationic dye the rate of rejection will decrease, while with anionic dye the rate of rejection increase with increase of pressure but noted that at pressure reach to 35 bar the rate of rejection decreased and this due to pass of dye molecule through the pores. In composite membrane the rate of rejection will decrease with increasing of pressure.

Regeneration cycles of composite membrane

From 1 to 7 cycle of regeneration the rate of rejection slightly increase, after 7 cycle the rate of rejection sharply increase due to the dye precipitation on the surface of membrane which lead to close of some pore of membrane as shown in Fig. 15.

The regeneration experiments are pergenerated to evaluate the reusability of N6.12/CS@ PES composite membrane using dye solutions. The used N6.12/CS@ PES membrane was washed by ethanol and water in every recycle. Figure 15 shows

Fig. 14 Effect of pressure on the rejection of Basic blue dye 41 (R1) and Alizarin red (R2) in a PES membrane and b N6.12/CS@ PES composite membrane
dye rejection are not changed after 7 cycles and separation efficiency of dyes is still 82% and f > 99.5% or PES and composite membranes. This due to the N6.12/CS@PES composite membrane was not destroyed even after 7 cycles (Fig. 15). Further verified the superior cycle performance of N6.12/CS@PES composite membrane for Basic blue dye 41 and Alizarin red treatment.

Dynamic and static mechanical properties

In order to preserve the structural integrity of generated membranes, the mechanical properties of membrane composites are equally necessary. In particular, mechanical properties of membranes depend mainly on the original rigidity of polymer chains, cross-linking molecular types and density [35, 36]. The mechanical properties of the static tensile modulus (membrane elasticity) and the thermomechanical properties of nylon6.12/chitosan @polyethersulfone (N6.12/CS@PES) and PES membranes were investigated in order to analyze the effect of the chemical modification of PES by chitosan and nylon6.12 surface coating on the mechanical properties of the resulting prepared membrane.

Dynamic mechanical analysis

DMA is used for studying glass transition temperature (T_g) of nanocomposites polymer and polymer and for yield values of the storage module (E'), loss modulus (E'') and tangent or dissipation mechanical loss factor (tan δ = E''/E'). The storage module values provide information on the energy contained in the material during deformation stresses and indicate the rigidity of polymer composites, while the E'' defines its viscous character [37].
Variations in the tensile storage module ($E'$) as a function of temperature for the PES and N6.12/CS@PES composite membranes is shown in Fig. 16a in the 25–150 °C range. The curves of storage modules display 3 different regions: the region with a high modularity is the glassy zone with very restricted segmental mobility and a sharp reduction in the value of $E'$ with an increase in the temperature, known as the transition zone [38]. As a consequence, this modulus decrease is due to an energy dissipation process involving mutual movements of the polymer chain. The third rubber region would have a viscous flow of polymer chains (flow region), i.e., higher chain mobility [38]. It also noted that storage modulus values for N6.12/CS@PES composite were higher than PES at all temperature regions. The values of the storage modules in the glass region (25 °C) and the rubber region (120 °C) for the PES and N6.12/CS@PES composite membranes are shown in Table 1. Composite membrane tensile storage modules are 30% and 67% larger than PES in the glass and rubber areas, respectively. The effect being more pronounced above the glass transition temperature and around the softening point of the matrix, which implies that the chemical modification of the PES by chitosan and the surface coating with nylon6.12 (composite sample) has been able to increase the crosslinking which prevents the free diffusion of the polymer chains and increases the stiffness of the polymer matrix.

Variations in the mechanical loss factor ($\tan \delta$) as a function of temperature for the PES and N6.12/CS@PES composite membranes is shown in Fig. 16b. The
position and height of the tan δ ‘s peak is also indicative of the composite material’s structure and properties. As shown in Fig. 16b tan δ curves of the PES and N6.12/CS@PES composite membranes, there is a single relaxation peak at 83.5 °C and 85.9 °C for the PES and N6.12/CS@PES composite membranes, respectively, and $T_g$ has been transferred to higher temperatures. This increase in thermostability of the composite membrane can again be interpreted as a decrease in the mobility of the polymer chain due to an increase in the degree of cross-linking. The composite membrane has a lower peak height than the PES membrane, which is directly proportional to the increase in crosslinking density [39].

In order to further confirm the hypothesis of the influence of the degree of crosslinking which prevents the mobility of the polymer chains, the degree of crosslinking ($D_X$) was calculated using the following equations based on the elasticity theory of the composite storage modules in the rubber plateau [40, 41].

$$D_X = \frac{E'}{3TR\rho}$$

$T$ is temperature equivalent to ($T_g + 50$), $E'$ is the storage modulus at $T$, $\rho$ is the polymer composite density, and $R$ is the gas constant. The values degree of crosslinking $D_X$ are listed in Table 1. The results show that the degree of crosslinking of N6.12/CS@PES composite membrane is greater than that of PES membrane by 32%. The above study, along with the FTIR findings, has shown that the degree of crosslinking plays a major role in the mechanical behavior of polymer composite membranes.

**Static mechanical properties**

The static tensile modulus (Young’s modulus) was also investigated at temperatures of 25 °C, 50 °C, 75 °C, 100 °C and 125 °C for PES and N6.12/CS@PES composite membranes, as shown in Table 2. Over all temperatures, the N6.12/CS@PES composite membrane displayed the highest Young’s module, demonstrating the high mechanical resistance of such a membrane. The Young’s modulus of composite membranes is larger than that of PES by 24%, 2%, 32%, 13% and 146% at 25 °C, 50 °C, 75 °C, 100 °C and 125 °C, respectively. Young’s modulus values decreased from 232.14 MPa to 0.17 MPa (100% decrease) for PES and from 287.74 MPa to 0.42 MPa (100% decrease) for N6.12/CS@PES composite membrane under 25 °C to 125 °C. This is due to the fact that at room temperature, the molecular motion of such polymer macromolecules is constrained (crosslinked) [42]. This leads to resistance to molecular flow, while the polymer networks are broken down with increased

| Table 2 Young’s modulus values for PES and N6.12/CS@PES composite membranes |
|-------------------------------------------------|
| Young’s modulus (MPa)                          |
| At 25 °C | At 50 °C | At 75 °C | At 100 °C | At 125 °C |
|----------------|
| PES          | 232.14   | 142.12   | 13.15     | 0.62      | 0.17      |
| Composite    | 287.74   | 144.65   | 17.34     | 0.71      | 0.42      |
temperature, and tend to be related to the broken bonds of the crosslinking. The observed changes in the values of modulus of elasticity are in agreement with the hypothesis described above.

**Dielectric properties**

Figure 17a and b show frequency dependence of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) for PES and N6.12/CS@PES composite membranes, respectively. It was observed from Fig. 17a that dielectric constant decreases with increase in frequency and it was more pronounced in N6.12/CS@PES composite than PES and became independent of frequency at higher frequencies (> 50 kHz). This could be because dipole polarization takes a long time since the sides of the polymers’ major chains gradually lose their ability to follow the field. As a result, their polarization contribution decreases, and the composites’ dielectric constant decreases [43, 44]. It was also observed that N6.12/CS@PES composite membrane has the highest dielectric constant only at lower frequencies (< 500 Hz). Interface polarization, i.e., the formation of bound loads at interfaces within the sample material, can be used to explain the high values of at low frequencies. The buildup of charge at interfaces between variable regions in heterogeneous materials that are not similar in conductivity to each other causes interfacial polarization. More components or stages, such as N6.12 + CS + PES, were created here, resulting in maximum heterogeneity. At the interface between the sample and the electrodes employed in net polarization, there is also a buildup of bound charges (electrode polarization). The additional capacitive component of the system is caused by the accumulation of space charges [44].

The frequency dependence of dielectric loss is shown in Fig. 17b. The N6.12/CS@PES composite membrane has the lowest dielectric loss over all frequencies range. It was also discovered that the dielectric loss of PES and N6.12/CS@PES composite membranes increased with frequency. This can be the result of increasing the relaxation loss of dielectric materials and also ionic polarization can occur at higher frequencies, thus encouraging charging carriers to instantly cross the composite surface causing an additional increase in dielectric loss values.

![Figure 17](image)

**Fig. 17** The variation of **a** dielectric constant and **b** dielectric loss with frequencies for the PES and N6.12/CS@PES composite membranes
Interfacial relaxation phenomena in heterogeneous materials, such as our composite membranes, are typically located at low frequencies and cannot be seen for the frequency range studied in room temperature measurements. However, there are many phenomena that typically hidden interfacial relaxations at these frequencies and room temperature, such as electrode polarization, conduction phenomena. The modulus formalism can be used for analyzing dielectric behavior to overcome these problems. The electric modulus $m^*$ formalism can be expressed as follows [45, 46]:

$$m^* = m' + im'' = \frac{\varepsilon'}{\varepsilon' + i\varepsilon''} + i\frac{\varepsilon''}{\varepsilon' + i\varepsilon''}$$

(3)

where $m'$ and $m''$ are the real and imaginary components of complex electrical modulus ($m^*$), respectively. Figure 18a and b show frequency dependence of $m'$ and $m''$ for PES and N6.12/CS@PES composite membranes, respectively. The values of real electric modulus ($m'$) is decreased with increasing frequency for both PES and N6.12/CS@PES composite membranes as expected. The relaxation peak is detected in the frequency range from approximately 70 Hz to 70 kHz for N6.12/CS@PES composite membrane. The relaxation time is calculated from the maximum frequency at peak point and found to be equal $3 \times 10^{-4}$ s.

**Conclusion**

The procedure for the synthesis of N6.12/CS @ PES composites membrane has been investigated via electros pinning by Chitosan with Nylon 6.12. The presence of N6.12/CS in the PES membrane was verified by the FT-IR spectra of the membranes. The asymmetric nature of the membranes was demonstrated using SEM micrographs. The hydrophilicity and mechanical strength of the Nylon 6 nanofiber membrane are improved by chitosan. The improved hydrophilicity of the nanofiber can minimize antifouling impact, making it a viable alternative for water filtration and increasing membrane performance at low pressures. The composite membrane has a greater dye rejection performance than the PES membrane. According to a water filter medium with a high rejection ratio against dyes, basic blue dye41 has

![Fig. 18](image)

**Fig. 18** The variation of **a** real electrical modulus and **b** imaginary electrical modulus with frequencies for the PES and N6.12/CS@PES composite membranes
a rejection ratio of 75.3 to 99.5%, while alizarin red dye has a rejection ratio of 71 to 82%. The composite membrane showed better static and dynamic mechanical properties at room and high temperatures owing to a high degree of crosslinking comparing to the PES membrane. The composite membrane also showed the highest dielectric constant at low frequencies and low dielectric loss at all frequencies range. These results indicated that the N6.12/CS @ PES composite membrane is a very promising membrane materials used to reject dyes from industrial waste water.

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