

# Hydrophilic Properties of PSF/SiO<sub>2</sub> Nanocomposite Membranes with Polymeric Additives

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## ABSTRACT

Polysulfone (PSF) shows great potential for forming membranes; however, its hydrophobic nature affects its function as an ultrafiltration membrane. One solution proposed to solve this problem is to add inorganic polymeric additives to PSF membranes. The present study prepared PSF membranes using SiO<sub>2</sub> nanoparticles by adding polyethylene glycol (PEG) or chitosan (CS) polymer additives. The nanocomposite membranes were compared using phase inversion and their hydrophilic properties and performance were examined by scanning electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy, and Fourier transformation infrared spectroscopy. The results indicated that water uptake increased and water droplet contact angle decreased and showed an improvement in the proper distribution of SiO<sub>2</sub> nanoparticles in the membranes. The comparison of improved and unimproved PSF/SiO<sub>2</sub> nanoparticles indicated that the pore-forming agents in the CS and PEG additives improved them. Hydrophilic results of the membranes showed that the addition of CS strongly increased their hydrophilic properties over those made with PEG.

**KEYWORDS:** Hydrophilicity, Nanocomposite membrane, Polymer additive, Polysulfone, SiO<sub>2</sub> nanoparticles.

## 1. INTRODUCTION

Membranes are important components of separation processes [1]. The good chemical and thermal stability of the polysulfone (PSF) polymer is well-known for materials used in the manufacture of ultrafiltration membranes [2,3]. One solution to decrease PSF hydrophobicity is the addition of inorganic polymeric additives to PSF membranes [4]. Silica, the main component of nanoparticles of silicon dioxide (SiO<sub>2</sub>) occurs abundantly in the earth's crust. It offers good chemical properties, low chemical reactivity, and good performance [5].

Studies have investigated the effect of polyethylene glycol (PEG) polymer added to a polyvinylidene fluoride [6], PSF [7], polycarbonate [8] and polyetherimide [9] and polymer-based membranes. Since synthetic polymers such as PSF decompose and degrade slowly in the environment, it is advantageous to use additives that increase their biodegradability. Chitosan is a N-deacetylated derivative of chitin and is biodegradable and hydrophilic and is naturally suited for film formation. Chitosan (CS) is an antifouling agent that has been shown to remove heavy metals, phosphorus, turbidity and natural organic matter [13-10].

Studies have shown that, contrary to expectation, additives do not always increase the porosity and permeability of the membrane [9] or enlarge the pore microstructure of the membrane [14, 15]. Some studies have observed closure of small pores with the use of additives [15]. Membrane structure has been shown to influence the molecular weight and concentration of some additives [15, 17].

The present study prepared and characterized PSF nanocomposite membranes using silicon dioxide (SiO<sub>2</sub>) nanoparticles. The addition of PEG polymer or CS was compared for improvement of membrane hydrophilic properties and nanocomposite membrane efficiency.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Granules of PSF (translucent; molecular weight = 22,000 gr/mol) were used as the polymer matrix (99% purity; Sigma-Aldrich, US). N,N-dimethylacetamide was used as a solvent (99.8% purity; Merck, Germany). Chitosan (CS) polymer and PEG with a molecular mass of 4,000 and a purity of 99.8% (Sigma-Aldrich; US) were used as polymer additives. SiO<sub>2</sub> nanoparticles (99.9% purity) with a particle size of 15-30 nm (US Research Nanomaterials) was used as an improver of hydrophilic properties and fine pore-forming of the membrane.

### 2.2. Preparation of membranes

All membranes were prepared by phase separation. Membranes were prepared using 23% wt PSF, 72% wt dimethylacetamide, 3% wt SiO<sub>2</sub> nanoparticles and 5% wt CS or PEG (Table 1).

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**Table 1.** Composition of different membranes' casting solution.

Membrane code number	PSF(wt%)	DMAc(wt%)	SiO <sub>2</sub> (wt% to PSF)	CS(wt%)	PEG(wt%)
1	23	72	3	-	-
2	23	72	3	-	5
3	23	72	3	5	-

The solutions were molded after preparation by pouring onto a flat glass surface and were cast to a thickness of 100  $\mu\text{m}$  using a film applicator. The film was immersed for phase separation and formation of the membrane in distilled water at 25°C. After 2 h, the membranes were removed from the water bath and washed several times with distilled water.

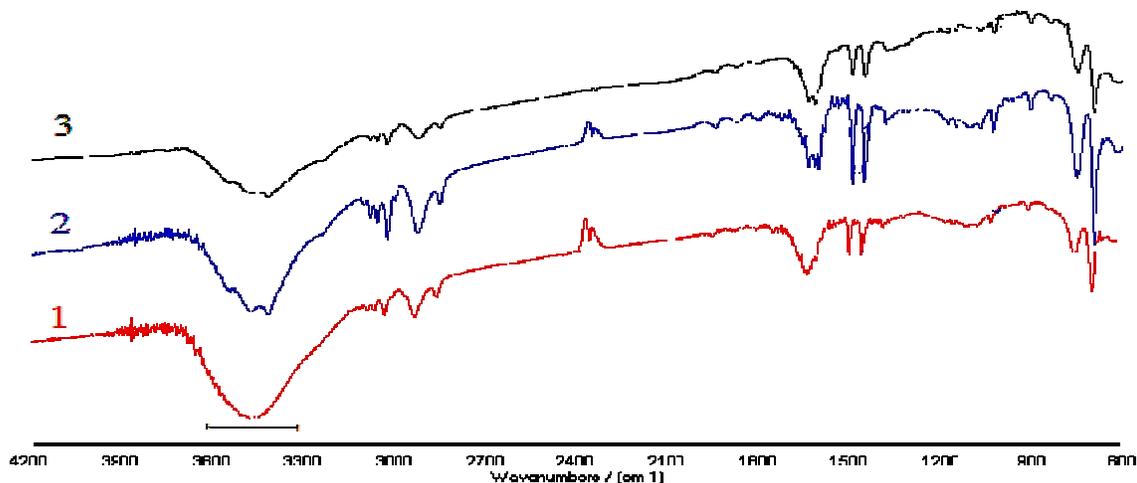
### 2.2.1. Preparation of PSf/PEG/SiO<sub>2</sub> nanocomposite membranes

SiO<sub>2</sub> nanoparticles were as dissolved in the dimethylacetamide solvent at 50-60 °C under vigorous stirring. PEG polymer was added to the nanoparticle solution at 50°C and dissolved after 8 h of stirring. PSF granules were added to the uniform solution at 80°C and dissolved after stirring for 5 h. The PSF/PEG/SiO<sub>2</sub> nanocomposite solution was exposed to ultrasonic irradiation for 1 h to increase the uniform distribution of nanoparticles in the PSF/PEG composite matrix. The uniform solution of PSF/PEG/SiO<sub>2</sub> nanocomposite was then molded to form a membrane.

### 2.2.2. Preparation of PSf/CS/SiO<sub>2</sub> nanocomposite membranes

Preparation of PSF/CS composite solution was done in accordance with the procedure described by Kumar et al. [3]. First, 1 g CS was dissolved in 50 ml 1% acetic acid solution. In another container, 3.8 g PSF was dissolved in 15.2 ml of DMAc solvent at 60°C by stirring for 4 h to obtain a uniform solution. Next, 1 ml of the CS solution was added to the PSF solution at 70°C and stirred at high speed.

The CS was precipitated (white) by adding 5 ml of DMAc to the solution and stirring was continued while maintaining the temperature until the CS was completely dissolved in PSF to prepare a PSF/CS viscous solution. The solution was filtered through G4 mesh while the solution was hot. SiO<sub>2</sub> nanoparticles (3% wt) were added to PSF/CS uniform viscous solution and stirring continued at 40°C until the nanoparticles dissolved completely.

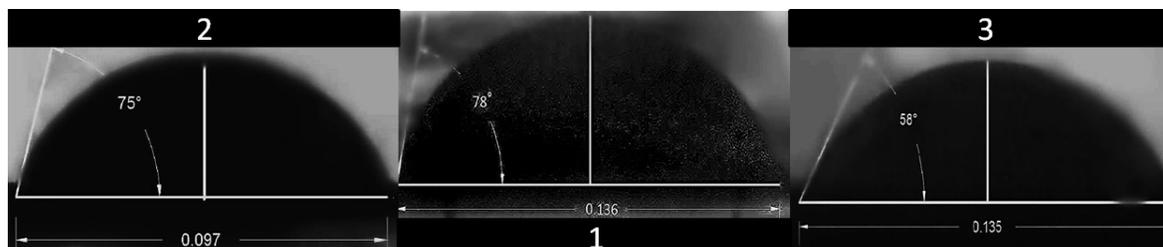


**Fig. 1.** FTIR spectra of 1) PSf/SiO<sub>2</sub>, 2) PSf/PEG/SiO<sub>2</sub>, 3) PSf/CS/SiO<sub>2</sub>.

After 1 h of stirring to ensure complete dispersion of the nanoparticles, the solution was subjected to ultrasonic irradiation for 1 h to prepare a uniform solution of PSF/CS/SiO<sub>2</sub> nanocomposite.

### 2.3. Characteristics of prepared membranes

The interaction between nanoparticles and polymer materials was studied using Fourier transformation infrared spectroscopy (FTIR) (model WQF-510; Rayleigh, China) at Islamic Azad University in Gorgan, Iran at 600-4200  $\text{cm}^{-1}$  and 0.1  $\text{cm}^{-1}$  magnification. The cross-section and surface structure of the membranes and membrane pore size was studied using scanning electron microscopy (SEM) (model LO 1430VP; UK, Germany) at Mohaghegh Ardabili University.



**Fig. 2.** Schematic representation of contact angle measurement: (1) PSF/SiO<sub>2</sub>, (2) PSF/PEG/SiO<sub>2</sub>, (3) PSF/CS/SiO<sub>2</sub>.

A Bruker X-ray diffraction unit (model D8 advanced; Germany) at Damghan University was used to study the structure of crystalline and amorphous membranes. Energy-dispersive X-ray spectroscopy (EDS) was conducted to confirm the existence of the elements, especially SiO<sub>2</sub> nanoparticles. The EDS micro-analyzer of an FE-SEM imaging detector (Mira 3-XMU; Germany) was used at Razi Metallurgical Research Center.

## 2.4. Hydrophilic properties of prepared membranes

### 2.4.1. Water contact angle

Measurement of the contact angle of the water droplets was performed as recommended by Kumar et al [18]. The FTA-200 dynamic contact angle analyzer was used to produce the droplets on prepared membranes having surface areas of 2 cm<sup>2</sup> (100 μm diameter). Contact angle measurement was performed three times and the average was recorded.

### 2.4.2. Measurement of water uptake

Membranes with areas of 1 cm<sup>2</sup> were dried in an oven and their dry weight was measured using a scale (0.00001 accuracy). The dried membranes were immersed in buffer solutions with pH values of 4, 7 and 11 for 24 h. The membranes were then removed from the buffer solutions, the excess water was removed from the surface of the membranes using filter paper and their wet weight was recorded using the scale (0.00001 accuracy) [18]. The water uptake of the membranes was prepared according to the following equation for water absorption:

$$\% \text{ uptake} = \left( \frac{W_w - W_d}{W_d} \right) \times 100$$

where  $W_w$  is the wet weight of the membrane after 24 h exposure to buffer solution and  $W_d$  is the dry weight of the membranes. For precision in measurement, the samples were measured three times and the average weight was recorded.

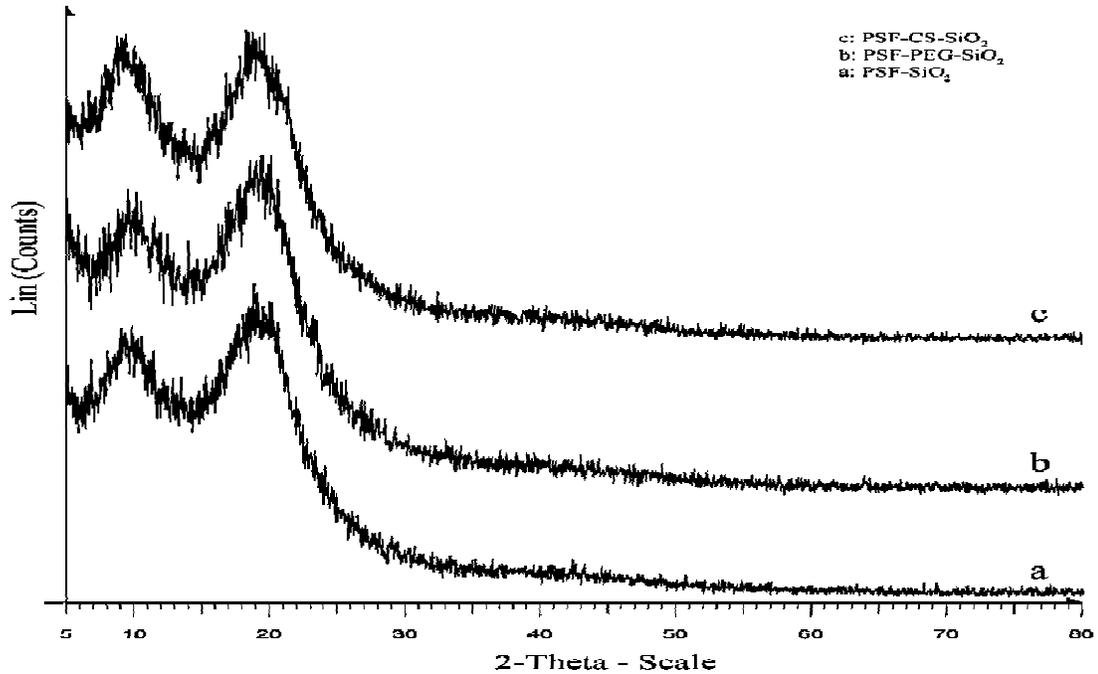
## 3. RESULTS

### 3.1. Study of FT-IR results

The FTIR spectra of the unimproved PSF/SiO<sub>2</sub> membranes and those improved with PEG and CS is shown in Fig. 1. The tensile bond of the Si-O element of the SiO<sub>2</sub> nanoparticles was confirmed by a peak at 1000-1100 cm<sup>-1</sup>. Peaks at 1105 cm<sup>-1</sup> and 1150 cm<sup>-1</sup> revealed the presence of the sulfonate groups in the PSF. Hydrogen bonds created by PEG and CS in the FTIR results of PSF/PEG/SiO<sub>2</sub> and PSF/CS/SiO<sub>2</sub> membranes were evident by the broad peaks at 3000-3400 cm<sup>-1</sup>.

### 3.1. XRD spectra analysis

Fig. 3 shows the XRD peaks for the crystalline regions of the membranes and the effect of nanoparticles on crystal or amorphous membranes.

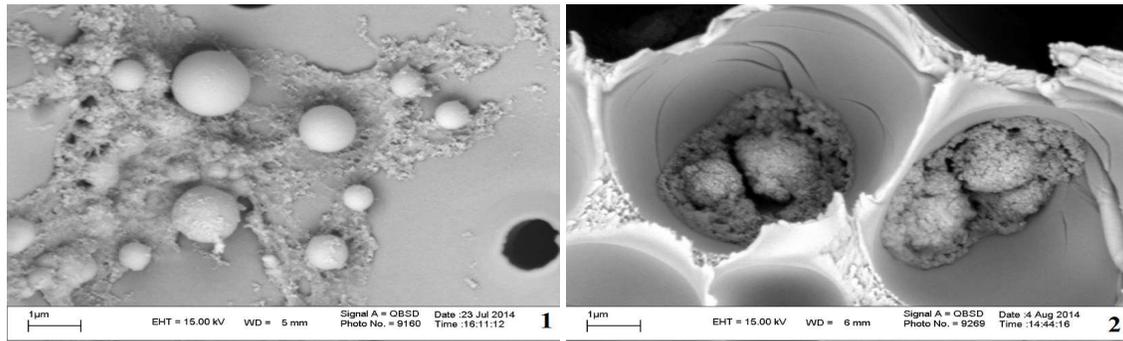


**Fig.3.** XRD pattern of all prepared nanocomposite membranes. a) PSF/SiO<sub>2</sub>, b) PSF/PEG/SiO<sub>2</sub>, c) PSF/CS/SiO<sub>2</sub>.

The figure shows the amorphous nature of SiO<sub>2</sub> nanoparticles was demonstrated and the results showed that the nanoparticles had no effect on the formation of crystalline regions in the prepared membranes.

### 3.2. SEM images analysis

Fig. 5 shows the SEM images of the cross-section and surface of the membranes show a smooth and flawless surface and an asymmetric spongy structure with uniform pores with no accumulation of nanoparticles. This was the result of the amalgamation of fine nanoparticles in the polymer matrix.



**Fig.4.** Comparison of SEM cross-sections of membranes for nanoparticle aggregation and pore size: (1) PSF/CS/SiO<sub>2</sub>, (2) PSF/PEG/SiO<sub>2</sub>.

The white spots in Fig. 4(1) indicate that most SiO<sub>2</sub> nanoparticles were uniformly dispersed within the PSF/CS/SiO<sub>2</sub> nanocomposite membrane. Fig. 4(2) shows that SiO<sub>2</sub> nanoparticles agglomerated in the PSF/PEG/SiO<sub>2</sub> nanocomposite membrane. SEM images of the improved membranes showed that PEG and CS act as promoters of membrane performance and as a pore-forming agent.

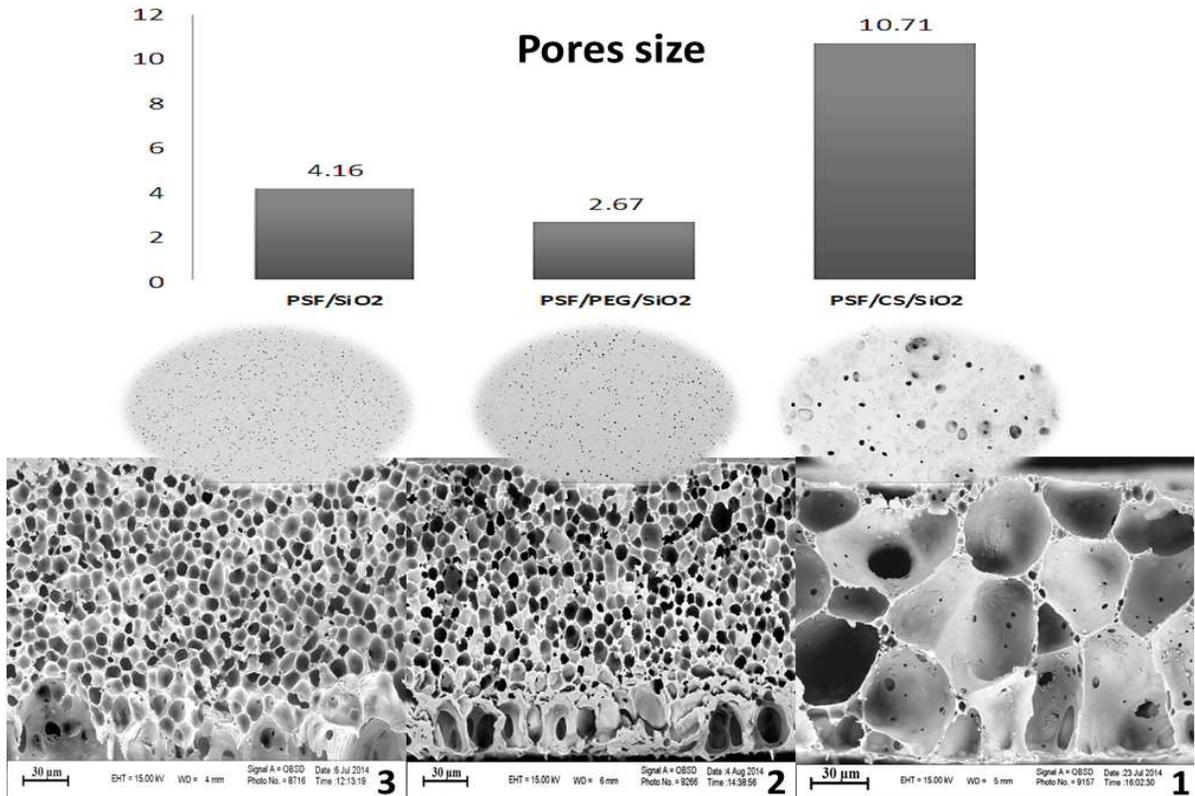


Fig.5. surface and Cross-section SEM images and pores size of: 1) PSF/CS/SiO<sub>2</sub> – 2) PSF/PEG/SiO<sub>2</sub> – 3) PSF/SiO<sub>2</sub> membranes.

The results showed that the addition of CS polymeric additive significantly increased the pores size of the PSF/SiO<sub>2</sub> sponge asymmetric structure (Fig. 5).

### 3.3. Investigation of EDS results

EDS analysis was used to confirm the existence of the elements in the SiO<sub>2</sub> nanoparticles in the prepared membranes.

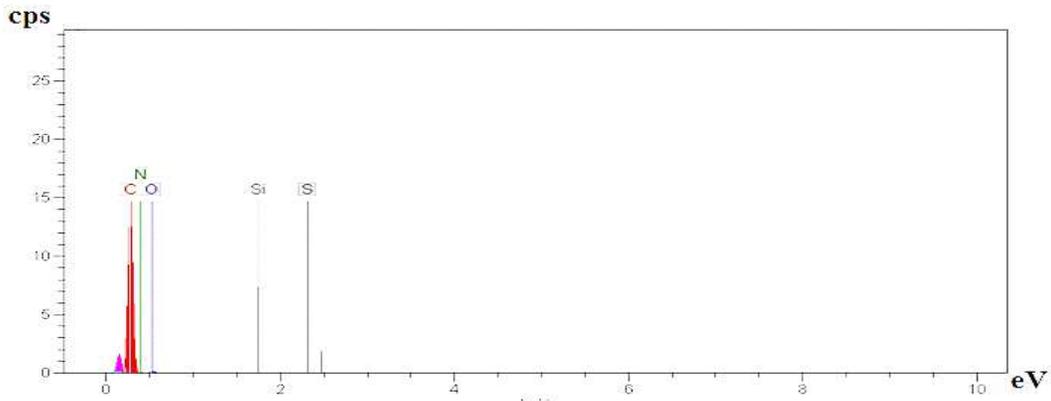
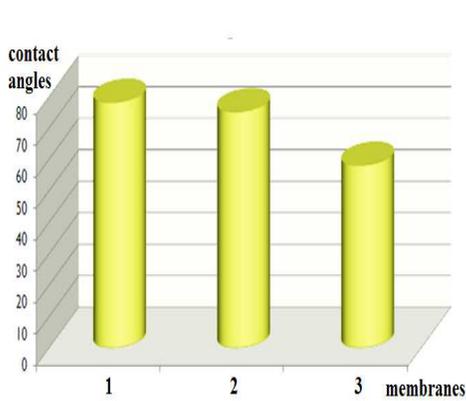


Fig. 6. EDS result of SiO<sub>2</sub> nanoparticles on the surface of modified membrane.

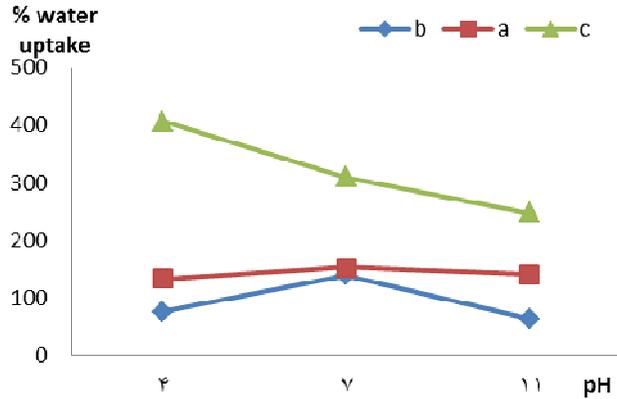
Fig. 6 shows the peak for Si of the SiO<sub>2</sub> nanoparticles and the peak for N related to the nitrogen element of CS.

### 3.4. Measurement of the contact angle of water drop and water uptake

Fig. 2 shows the water droplet contact angle with the prepared membranes showed that adding CS polymer additives to PSF/SiO<sub>2</sub> membrane strongly decreased the water droplet contact angle from 78° to 58°.



**Fig. 7.** Contact angle of membranes: 1) PSf/SiO<sub>2</sub>, 2) PSF/PEG/SiO<sub>2</sub>, 3) PSF/CS/SiO<sub>2</sub>



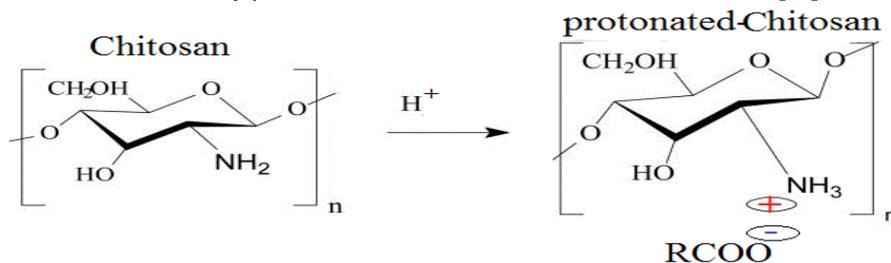
**Fig. 8.** pH dependent of a) PSf/SiO<sub>2</sub>, b) PSF/PEG/SiO<sub>2</sub> and c) PSF/CS/SiO<sub>2</sub> membranes.

The results for water uptake of the membranes at pH 4, 7 and 11 are shown in Fig. 8. The addition of CS to the PSF/SiO<sub>2</sub> membrane dramatically increased water uptake for different pH values compared the unimproved membranes and the membranes improved with PEG polymer additive (Fig. 8).

#### 4. DISCUSSION AND CONCLUSIONS

The SEM images showed good distribution of SiO<sub>2</sub> nanoparticles in the prepared membranes. The asymmetric spongy structure of PSF/CS/SiO<sub>2</sub> nanocomposite membrane was well-dispersed and uniform. FTIR analysis showed a good interaction between the SiO<sub>2</sub> nanocomposite membranes and polymer additives. In the PSF/CS/SiO<sub>2</sub> nanocomposite membrane, PSF and CS functional groups interacted with SiO<sub>2</sub> nanoparticles. FTIR peaks for PSF/CS/SiO<sub>2</sub> decreased in intensity. The formation of hydrogen bonds between the functional groups of the CS and SiO<sub>2</sub> nanoparticles increased the peak for CS to 3000-3400 cm<sup>-1</sup> in width. This indicates good interaction between the nanoparticles in PSF/CS/SiO<sub>2</sub> as confirmed by FTIR spectroscopy.

Investigation of the hydrophilic properties of the membranes showed that the addition of CS strongly increased the hydrophilic attributes. This was confirmed by the SEM images which represent an increase in the spongy pore sizes of the PSF/CS/SiO<sub>2</sub> membrane and by the decrease in contact angle of the water droplets and increase in water uptake. In the PSF/CS/SiO<sub>2</sub> nanocomposite membranes, the increase in water uptake at pH 4 was the result of the formation hydrogen bonds in the -NH<sub>2</sub> groups of CS in acidic solution (Fig. 9). When CS is placed into an acidic environment, the -NH<sub>2</sub> functional groups protonate and conflict with the -NH<sub>2</sub> functional group; the main chain of CS easily penetrates the water and increases water absorbance [18].



**Fig. 9.** Schematic of protonation CS mechanism in acidic solution (pH = 4).

For PSF/CS/SiO<sub>2</sub> nanocomposite membranes, there was a slight decrease in water uptake at pH 11 over that for pH 7 from the formation of CS functional groups in the buffer solutions [3]. The results of this study suggest that CS is a good hydrophilic additive because it is natural, accessible, inexpensive and biodegradable polymer. It is a good pore-forming agent for preparing nanocomposite membranes for use in separation of water.

#### 5. Acknowledgement

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