

Nano Composite Membrane on Polysulphone Matrix

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Recently, membrane technology started to be considered the leading technology in the field of separation techniques. In the present paper, Polysulfone-Sulfonate Polyetheretherketone-Polyaniline-Carbon Nanotube (PSf-SPEEK-PANI-CNT) nanocomposite membrane, has been obtained by phase inversion via immersion-precipitation from a dispersion of the SPEEK-PANI-CNT nanocomposite material, in a solution of Polysulfone in N, N-dimethylformamide (DMF). The morphology of membrane was characterized by using SEM techniques. Due to the high degree of sulfonation, the production SPEEK membranes are soluble in water, which restrict their application field. The PSf-SPEEK composite membrane has a good thermal resistance, the thermal stability up to 460-480°C, and the residual mass in this case was (11.96%). The pore shape of PSf-SPEEK composite membrane looks like a water lily flower with longitudinal pores sizes ranging between 504.0nm and 1.837 μm. These sizes refer to the availability of using this composite membrane in ultrafiltration applications with high permeate flow.

Keywords: nano composite, membrane, polysulfone, technology

Recently, membrane technology is the leading technology of separation techniques [1]. A recent advance in membrane technology is the focus on the development of membrane materials which are the key determinants of separation performance and water productivity [2-4].

Polysulfone is selected as the support material due to its hydrophobic character and relatively high surface tension for improving adhesion to coating layer [5] and its excellent characteristics: good solubility in a wide range of solvents, high thermal resistance (150-170°C), good resistance in pH range, good resistance in oxidative medium, high mechanical resistance of the films (fracture, flexure, torsion), moderate reactivity in aromatic electrophilic substitutions reactions (sulfonation, nitration, chloromethylation, acylation, etc.) [6-8]. The separation ability of a membrane is dependent on its composition [9-12].

Polyetheretherketone (PEEK) is one of the conventional thermoplastic polymer that has excellent mechanical properties. The aromatic backbone of PEEK give it chemical modification through electrophilic substitution by sulfonation. To increase the hydrophilicity and ion transport of the PEEK material, charged groups are introduced through sulfonation [13-15]. The aromatic backbone helps maintain thermal and mechanical stability, as well as allowing for chemical modification such as through simple electrophilic substitution by sulfonation.

The sulfonation groups ($-SO_3^-$) can be introduced into the PEEK polymer chain using several methods. Sulfonation can be done by pre- or post- polymerization [16]. Sulfonated poly (ether ether ketone) (SPEEK) has high thermal stability, high mechanical strength, easy to handle and cheap. Nevertheless, raw material for SPEEK membrane, poly (ether ketone) (PEEK), is a hydrophobic polymer and not suitable to fabricate as membrane. Therefore, PEEK has to be modified by the sulfonation process using concentrated sulfuric acid [13].

Among the family of conducting polymers, polyaniline (PANI) is one of the most useful since it is environmental stable in both its doped, conducting form and its de-doped, undoped form of polyaniline is hydrophobic, while in the doped form polyaniline has been shown to be hydrophilic. Together, these properties make polyaniline a promising candidate for liquid separation. In addition, the polymer is nontoxic, has high thermal stability and low manufacturing cost. The subject of many publications focused on the improvement of its process ability in the past several years, such as substitution of aromatic ring of polyaniline with $-CH_2-$, $-OCH_2-$, $-SO_2-$ or long alkyl chain that leads to higher solubility in organic solvents and even in water [17,18].

Simultaneously, undoped polyaniline (emeraldine salt form) shows better solubility in common non polar or weakly polar organic solvents and surprisingly desired bulk polymers (such as Polysulfone) are also dissolved in these solvents. Therefore, the development of polyaniline nano composites and blend via solution blending is expected to make a critical impact in fabricating higher performance membranes with increased permeability, selectivity.

The most stable form of PANI is emeraldine, in which every second nitrogen atom is oxidized, and polymer chain contains equal number of oxidized and reduced units. Charge carriers are formed in polymer during its oxidation. Nitrogen atoms of PANI serve as oxidation centers. During oxidation, i.e., removal of electron, positive polaron is generated in the chain; it deforms chain structure considerably [24-26].

Carbon nanotubes (CNT) have been a great source of researches due to its unique mechanical, electrical and thermal properties, which can be extremely applicable to engineering development. There are two types of carbon nanotubes, single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). However, MWCNT, poor stability.

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The sulfonation process makes the polymer soluble in many other solvents such as dimethylsulfoxide (DMSO). It is noteworthy that the dissolution properties of SPEEK are strongly dependent upon the degree of sulfonation, DS, such that below 30% sulfonation the samples are insoluble, at least at moderate temperatures, in all common solvents. Above 30% sulfonation the samples are soluble in hot dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethylsulfoxide (DMSO); above 40% in the same solvents at room temperature, above 70% in methanol and at 100% in hot water [27, 28].

The degree of sulfonation (DS) is defined as the percentage of repeat PEEK units that have been sulfonated. A higher degree of sulfonation indicates that more repeat units have been sulfonated. This can be determined by using a titration method, H-NMR spectroscopy, FTIR spectroscopy, or by weight loss.

This study is dedicated to combine the advantages of polysulfone as a membrane material and SPEEK, PANI, and CNT as a composite material. Although several studies on SPEEK were previously conducted, this chapter reports the synthesis and characterization of SPEEK membrane was prepared via evaporation of SPEEK (350P) - gel form.

Experimental part

PEEK (150P), PEEK (350P), sulfuric acid (96%) (Merck) was used as a solvent for PEEK. Carbon nanotube was used as a modified material polysulfone was supplied by BASF (Ultrason S3010), N,N-dimethylformamide (DMF) (Merck) was used as a solvent for Polysulfone. Aniline (Merck), hydrochloric acid (HCl) (Merck) and potassium persulfate (Fluka) were used for aniline polymerization.

Ethanol was used as a non-solvent for membrane phase inversion, and finally pure water was obtained by Millipore module.

Characterization techniques description

The membranes were characterized by FT-IR Spectroscopy analysis (Bruker Tensor 27 with ATR annex), thermal analysis (TGA-DSC) using a Universal V4.5A TA Instrument, EDAX analysis and Scanning Electron Microscopy (FEI Instrument, the samples were covered with a thin layer of gold) [21-23].

Preparation of nano composite materials

After PEEK sulfonation (2g) by reaction with concentrated sulfuric acid 96% (20 mL) for five days, appeared an auburn-golden solution, figure 1a, CNT trace

was added. In order to make the interaction structural between SPEEK and PANI, aniline (60 mL) was added sequentially to the present sample, where was observed that appears high exothermic reaction figure 1e. PANI was obtained in-situ by Chemical polymerization of Aniline, via added the present sample to a solution of 500 mL of distilled water, 5mL of concentrated hydrochloric acid, and 2g of potassium per sulfate figure 1b.

After five days the nano composite material was separated by using a vacuum device with filter paper (0.45 μ m) (fig 1a). Nanocomposite material have been saved in glass container was wrapped with aluminum foil to keep on from humidity.

The nanocomposite materials were washed many times with distilled water after pouring in a dialysis tube and soaking in a distilled water at ambient temperature (22°C) until the conductivity of washing water was closed to zero (fig 3 f), by using a conductivity meter. The nano composite material was dried at 60°C for 24 h figure 1b.

Visually, the process was controlled by monitoring the color change of solution, from auburn-golden solution to white- brown, blackish material after the aniline was added, and then, violet, green for a moment of time, after it was added to a solution of water, hydrochloric acid, and potassium per sulfate, and finally to brown blackish, which confirmed the sulfonated of PEEK and polymerization of aniline.

It should be taken into account that the color of polyaniline is changing according to the solution pH [20]. Oxidative polymerization of aniline in basic, neutral and weakly acidic media gives brown powder with low conductivity, while, the synthesis in highly acidic medium yields highly conductive PANI, since only under these conditions conducting dark-green emeraldine can be obtained. In contrast with oxidizing agents, persulfates are used more widely, due to having an oxidation potential of +2.01V [17].

It should be noted here, in a vast majority of cases, PANI is synthesized by oxidative polymerization of aniline. Oxidation of aniline is an exothermic process and can easily be followed by temperature changes. The temperature dependence provides information on the intensity of oxidation processes in the individual steps of the synthesis. The monomers used in oxidative polymerization are characterized by pronounced electron donor properties and high oxidation tendency.

It should be also kept in mind that the formation of chain may proceed in two ways. The first one is recombination

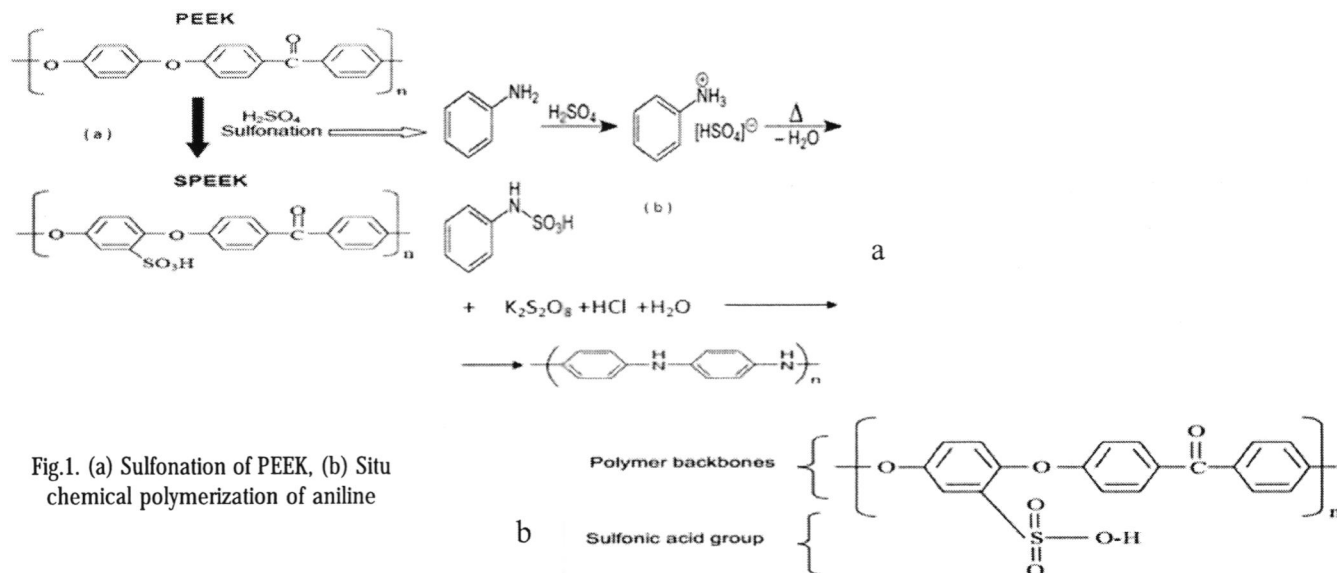


Fig.1. (a) Sulfonation of PEEK, (b) Situ chemical polymerization of aniline

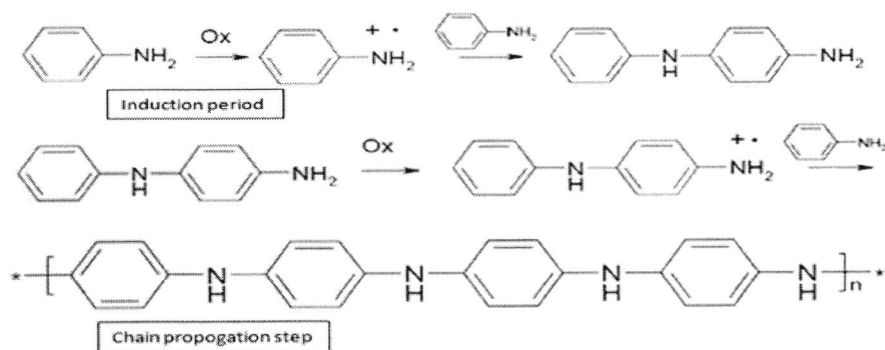


Fig.2. Aniline oxidative polymerization

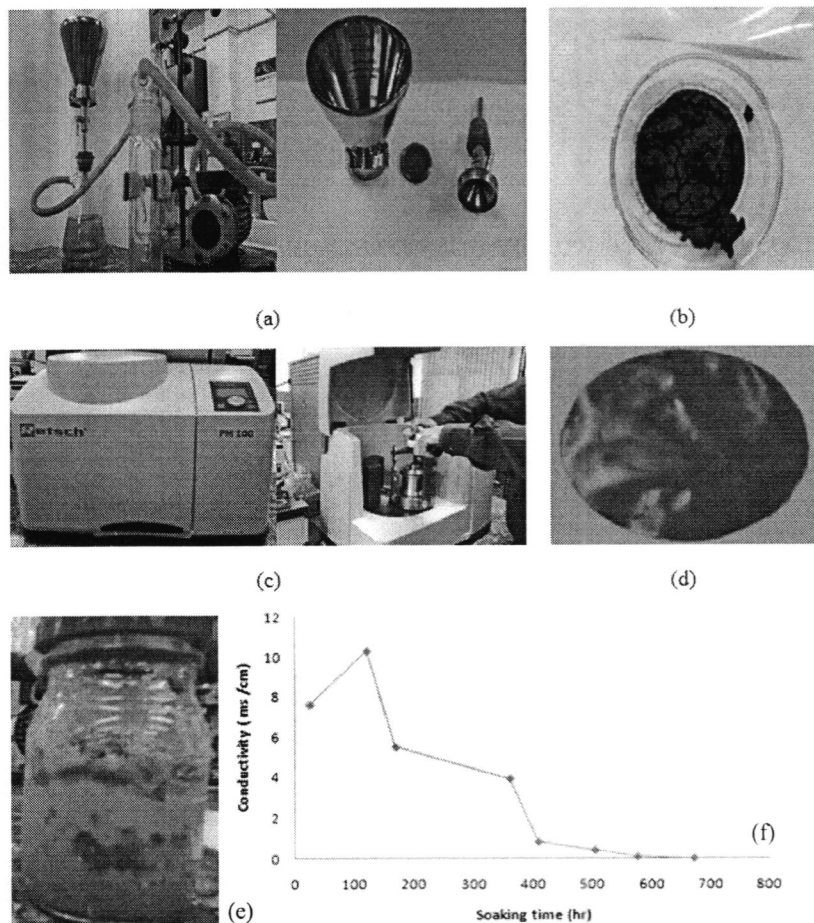


Fig 3. (a) Vacuum device was used to separate the nanocomposite materials; (b) Nano composite materials; (c) RetschR PM 100; (d) Nano composite membrane; (e) Sulfonation of aniline (f) Conductivity of nano composite material washing water

of cation radical oxidation sites. In this case, polymer growth process is classed as polycondensation, since fragments of any length may recombine. The second way of chain growth belongs to electrophilic substitution; in case of aniline, oxidized nitrogen-containing structure attacks phenyl ring of another molecule and substitutes one proton of the ring. Both the ring and nitrogen-containing structure lose one proton; after that, monomer units bind with each other, and the chain becomes longer [18].

Presently, electrochemical and chemical synthesis of conducting PANI by oxidative polymerization is usually described in figure 2 [20].

Aniline oxidation process usually involves. (1) Oxidation of nitrogen atom of monomer followed by oxidation of end nitrogen atoms of oligomer and polymer; (2) addition of monomer in the *nitrogen-carbon* fashion as a result of chain reaction (electrophilic substitution of proton in aromatic ring of monomer by oxidized polymer fragment) [17,19].

In the course of chain-growth polymerization, monomer units are sequentially added to the polymer chain bearing active end group and there are many types of linkage between monomer units, in the case of aniline, *head-to-*

head, *tail-to-tail*, and *head-to-tail* configuration is possible [17].

Preparation of nano composite membrane

Nano composite membrane solution was achieved after adding 0.87 g of nano composite material to a solution of 20% Psf in DMF (80mL) in the autoclave of colloidal mill (Retsch[®] PM 100) with quartz grinding machinery of 1mm diameter (80mL) (fig. 3c). After 3 h of homogenous mixing at 300 RPM the autoclave was opened.

A small quantity of nano composite membrane solution was deposited on a spectral glass after the blade was fixed and it was extended to a standard thickness (250µm) by using a scalpel. After submerging in the coagulation bath for 30 min at ambient temperature (25°C), the obtained brown, blackish nano composite membrane was washed with distilled water to remove traces of the solvent and the coagulant figure 3 d.

Results and discussions

FT-IR and EDAX spectrum

FT-IR Spectra of Nano composite materials are shown in fig 4. As shown in figure 4 (a) the presence of sulfonic

acid groups $O = S = O$ was observed with the absorption bands at 1021.06, 1077.14, 1158.29, 1183.73 cm^{-1} .

The C=O stretch mentioning of PEEK formation was assigned in bands 1647.51, 1652.68, 1670.35, 1684.11, 1698.36, 1716.66, 1733.57, 1748.91, 1760.65 cm^{-1} .

The presence of PANI was observed with the absorption secondary band of N-H at 3259.23 cm^{-1} and the absorption primary band at 3421.27 cm^{-1} . It is worth noting, that the carbon nanotubes have not an infrared spectrum with bands [20], and the spectrum region between 3000-3600 cm^{-1} , shows the formation of hydrogen bonds [17]. EDAX spectrum figure 5 indicates that the elemental distribution values for nano composite membrane recorded higher values than 20% PSf membrane.

TGA of nanocomposite membrane

The thermogravimetric curves of 20% PSf membrane and nanocomposite membrane are presented in figure 4. In curve a, the weight loss started at 100°C and persisted until 240°C, may be correspond to the loss of adsorbed bound water and other organics. There are two different stage ranges of weight loss, 440 – 520°C and 520 – 580°C. The stages 520 to 640°C represented a weight loss process of PSf. Figure 4 (b), shows four different stages of weight loss, the first stage ranges between 100 and 240°C was associated with adsorbed bound water and other organics. The observed low weight loss between 280 – 360°C was attributed to the decomposition of sulfonic acid groups.

The two different stage ranges of weight loss, 450 – 520°C and 520 – 600 were associated with backbone

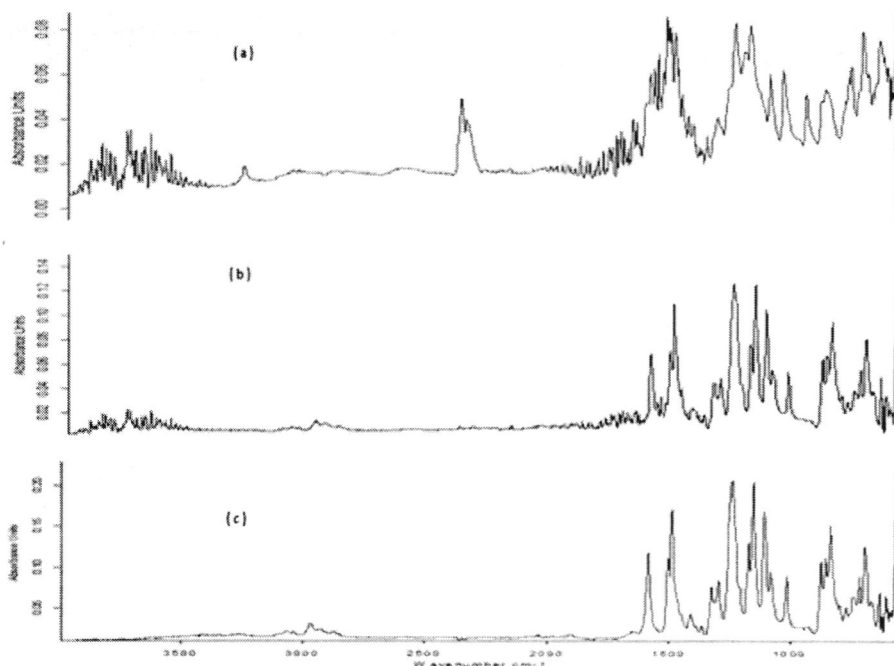


Fig 4. FT-IR spectra of (a) nano composite materials (SPEEK-PANI-CNT); (b) nano composite membrane; (c) 20% PSf membrane

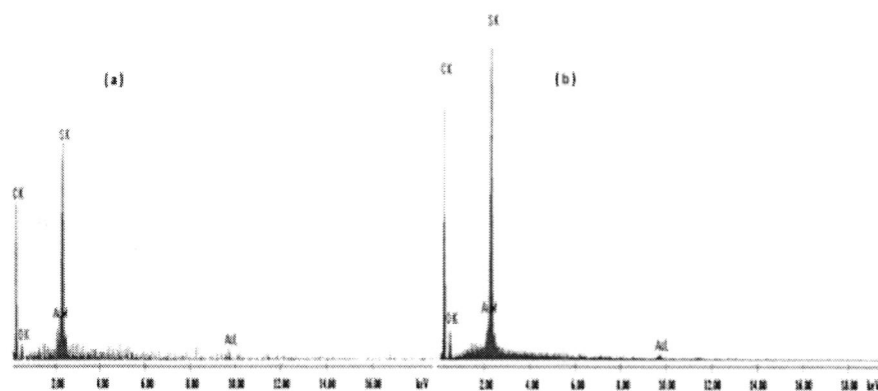


Fig 5. EDAX image of 20% PSf membrane (a) and nanocomposite membrane (b)

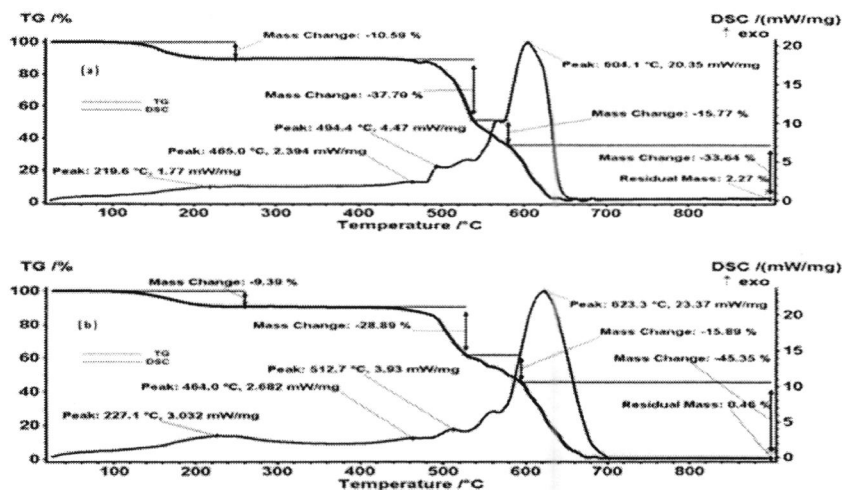


Fig 6. TGA and DSC curve of (a) 20% PSf membrane; (b) nanocomposite membrane

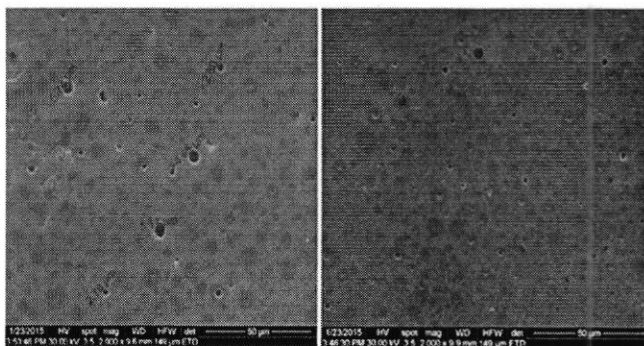


Fig 7. SEM images of (a) 20% polysulfone membrane, (b) nanocomposite membrane

decomposition of PSF, PANI, and PEEK. The thermogravimetric curve of the nanocomposite membrane did not show imperceptible change in thermal resistance if compared with polysulfone membrane.

Membrane morphology

SEM remaining one of the most used techniques for the characterization of the morphology of membrane (fig. 7) shows the size of the opened pores, observed at the surface for 20% PSf membrane and nanocomposite membrane. From figure 7 (a) it seems that the size of pores ranges between 2.78 and 5.74 μm for 20% PSf membrane and between 784.6 nm to 4.17 μm for nanocomposite membrane figure 7 (b).

Polysulfone composite membrane of sulfonated poly ether ketone, modified by dispersed polyaniline

PEEK (350P, gray color) was dried in a vacuum oven at 100. PEEK pellets (10 g) were gradually added into 100 mL H_2SO_4 (96%) with vigorously stirred at ambient temperature ($\sim 22^\circ\text{C}$). After a prescribed time (9 days), the sulfonated polymer was recovered by precipitating the acid polymer solution into a large excess of ice water under mechanical agitation for a desired time (1-2h), where to be observed formation a white SPEEK.

A SPEEK was left to settle overnight. SPEEKs were washed with deionized water by placing the polymers in dialysis tubing and dialyzing the acid out of the polymers until the rinse water was at pH 6-7 [26]. Then, the SPEEK samples were dried at 70°C for 7 days, where observed formation a yellow SPEEK (fig. 8).

Solution preparation

a) PANI solution preparation

2.699 g of Polyaniline (Aldrich, emeraldine base, Mwca.20.000) was dispersed in 100mL of N, N-dimethylformamide (Sigma-Aldrich) at 100°C with magnetic stirrer for a desired time.

b) SPEEK solution preparation

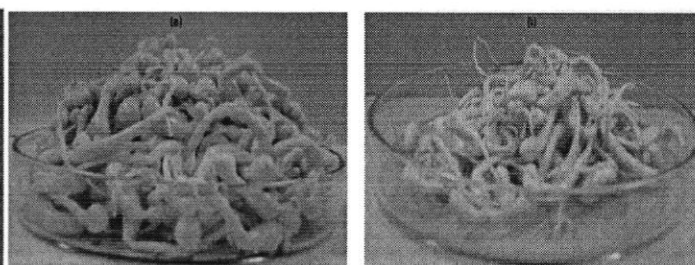


Fig.8. SPEEK; (a) before drying; (b) after drying

3g of SPEEK was dissolved in 420mL of N, N-dimethylformamide at the desired time (14 days) and ambient temperature ($\sim 22^\circ\text{C}$).

c) 20% PSf solution preparation

100 g of PSf was dissolved in 450 mL N, N-dimethylformamide at the desired time (14 days) and ambient temperature ($\sim 22^\circ\text{C}$).

d) PSf - SPEEK solution preparation

150 mL of SPEEK was mixed with 200mL of 20% PSf solution by using a magnetic stirrer at desired time 72h.

e) PSf - SPEEK-PANI solution preparation

100 mL of PANI was dispersed in a solution of 100mL SPEEK and 250 mL 20% PSf with magnetic stirrer at desired time 72h.

Preparation of composite membranes

Small solution (c, d, and e) quantities were deposited on a spectral glass after the blade was fixed and it was extended to a standard thickness ($250\mu\text{m}$) by using a doctor knife.

After submerging in the coagulation bath for 30 min at ambient temperature (22°C), the obtained composite membranes were washed with distilled water to remove traces of the solvent and the coagulant.

TGA of composite membrane

The thermogravimetric curves of 20% PSf membrane and composite membrane are presented in figure 9. In curves a, and c the weight loss started at 100°C and persisted until 240, may be correspond to the loss of adsorbed bound water and other organics. In curve a, and c the sample is stable up to 140°C .

The first decomposition percents for curves a and c are (9.43%) and (5.87%) respectively. Between 240-450 curve a, and c has been no transformation. There are two different oxidative degradation presented in curves a, and c between 450-544.541 $^\circ\text{C}$ and 544.541-690 $^\circ\text{C}$ respectively. These processes that are accompanied by adverse exothermic DSC curves.

Curve b, has a different behavior. It started with an increase in mass loss (33.82%). Curve b, shows good thermal stability up to 460-480 $^\circ\text{C}$. Then you can see that there are two phases of oxidative degradation taking place

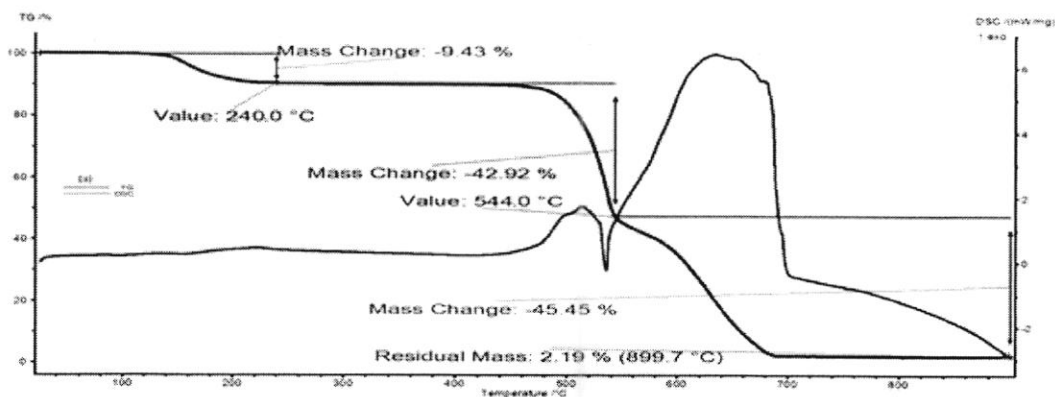


Fig 9. TGA and DSC curve of (a) 20% PSf membrane

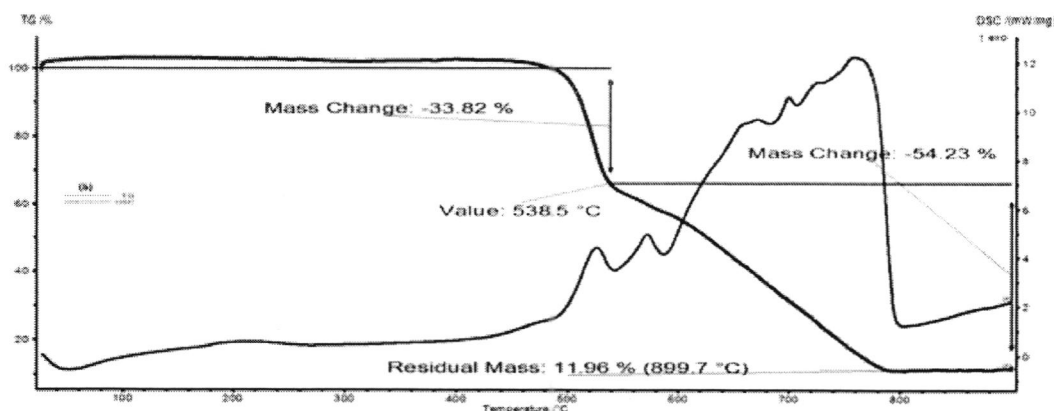


Fig 9. TGA and DSC curve of (b) PSf-SPEEK composite membrane; (c) PSf-SPEEK-dispersed PANI composite membrane

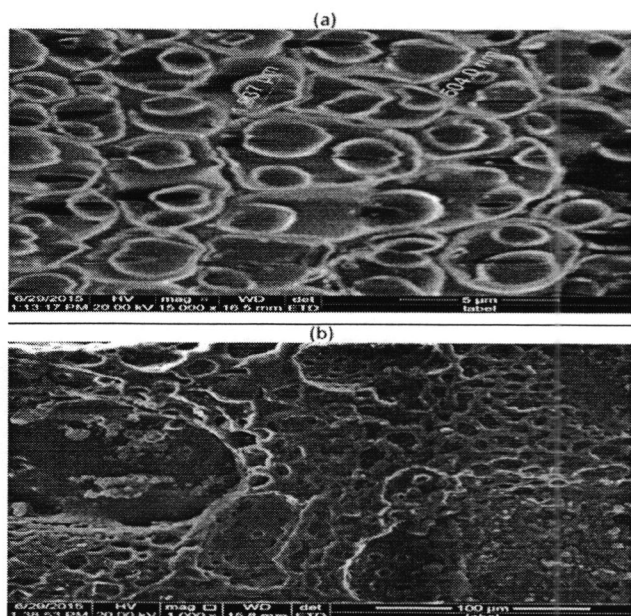
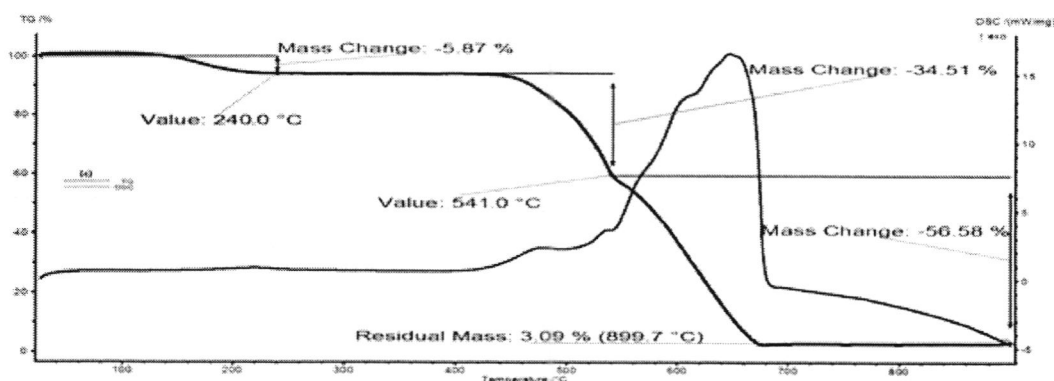


Fig 10. SEM images of (a) PSf-SPEEK composite membrane, (b) PSf-SPEEK-dispersed PANI composite membrane

are accompanied by more peaks exothermic DSC curve, indicating that we have a sequence of chained processes, overlapping. The residual mass in this case was (11.96%).

The thermogravimetric spectra (curve b), showed that PSf-SPEEK composite membrane has a good thermal resistance, the thermal stability up to 460-480°C, and the residual mass in this case was (11.96%).

Composite membrane morphology

The SEM presented in figure 10, shows the shape and size of polysulfone composite membrane pores. Figure 10 (a) shows that the pore shape of PSf-SPEEK composite membrane looks like a water lily flower with longitudinal pores sizes ranging between 504.0nm and 1.837 μm .

These sizes refer to the availability of using this composite membrane in ultrafiltration applications with high permeat

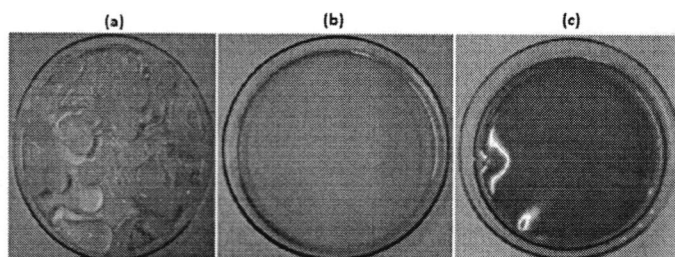


Fig.11. (a) White-gel form SPEEK, (b) SPEEK membrane was formed from drying at 70°C for 72 h, (c) SPEEK membrane was formed from drying at 100°C for 24 h

flow. While the pore shape of PSf-SPEEK-dispersed PANI composite membrane looks like microscopy bony tissue figure 10 (b).

SPEEK membrane synthesis via evaporation of SPEEK - gel form

PEEK sulfonation

PEEK (350P, gray color) was dried in a vacuum oven at 100. PEEK pellets (10 g) were gradually added into 100 mL H_2SO_4 (96%) with vigorously stirred at ambient temperature ($\sim 22^\circ\text{C}$). After a prescribed time, more than 1 month (56 days), the sulphonated polymer was recovered by precipitating the acid polymer solution into a large excess of ice water under mechanical agitation for a desired time (1-2h), where to be observed white-gel form of SPEEK figure 11a. A White-gel form of SPEEK was left to settle overnight.

SPEEKs were washed with deionized water by placing the polymers in dialysis tubing and dialyzing the acid out of the polymers until the rinse water was at pH 6-7 [13,26].

Preparation of SPEEK membrane

Membranes were formed by drying white-gel form SPEEK in a vacuum oven at 70°C and 100°C, where yellow-white and yellow-orange membranes were formed respectively figure 11b,c.

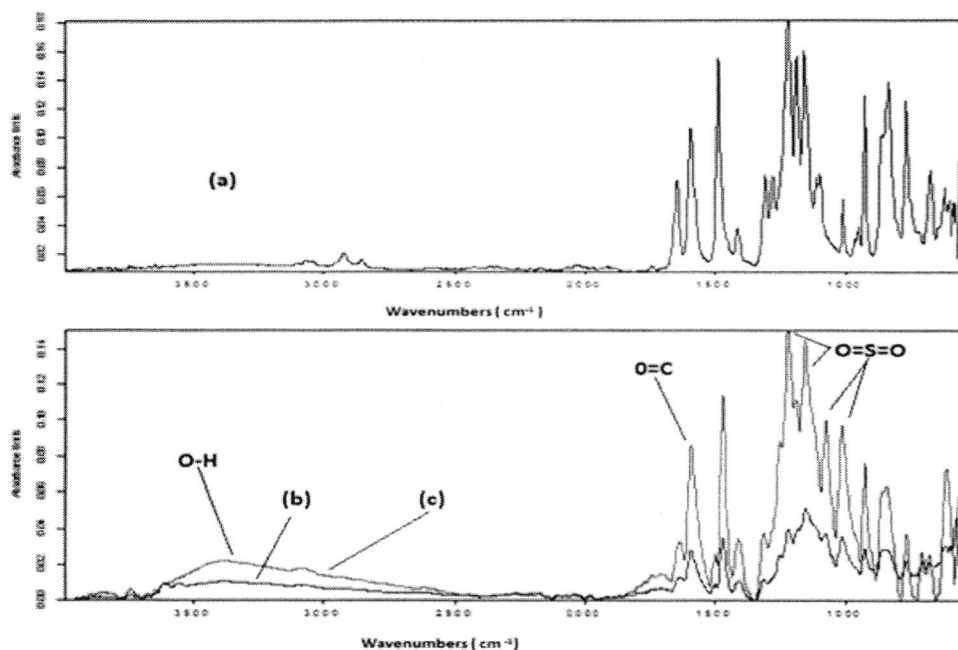


Fig 12. FTIR spectra, (a) PEEK (350P), (b) SPEEK membrane was formed from drying at 70°C for 72 h, (c) SPEEK membrane was formed from drying at 100°C for 24 h

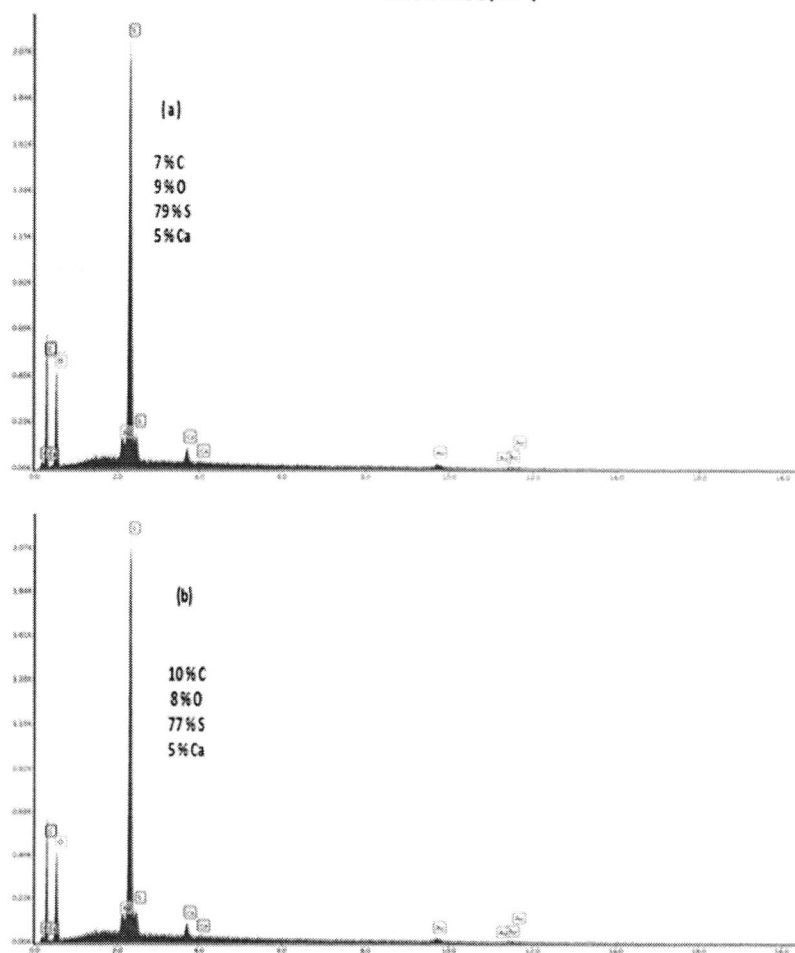


Fig 13. EDAX image of (a) SPEEK membrane was formed from drying at 70°C for 72 h, (b) SPEEK membrane was formed from drying at 100°C for 24 h

Confirmation of the presence of sulfonic acid group in SPEEK polymer

In order to identify the presence of the sulfonic acid group, Fourier transform infrared (FTIR) spectroscopy was used in the present study figure 12. The broadband in SPEEK samples appearing at 3460 cm^{-1} was assigned to O-H vibration from sulfonic acid groups. A new absorption band at $1080, 1020$ and 1255 cm^{-1} in SPEEK were assigned to the sulfonic acid group $\text{O}=\text{S}=\text{O}$ [6]. As their intensities with respect to the backbone carbonyl ($\text{C}=\text{O}$) band at 1651 cm^{-1} increased with temperature of drying membrane samples. There is no change in the carbonyl band at 1651 cm^{-1} for SPEEK compared with PEEK. EDAX spectrum

analysis shows the sulfonic acid group element distribution of the SPEEK membrane material figure 13.

Morphology of SPEEK membranes

The performance of SPEEK membrane should be closely related to its internal structure, especially its morphology. Figure 14 (a) and (b) shows scanning electron microscopy (SEM) micrographs of SPEEK membranes. The (SEM) of SPEEK membranes, did not show any evidence of the presence of microporous structure. The production of non-porous structure is due to the fabrication technique of the membrane itself, dry technique, which was implemented in this study. Generally, the membrane produced by this

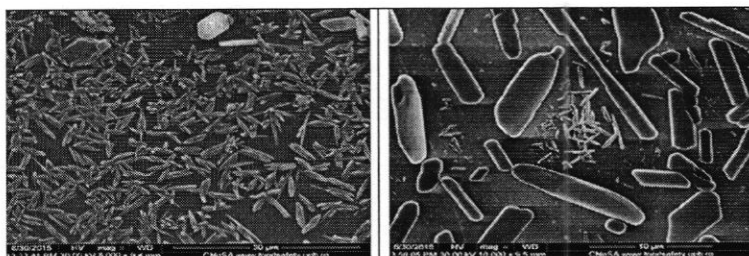


Fig 14 a. SEM of SPEEK membrane was formed from drying at 70°C for 72 h

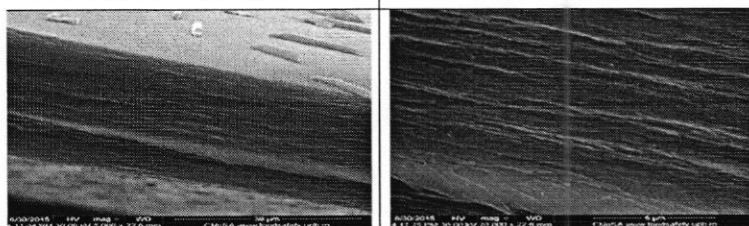
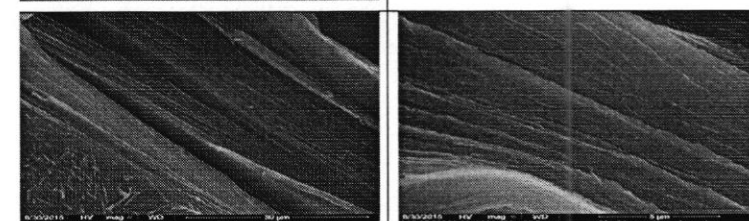
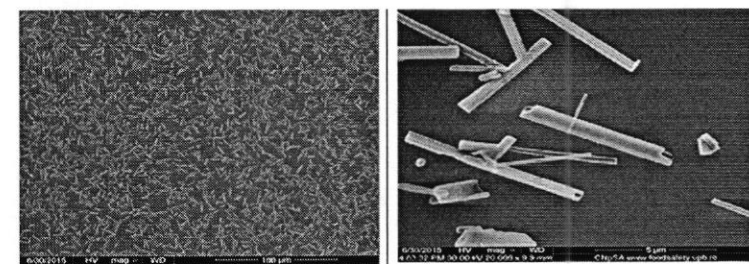


Fig 14b. SEM of SPEEK membrane was formed from drying at 100°C for 24 h



technique is in a dense structure due to the slow removing of solvent molecules when it is evaporated from the polymer membrane. Figure 14 shows that there is an imperceptible effect of drying temperature on the membrane structure as shown from formation a nanotube structure on the surface of the membrane when it was dried at 100°C (fig. 14 (b)).

Conclusions

In the present paper, nanocomposite membrane of PSF-SPEEK-PANI-CNT, has been produced by phase inversion via immersion-precipitation from a dispersion of the nanocomposite material of SPEEK-PANI-CNT, in a solution of Polysulfone in N, N-dimethylformamide (DMF).

Composite membrane of PSf-SPEEK-dispersed PANI, has been produced by phase inversion via immersion-precipitation from a dispersion PANI, in a solution of PSf-SPEEK.

And finally, as a side product for a long sulfonation period of PEEK (350P), more than one month (56 days), SPEEK membrane was prepared via evaporation of SPEEK (350P) - gel form at different temperatures.

In general the following conclusions extract from the present study:

- in order to make the interaction, structural between SPEEK and PANI, PANI was produced in -situ by chemical polymerization of aniline, through addition the aniline sequentially to the SPEEK solution, Where observed appears the highly exothermic reaction. Visually, the process was controlled by monitoring the color change.

- the prepared nanocomposite membranes were structurally characterized using FT-IR, TGA, SEM, and EDAX techniques. FT-IR Spectra is mentioning of SPEEK and PANI.

Formation. It is worth noting, that the carbon nanotubes have not an infrared spectrum with bands. Nanocomposite membrane did not show imperceptible change in thermal resistance if compared with Polysulfone membrane.

- the morphology of membrane was characterized by using SEM techniques. The SEM images show a little imperceptible change in pore size for nanocomposite membrane if compared with Polysulfone due to the presence of the CNT. On the other hand, The thermogravimetric curve of the Nanocomposite membrane did not show imperceptible change in thermal resistance.

- the EDAX spectrum indicates that the elemental distribution values for nano composite membrane recorded higher values than 20% PSF membrane.

- the PSf - SPEEK composite membrane has a good thermal resistance, the thermal stability up to 460-480°C, and the residual mass in this case was (11.96%).

- the pore shape of PSf-SPEEK composite membrane looks like a water lily flower with longitudinal pores sizes ranging between 504.0nm and 1.837 µm. These sizes refer to the availability of using this composite membrane in ultrafiltration applications with high permeate flow.

- the SPEEK membrane was prepared via evaporation of SPEEK (350P) - gel form at different temperatures has a dense structure due to the slow removing of solvent molecules when it is evaporated from the polymer membrane. Drying temperatures have an imperceptible effect on the membrane structure is shown from formation a nanotube structure on the surface of the membrane when it was dried at 100°C.

- membranes were formed by drying white-gel form SPEEK at 70 and 100 °C, have a yellow-white and a yellow-orange color, respectively.

- due to the high degree of sulfonation, the production SPEEK membranes are soluble in water, which restrict their application field.

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