# Tailoring the Characteristics of Poly (phenylene-ether-ether) Sulfone Membrane for Efficient Glycerol/Biodiesel Separation

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**ABSTRACT:** *Poly (phenylene-ether-ether) sulfone membrane was fabricated and characterized to efficient glycerol/biodiesel separation produced from waste cooking oils trans-esterification. The membrane preparation was processed by phase inversion technique. The morphology, physico-chemical properties and separation behavior of membranes was studied at various PPEES concentration. A uniform surface was observed for the prepared membranes by scanning electron microscopy. AFM images exhibited that surface roughness was decreased from 9.24 to 7.26 nm by increase of PPEES concentration from 12 to 15 %wt. Similar trend was found for the membrane Flux, water content and porosity by increase of PPEES content ratio up to 15 %wt. The efficiency of glycerol removal and mechanical strength was also improved by increase of polymeric matrix concentration.*

**KEYWORDS:** *Poly (1, 4-phenylene ether-ether-sulfone); Polymeric membrane; Glycerol/biodiesel separation; Physico-chemical characterization.*

## INTRODUCTION

Nowadays, the attentions have been given to look for alternative fuels widely. Biodiesel is considered as the most alternative fuels due to its unique features. Non-toxic, renew ability; bio-degradability and safe environmentally compared to petroleum fuel make it favourable. The pollutants emission for biodiesel fuel is much lower than other petroleum ones [1-6]. Different methods have been used for biodiesel production that the most notable technique is transesterification as reaction of triglycerides with low molecular weight alcohols [2, 5, 7-13]. But, produced biodiesel contains various impurities such as glycerol, methanol, residual catalyst, un-reacted triglyceride and small amounts of soap/water which should be purified due to its affect on engine performance [1]. Water and

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acid washing, extraction, adsorption and membrane separation are important ways to biodiesel purification. Nowadays, membranes have received more attention in industries and human life due to low energy consumption, easy conversion to industrial scale, and low maintenance cost. It is also well known as new technique in purification of biodiesel [9]. Several researches have been done to purification of produced biodiesel by membrane technology. The polyacrylonitrile membrane, polyethersulfone membrane and the composite PES-$TiO_2$ and PI/MWCNTs membranes showed efficient glycerol/biodiesel separation without significant decreasing trend in flux [4, 6, 7, 12-14]. Also in other studies, ceramic based membranes were utilized for biodiesel separation which showed good chemical, thermal and mechanical stabilities in biodiesel purification although its high cost compared to polymeric membranes make that unfavourable [14, 15]. The reported studies showed that membrane process is appropriate alternative for biodiesel production/purification. In this study, poly phenylene-ether-ether sulfone (PPEES) based membranes were prepared via phase inversion by immersion precipitation technique in order to glycerol/biodiesel separation effectively. The effect of PPEES concentrations in the casting solution on morphology, physico-chemical and separation characteristics in glycerol removal from biodiesel was studied. The used biodiesel in the experiments was produced from waste cooking oils by trans-esterification method and using alkaline catalyst.

## EXPERIMENTAL SECTION

### *Materials*

Poly (1, 4-phenylene ether-ether-sulfone) (PPEES, SIGMA Aldrich) and N-Methyl-2-pyrrolidone (NMP) by Merck were employed as polymer binder and solvent, respectively. Polyvinyl pyrrolidone (PVP, MW: 25,000, Merck Inc., Germany) was also used as pore former. All other chemical were prepared from Merck Inc., Germany.

### *Biodiesel production*

The used biodiesel was produced from waste cooking oils through transesterification technique [12, 13]. For the aim, waste cooking oil was fed into the reactor and preheated before adding sodium hydroxide as catalyst and methanol as reactant. The molar ratio of methanol to cooking oil was (9:1) and and the amount of used catalyst was determined 1.5 wt%. The reaction time was 2 h and reaction temprature was adjusted at 60 ℃. After the reaction, products was allowed to settle for 8 h. The lower phase/polar glycerol layer was removed and the upper phase/non-polar layer was neutralized with sulphuric acid. Finally, one part of produced biodiesel was purified by membrane process and the other part purified by water washing to comparison of separation efficiency.

### *Fabrication of membrane*

PPEES membranes were fabricated through phase inversion method. The casting solutions conaning of PPEES, NMP and PVP were casted on a clean glass plate at room temperature by a casting knife with 200 μm thickness. The prepared films were then immersed in disttiled water as non-solvent coagulation bath. Finally, prepared membranes were kept in distilled water. The composition of casting solution is shown in Table 1.

### *Dead end membrane cell*

A self-made dead-end membrane test cell was utilizied to study the characteristic of prepared membranes in glycerol/biodiesel separation (Fig. 1). The membranes were placed at the end of cell and fed by biodiesel. The driving force was also provided by nitrogen gas.

## MEMBRANE CHARACTERIZATION

### *Flux (J) and Rejection (R)*

The flux (J) is defined as the amount of permeate produced ($\Delta V$) per unit area of membrane surface (A) and per unit time ($\Delta t$). The flux is defined as follows [17]:

$$J = \frac{\Delta V}{A \Delta t} \left( \frac{L}{m^2 \cdot h} \right) \quad (1)$$

The glycerol concentration in feed and permeate were also measured by using of the UV-Visible instrument. The glycerol rejection is calculated by comparing glycerol concentration between feed ($C_F$) and permeate ($C_P$) as follows [17-19]:

$$R\% = \left( 1 - \frac{C_P}{C_F} \right) \times 100 \quad (2)$$

### *Membrane water content and Porosity*

The water content was calculated as weight difference between the wet and dried membranes by Eq. (1) [19-23].

***Table 1: Composition of casting solution for fabrication membranes.***

| Samples | PPEES (wt.%) | PVP (wt.%) | NMP (wt.%) |
|---|---|---|---|
| 1 | 12 | 2 | 86 |
| 2 | 13 | 2 | 85 |
| 3 | 14 | 2 | 84 |
| 4 | 15 | 2 | 83 |

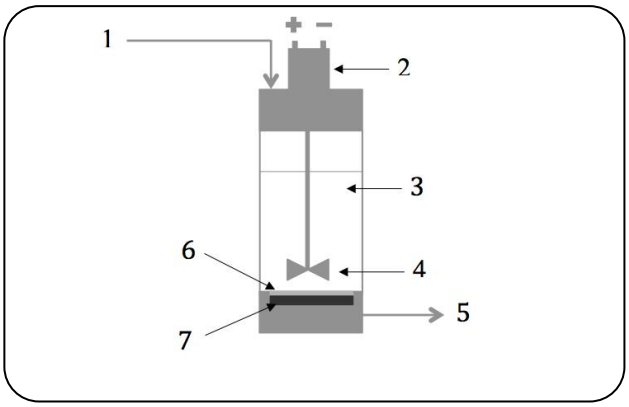



***Fig. 1: Schematic diagram of used dead-end filtration cell: (1) Nitrogen gas input, (2) electrical motor, (3) feed solution, (4) blades, (5) permeate, (6) membrane, (7) support layer.***

$$\text{Water content}\% = \left(\frac{w_{wet} - w_{dry}}{w_{dry}}\right) \times 100 \quad (3)$$

Where $W_{wet}$ is the weight of wet membrane and $W_{dry}$ is the weight of dried membrane.

The membrane porosity (*Pr*) was also calculated as a function of the membrane weight [24]:

$$P_r = \left(1 - \frac{w_{dry}}{s \times d \times \rho}\right) \times 100 \quad (4)$$

Where *s* is the area of membrane, *d* the membrane thickness and $\rho$ the density of the membrane.

***Scanning Electron Microscope (SEM)***

The surface and cross-section of membranes was examined by scanning electron microscope (SEM, Cambridge). The samples were sputtered by gold to observation by microscope.

***Atomic Force Microscopy (AFM)***

The surface roughness of prepared membranes was studied by Atomic Force Microscopy (AFM, Auto Pro CP, and USA, μm×5 μm, contact mode).

***Mechanical property***

The tear resistance as a mechanical property of the prepared membranes was investigated by Universal Testing Machine (UTM, SDLATAS, M 350-5 KN, 1 mm/min) at ambient temperature (26.1 °C and 23% R.H). The samples were cut in standard shape (80 mm × 15 mm) and used for measurement.

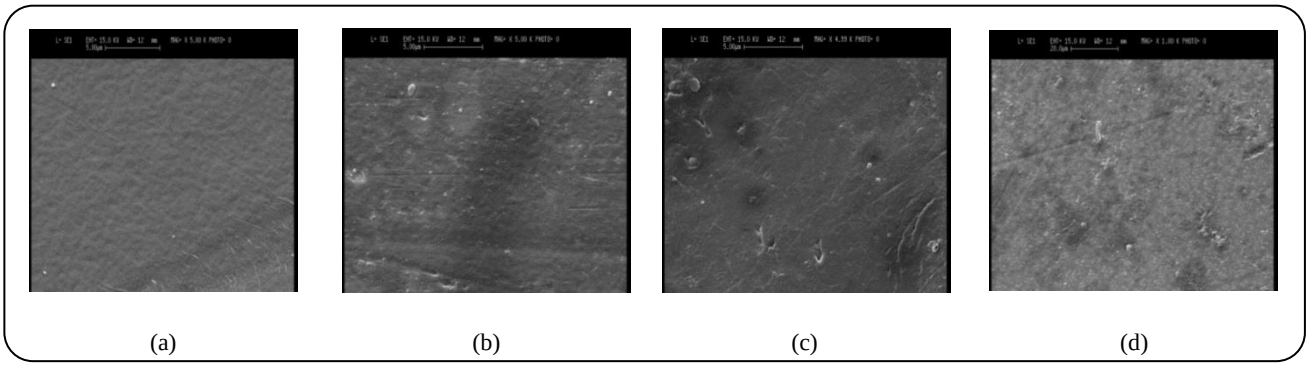
## RESULTS AND DISCUSSION

***Morphological study***

Figs. 2 and 3 show the surface and cross-sectional images of prepared PPEES membranes. A uniform surface was observed for the prepared membranes. SEM images showed a dense top layer, porous sub-layer and fully developed macro-pores for the fabricated membranes. The increase of PPEES concentration led to decrease of finger-like pores and formation of dense sub-layer for the membranes which assigned to improvement in casting solution viscosity that reduces the exchange rate between NMP and water during phase inversion process [25-27].

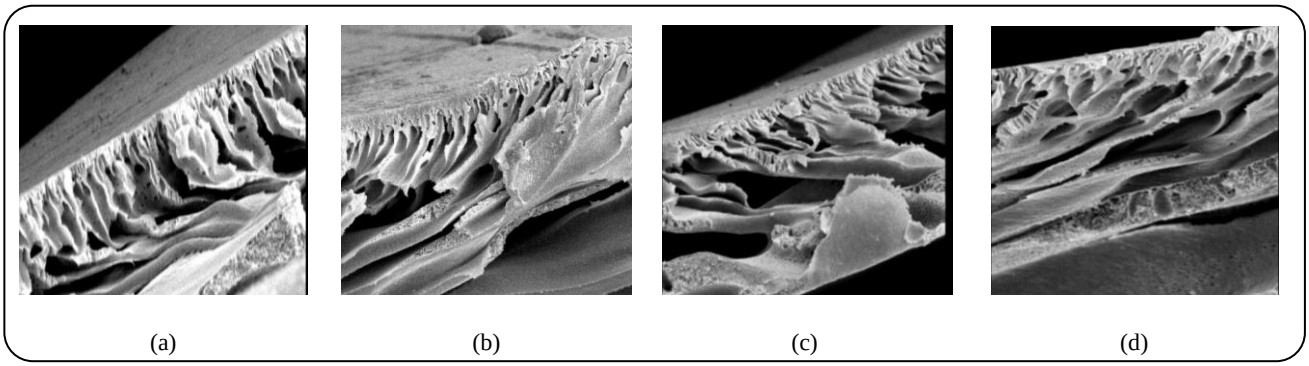
***Atomic Force Microscopy Analysis (AFM)***

AFM images (Fig. 4) showed that increase of PPEES concentration caused to decreases of membrane surface roughness and surface porosity obviously. The amount of calculated roughness parameter is given in Table 2. The amount of average roughness was declined from 9.24 to 7.36 nm by increase of PPEES concentration from 12 to 15 %wt in the casting solution. The membrane with low surface roughness has stronger antifouling ability. This may be due to decrease of exchange rate between the NMP and distilled water at higher PPEES concentration. Besides, increase of casting solution viscosity by more PPEES concentration slows down the exchange rate between solvent/non-solvent which leads to formation of a membrane with smooth surface, small pore size and dense structure [26, 27].



(a) (b) (c) (d)

***Fig. 2: SEM surface images of membranes at various PPEES concentration: (a) 12 %wt; (b) 13 %wt; (c) 14 %wt; (d) 15 %wt.***



(a) (b) (c) (d)

***Fig. 3: SEM cross sectional images for fabricated membranes at different concentration of PPEES: (a) 12 %wt; (b) 13 %wt; (c) 14 %wt; (d) 15 %wt.***

***Membrane water content and porosity***

As shown in Fig. 5, membrane water content was declined by increase of PPEES concentration. Decrease of free spaces in membrane body at high PPEES ratio caused to less water accommodation. Moreover, the porosity for prepared membranes was presented in Fig. 5. Prepared membranes showed porosity in range of 25 to 48%. Increase of PPEES concentration caused to porosity decreasing which is assigned to decrease of exchange rate between solvent/non-solvent during phase inversion [26-28].

***Mechanical property of prepared membranes***

It was found that (Fig. 6) mechanical stability of fabricated membranes was improved by increase of binder content ratio which is assigned to decrease of its porosity and formation of great links between polymer chains at high PPEES ratios which improve the mechanical property.

***Membrane flux and rejection***

The membrane flux (Fig. 7) was declined at higher PPEES concentration due to decrease of membrane porosity which makes difficult the fluid passage through the membrane and declines the flux. The separation efficiency for the prepared membranes as ratio of membrane glycerol rejection to water washing process is also shown in Fig. 8. The separation efficiency was enhanced sharply by increase of PPEES concentration. Decrease of membrane surface roughness at higher PPEES concentration, declines the possibility of stagnant layer formation on surface which improves the rejection. A membrane with a smooth surface has more ability to improve the antifouling performance. The prepared membrane containing 13 %wt PPEES, with highest flux, and suitable separation efficiency showed more appropriate performance.

**CONCLUSIONS**

Poly phenylene-ether-ether sulfone membrane was fabricated and characterized to efficient glycerol/biodiesel separation produced from waste cooking oils trans-esterification. The effects of PPEES concentration on morphological, physico-chemical properties and separation behaviour of fabricated

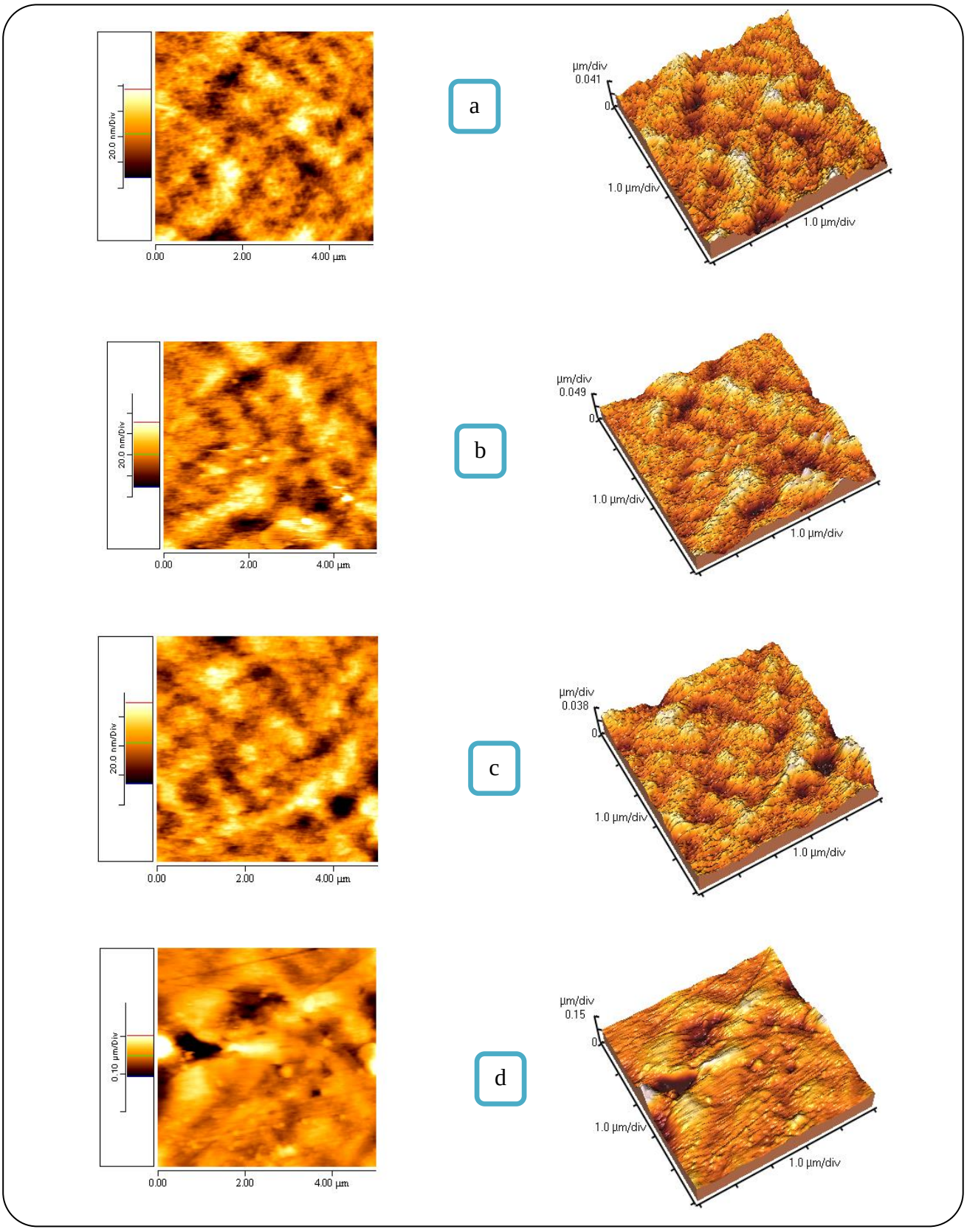



***Fig. 4: AFM images for homemade PPEES based membranes: (a) 12 %wt; (b) 13 %wt; (c) 14%wt; (d) 15 %wt.***

***Table 2: The calculated surface roughness parameters for the prepared membranes.***

| PPEES Concentration (wt.%) | Average roughness (nm) |
|---|---|
| 12 | 9.24 |
| 13 | 8.46 |
| 14 | 8.06 |
| 15 | 7.36 |

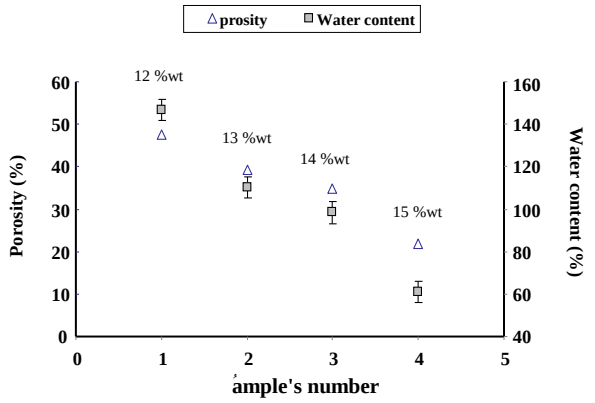



***Fig. 5: The effect of PPEES concentration on water content and porosity of prepared membranes.***

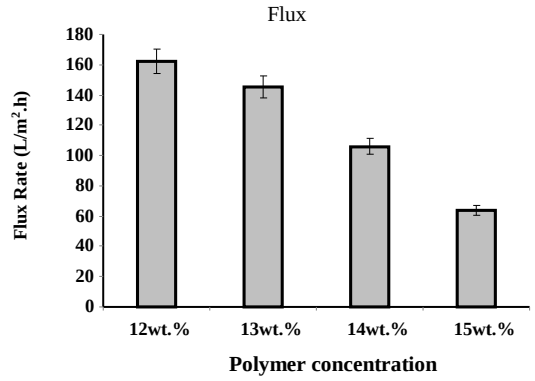



***Fig. 7: Flux of fabricated PPEES membranes: the effect of binder ratio.***

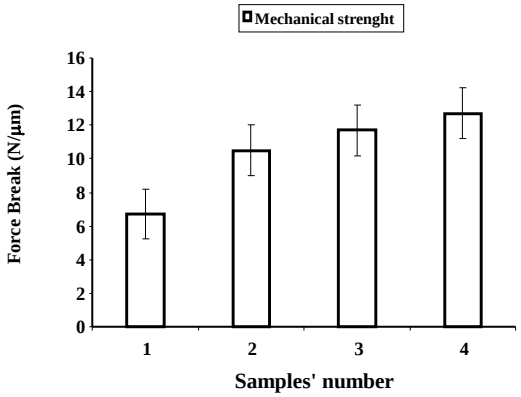



***Fig. 6: The effect of PPEES content ratio on mechanical strength property of membranes.***

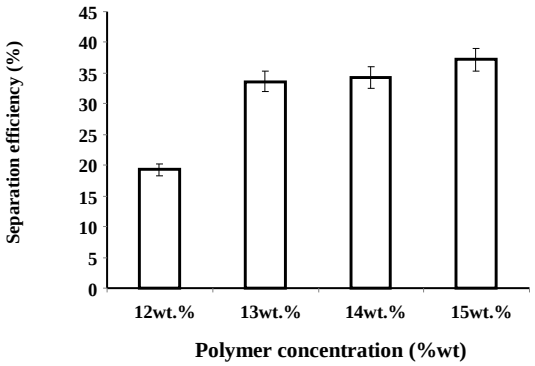



***Fig. 8: The separation efficiency for prepared membranes with different PPEES concentration.***

membranes was studied. A uniform surface was observed for the prepared membranes. AFM images exhibited that surface roughness was decreased from 9.24 to 7.26 nm by increase of PPEES concentration from 12 to 15 %wt. Also membrane Flux, water content and porosity showed similar trend by increase of PPEES content ratio whereas membrane rejection and mechanical stability was improved by increase of PPEES concentration. The prepared membrane with 13 %wt PPEES, showed more appropriate performance in glycerol removal compared to others.

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