



Experimental survey of temperature, time and cross-linking agent effects on polydimethylsiloxane composite membranes performances in sulfur removal

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Abstract

Four types of the multi composite membranes were fabricated to decrease the sulfur content in diesel fuel, which the investigated polymers are polydimethylsiloxane (PDMS), polyethyleneglycol (PEG), polyethersulfonic (PES) and cross-linked polyacrylonitrile (PAN) with tetra-ethyl-ortho-silicate (TEOS). The effects of the operating parameters such as the cross-linking temperature (65–85 °C) and cross-linking time (0.5–2.5 h) were studied on the membranes performances. The results showed that the sulfur selectivity of PDMS/PEG/PES/PAN membranes were improved through increasing temperature and time. In addition, most of the total flux and the lowest amount of sulfur in the back flow is related to composite membranes of PEG + PDMS.

Keywords Composite membrane · Sulfur content removal · Cross-linking agent · PDMS · PEG · PAN

Introduction

The used membrane materials for removing sulfur are mostly including hydrophobic membranes such as polyurethane, polyurea/polyurethane, polyamide, natural rubber, polystyrene-butadiene and polydimethylsiloxane. Hydrophilic properties of the membranes clearly increase the selectivity to the sulfur compounds which usually are more polar than hydrocarbons. The most common methods for making membranes with high selectivity and flux include cross-linking, blending, filling and copolymerization. Lin et al. studied the solubility of gasoline blending in polyethylene glycol [1]. They concluded that sulfur recovery rate by increasing the amount of cross-linking agent and the cross-linking time increases. Lin et al. used polyethylene glycol and polyurethane polymers for fluidized bed catalytic cracking unit gasoline desulfurization [2]. Wu et al. improved the stability of the interface between the active

layer of polydimethylsiloxane and base layer of polyethersulfone by the aminosilane and amino propyl trimethoxysilane [3]. Their results showed that with increase of cross-linking agent penetration flux is uniformly reduced. The effect of tetraethyl ortho silicate on the increasing selectivity in the Polydimethylsiloxane membrane has been studied by Xu et al. [4]. In another study, manufacturing of polydimethylsiloxane and polyamide composite membrane in separation of heptane from thiophene was studied [5]. The transport properties of gases in polydimethylsiloxane (PDMS)/zeolite a mixed matrix membranes (MMMs) were determined based on pure gas permeation experiments in study of Rezakazemi et al. 2012. The permeation rates of C₃H₈, CH₄, CO₂, and H₂ were evaluated through a dense homogeneous pure PDMS membrane and PDMS/4A MMMs to assess the viability of these membranes for natural gas sweetening and hydrogen purification. SEM investigations showed good adhesion of the polymer to the zeolite in MMMs. Permeation performance of the membranes was also investigated using a laboratory-scale gas separation apparatus and effects of feed pressure, zeolite loading and pore size of zeolite on the gas separation performance of the MMMs were evaluated [6]. Rezakazemi et al. cross-linked polydimethylsiloxane (PDMS) membranes supported on cellulose acetate (CA) and polyamide (PA) microfiltration membranes were prepared by pre-wetting technique for pervaporation (PV)

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dehydration of ethanol. The experiments were carried out to investigate the effects of support layer and permselective thickness on the separation performance of membranes at different operating conditions particularly initial ethanol concentrations and temperatures. The results revealed that increasing feed concentration and temperature increases total permeation flux. PDMS/PA membrane showed better overall performance than PDMS/CA membrane [7]. Chen et al. investigated cross-linked polydimethylsiloxane (PDMS)–polyetherimide (PEI) composite membranes preparation, in which asymmetric microporous PEI membrane prepared with phase inversion method acted as the microporous supporting layer in the flat-plate composite membrane. Membrane characterization was conducted by Fourier-transform infrared and scanning electronic microscopy analysis. The composite membranes were employed in pervaporation separation of *n*-heptane–thiophene mixtures. Effect of amount of PDMS, cross-linking temperature, amount of cross-linking agent, and cross-linking time on the separation efficiency of *n*-heptane–thiophene mixtures was investigated experimentally [8].

Rostamizadeh et al. investigated Gas permeability through synthesized polydimethylsiloxane (PDMS)/zeolite 4A mixed matrix membranes (MMMs) with the aid of artificial neural network (ANN) approach. Kinetic diameter and critical temperature of permeating components (e.g., H₂, CH₄, CO₂ and C₃H₈), zeolite content and upstream pressure as input variables and gas permeability as output were inspected. Collected data of the experimental operation was used to ANN training and optimum numbers of hidden layers and neurons were obtained by trial–error method. As a result, ANN can be recommended for the modeling of gas transport through MMMs [9].

Rezakazemi and Mohammadi developed robust artificial neural network (ANN) to forecast sorption of gases in membranes that comprised porous nanoparticles dispersed homogeneously within polymer matrix. The main purpose of this study was to predict sorption of light gases (H₂, CH₄, CO₂) within mixed matrix membranes (MMMs) as function of critical temperature, nanoparticles loading and upstream pressure. The prediction results were remarkably agreed with the experimental data with MSE of 0.00005 and correlation coefficient of 0.9994 [10].

In other work of Rezakazemi et al., a facile strategy for the synthesis of binary fillers nanocomposite membranes containing fumed silica (FS) and octatrimethylsilyloxy polyhedral oligomeric silsesquioxane (POSS) nanoparticles was proposed to prepare high-performance PDMS–FS–POSS nanocomposite membranes. To fully explore the synergistic effect between POSS and FS nanoparticles, thermal stability by thermo-gravimetric analysis (TGA) and dispersion quality by scanning electron microscopy (SEM) were investigated, while the crosslinked network was studied by

Fourier-transformed infrared spectroscopy (FTIR). The results showed that the thermal stability of these novel nanocomposite membranes was much better than that of the neat membrane thermodynamically, dipole–dipole interaction between the functional groups is the main parameter leading to better dispersion and thermal stability [11]. Furthermore, it was found that the separation properties of different gases (H₂, C₃H₈, CO₂ and CH₄) across the nanocomposite membranes were enhanced with increasing FS content. All the improvements observed can be attributed to synergistic interactions between FS and POSS [12]. Rajesha et al. synthesized oxide–zeolite composite membranes for benzophenone-3 removal from water. They concluded that membrane performances were significantly improved after the addition of ZnO–zeolite in the cellulose acetate solution [13]. Ghasemian et al. used polyvinylidene fluoride (PVDF) and nano-porous silica particle. Their results show that PVDF/SiO₂ nano-composite membranes exhibited enhanced anti-fouling property compared to neat PVDF membrane [14]. Xu et al. manufactured a gradient cost-efficient composite membrane. They concluded that when the additive amount of OMWCNTs was 1 wt%, the composite membranes presented an excellent flux [15].

In this study, the total sulfur in diesel product of an oil refinery was reduced from 6380 ppm to 1700 ppm using composite membranes of PDMS, PDMS + PEG, PDMS + PES and PDMS + PAN, as well as the cross-linking technique by TEOS in a module of flat sheet membranes. The effect of operational variables such as cross-linking temperature and cross-linking time on the total flux of the stream and total sulfur in the retentate stream was evaluated.

Materials and methods

Materials

To manufacture the composite membranes, the following laboratory material were used:

1. Tetraethyl ortho-silicate (TEOS) with an average molecular weight of approximately 208 g/mol (Merk, Germany).
2. Oligomers of Polydimethylsiloxane (PDMS) with an average molecular weight of approximately 40,000 g/mol and viscosity 5000 MPa s (Aldrich, USA).
3. Polyethylene glycol (PEG) with an average molecular weight of approximately 4000 g/mol (BASF, Germany).
4. Polyethersulfone (PES) with an average molecular weight of about 58,000 g/mol (flakes, BASF, Germany).

5. Polyacrylonitrile (PAN) with an average molecular weight of about 45,000 g/mol (Merk, Germany).
6. Polyvinylpyrrolidone (PVP) k90 as a filler with an average molecular weight of approximately 360,000 g/mol (Merk, Germany).
7. Dimethyl acetamide (DMac) as a solvent (Merk, Germany).
8. Dibutyltin dilaurate (fluka, Switzerland).
9. Ammonia (Merk, Germany).
10. Asymmetric nano filter based membrane of polyester (plasmachem GmbH, Germany).
11. *N*-heptane (Romil, UK).
12. SPAN 80 (MERK, Germany).
13. Distilled water.

Composite membrane preparation

A certain amount of span 80 as surfactant, silicone propulsion (tetraethyl-ortho-silicate) with weight percentages of 8% with oligomers of polydimethylsiloxane and polyethylene glycol in *n*-heptane (solvent) at room temperature for making homogeneous solution mixed together. Ammonia in water (anti-solvent) with half the molar concentration of the solution is solved to build a solution with pH 9. However, a certain amount of this solution is added into a homogeneous solution under difficult conditions of stirring. Mass ratio between solvent and polymer is about 3.5 and the mass ratio between the polymers used in this study is equal. The use of ammonia as catalyst cause agglomerate silica has been done at the interface of water/homogeneous solution. After mixing for 30 min, a small amount of Dibutyltin dilaurate as bubble removing is added to this mixture. The mass ratio between the polymer, Dibutyltin dilaurate, Span 80 and the solution with pH 9 is 10/0.1/0.3/1, respectively. After removing bubbles in homogeneous solution, the solution is laying the base

layer and the film device is used. The solution to build a base film by deposition technique made by immersion; therefore, a 15% the mass of solution polyethersulfone and 3% the mass of the Polyvinylpyrrolidone as filler in the dimethylacetamide solvent is made. This solution is built on the base of nano-filter asymmetric polyester, and after using the film immersed quickly in distilled water to remove residual dimethylacetamide. Membranes initially are placed in the open air for 24 h and then to complete the cross-linking process and evaporate the remaining solvent at the time of cross-linking (0.5–2.5 h) determined and at the time of cross-linking time (65–85 °C) placed inside an electric furnace. Finally, the membranes are washed with distilled water and placed between sheets of filter paper and dried. All membranes before used in the membrane module and the membrane performance be measured should be placed in a free of dust and dry environment.

Laboratory devices for research is shown in Fig. 1.

Feed tank (position 1) is containing about three liters of diesel with the total sulfur content of 6380 ppm. After using any appropriate membrane, the remaining diesel is poured inside the feed tank and the feed will be replaced with new diesel to experiment with new membrane. In position 2, the pump has been used that leads diesel with different flow rates and pressures set (5–9 times) into the membrane module (position 5). Membrane modules is manufactured from stainless steel and membranes used with active area of 2100 cm². The pressure gauges represents (position 4 and 6) the diesel and backflow pressures, respectively. Needle valves are installed at 7 positions to control the backflow and a valve is inserted in position 3 for the input flow to the module. The membranes in the input feed to the modulus to be kept wet approximately 1 h before the start of each test to achieve steady state conditions. For each test approximately 3 h were taken and the operating temperature range is between 65 and 85 °C.

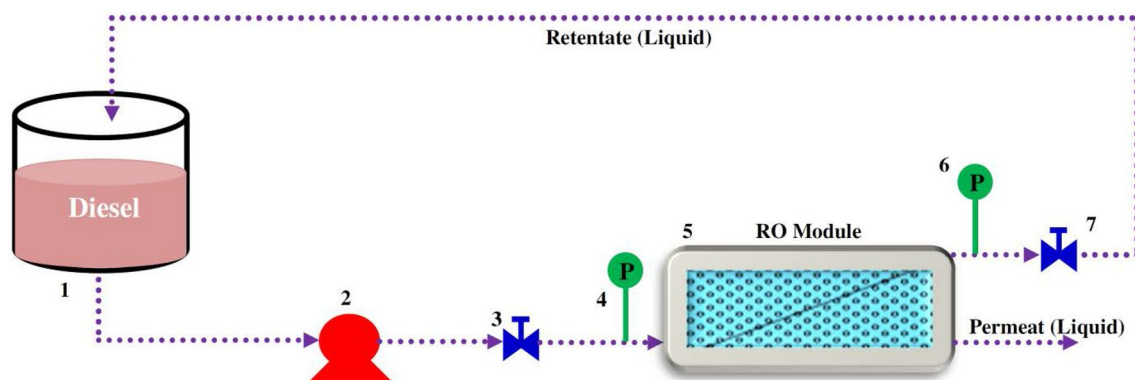


Fig. 1 Schematic diagram of experimental apparatus

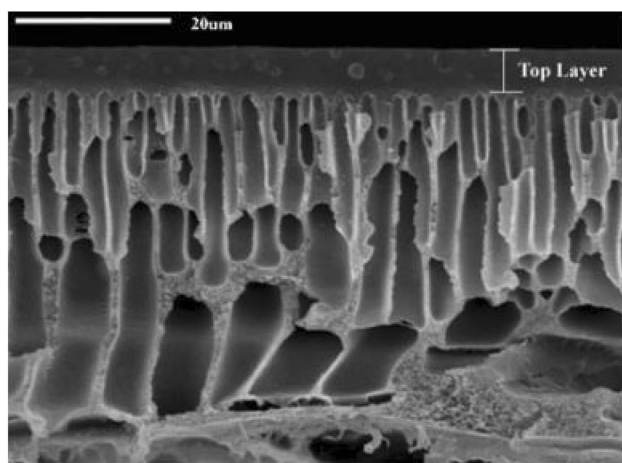


Fig. 2 The cross section morphology of the PDMS composite membrane

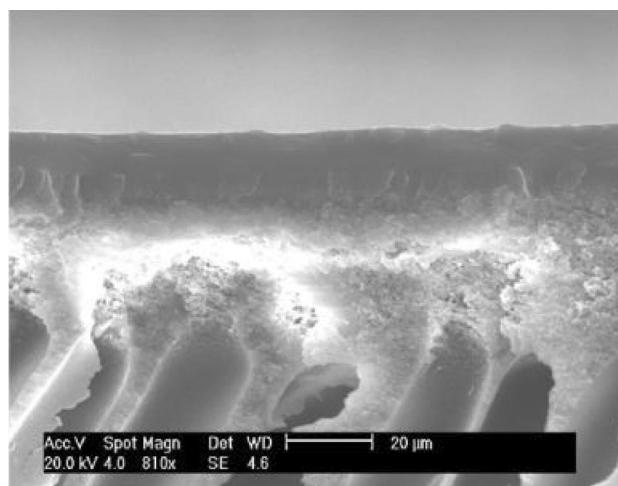


Fig. 4 SEM images of the cross-section of composite PDMS membrane

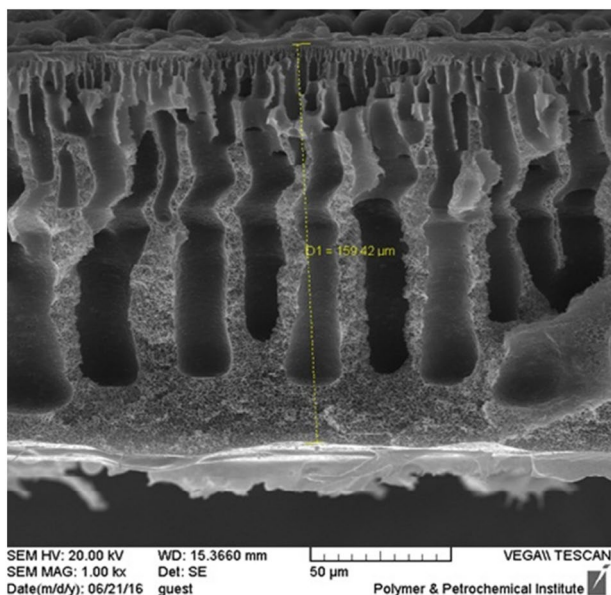


Fig. 3 Scanning electron microscope image of the composite membrane of PDMS

Results and discussion

Figures 2, 3, 4, 5 are scanning electron microscope images of PDMS composite membrane at a temperature of cross-linking 75 °C and cross-linking time of one hour and the amount of TEOS 8% by weight. These images show the porosity in internal layer of membrane. As demonstrated in the SEM photographs, there is a clear boundary between the PDMS top layer and support layer. Meanwhile, the cross-sectional structure of the composite membrane of

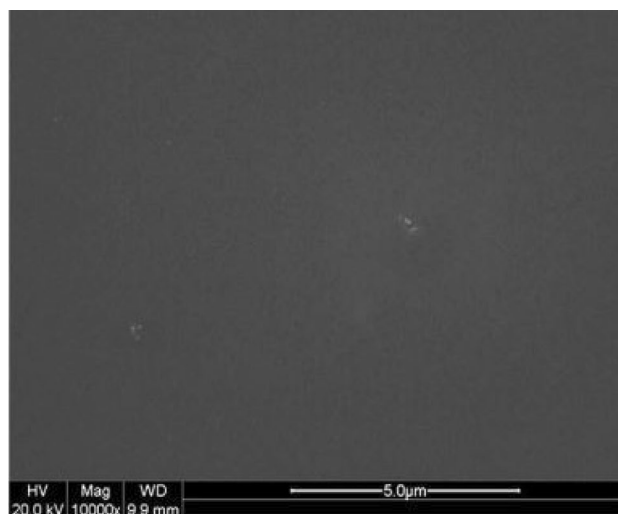


Fig. 5 The surface morphology of the PDMS composite membrane

PDMS with TEOS as agent, consisted of an ultrathin skin layer and a porous finger-like structure. The top dense layer is clearly demonstrated in Figs. 2 and 4. Using Soaking method, porosity of the membrane, 33.308%, was obtained. Furthermore, the thickness of the PDMS top layer was determined to be about 4.5 μm from the SEM photograph by the scale tab. Note that, top-layer thickness increased as the PDMS concentration increased. Also, the thickness of membrane support obtained as 130 μm.

The surface morphology of the composite membrane is shown in Fig. 5. From this figure, the originally porous surface was covered by a flat featureless PDMS layer, and the top PDMS layer, functioning as the basis of selectivity, had a nonporous and tight structure. The surface of the

composite is dense and there is no pinhole or crack, which is important for practical application.

Figure 6 shows that the total flux changes with the use of TEOS as cross-linking agent in the manufacture of membranes, which in accordance with Fig. 6 with increasing consumption of TEOS output flux from retentate stream is reduced. This result implied that, when the TEOS content increased, more TEOS chains occurred in cross-linking reaction, and the top membrane layer, functioning as the basis of permselectivity, became a nonporous and very tight structure. Accordingly, the free volume of PDMS composite membrane decreased, which led to the flux decrease. Meanwhile, top-layer thickness increased as the TEOS concentration increased. By all given reasons, the flux decreased as TEOS content increased. According to Fig. 6, it can be seen that the highest flux is related to the blending polymers PDMS + PEG, which it uses the technique of blending polymers with the PDMS as a hydrophobic polymer and PEG as a hydrophilic polymer.

Figure 7 shows sulfur is reduced in the back flow with the use of TEOS as a cross-linking agent. According to Fig. 7, increasing the amount of TEOS in manufacturing composite membranes reduces the amount of sulfur in the return flow. Because by increasing the amount of TEOS as cross-linking agent, the selectivity of composite membrane increased and consequently total sulfur in retentate flow decreases.

Figure 8 shows sulfur changes in the back flow with cross-linking temperature that 8% weight of TEOS is used as cross-linking agent in the construction of composite membranes, which according to Fig. 8 increasing cross-linking temperature reduces total sulfur flux.

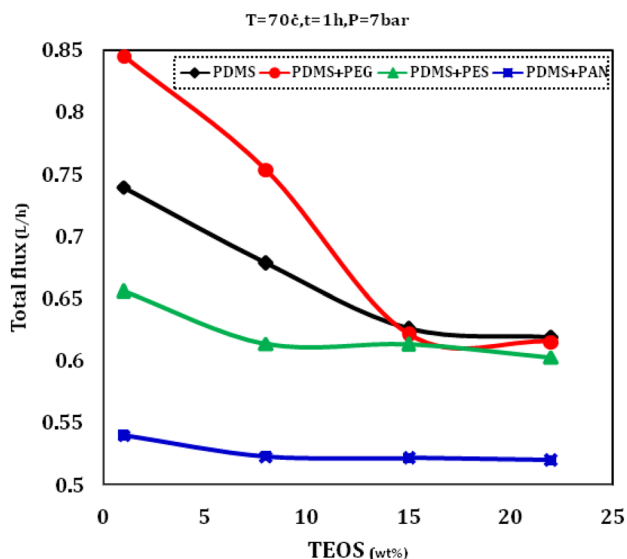


Fig. 6 Total flux changes with consuming value of mass percentage of crosslinking agent at 70 °C and crosslinking time of 1 h and membrane module pump pressure in 7 bar

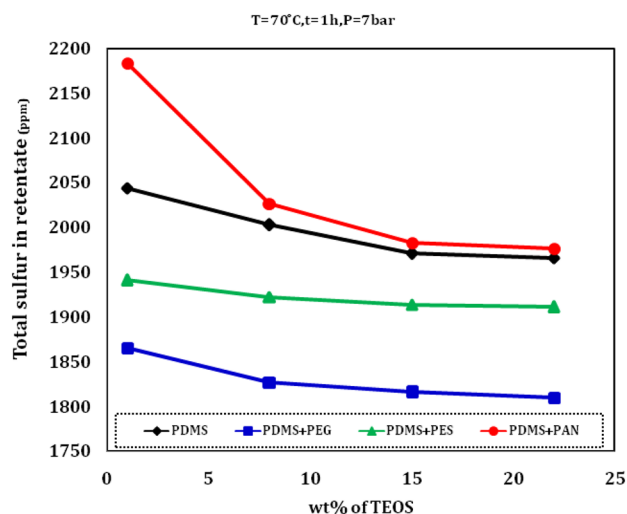


Fig. 7 Sulfur changes in the back flow using mass percentage of crosslinking agent, at 70 °C, crosslinking time of 1 h and membrane module pump pressure in 7 bar

As cross-linking temperature (65–85 °C) increases, the degree of equilibrium swelling decreases and thus the selectivity of the composite membrane increases. Some observations show reducing the chain length between the cross-linking. Reducing chains between cross-linking increases the elastic resistance of swelling stress in composite membranes and thus the swelling degree of the membrane reduces. Thereby, reducing the degree of swelling increases the selectivity of the composite membranes to sulfur compounds and ultimately the amount of sulfur in the backflow reduces.

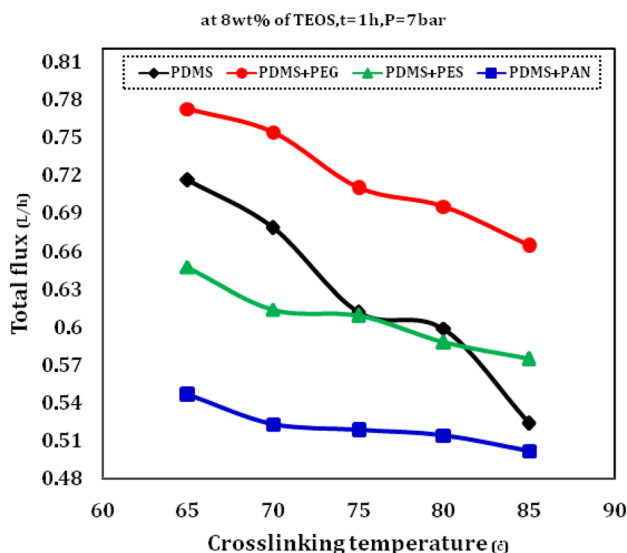


Fig. 8 Total flux changes with crosslinking temperature at 8% mass of the cross-linking agent and crosslinking time of 1 h and membrane module pump pressure in 7 bar

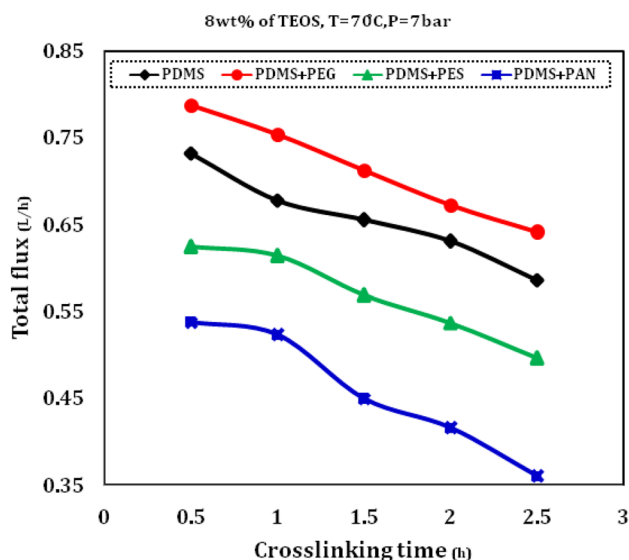


Fig. 9 Total flux changes with crosslinking time at 8% mass of cross-linking agent and crosslinking temperature of 70 °C and membrane module pump pressure in 7 bar

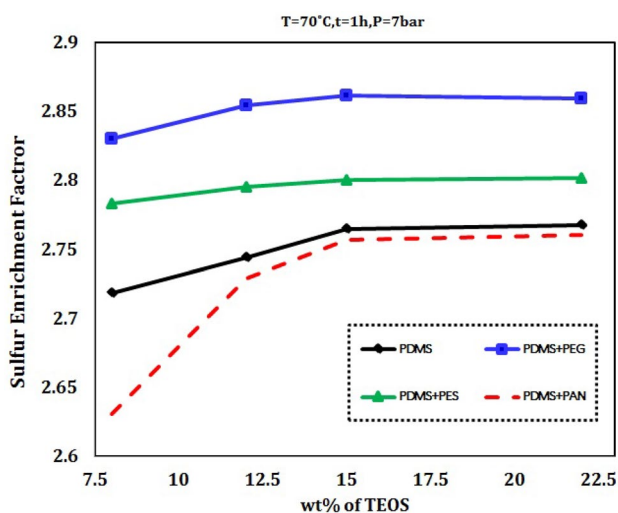


Fig. 10 Sulfur enrichment factor as a function of TEOS percentage

Figure 9 shows total flux changes with cross-linking time in the case of 8% weight TEOS as a cross-linking agent is used in the construction of composite membranes. According to Fig. 9, the total flux is reduced with increasing cross-linking time from 0.5 to 2.5 h.

The effects of crosslinking dosage, crosslinking time and temperature are illustrated in Figs. 10, 11, 12. As can also be seen in these figures, the blended PDMS + PEG polymer shows a higher enrichment factor than other cases. In consequence to previous descriptions, when the total sulfur in retentate flow decreases so the enrichment factor will be increased. The sulfur enrichment factor is defined as the

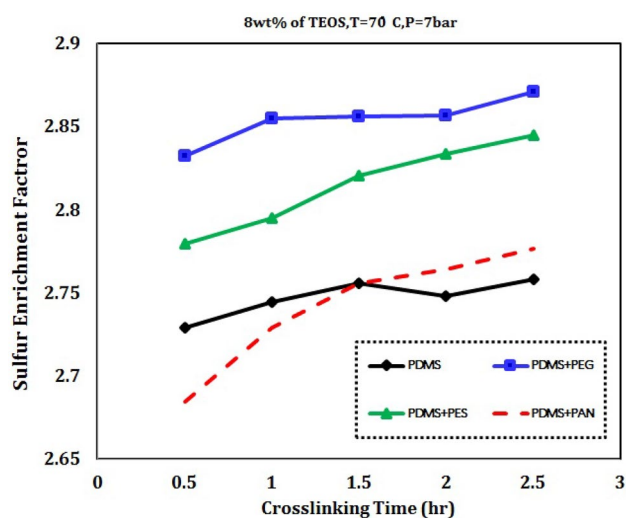


Fig. 11 Sulfur enrichment factor as a function of time

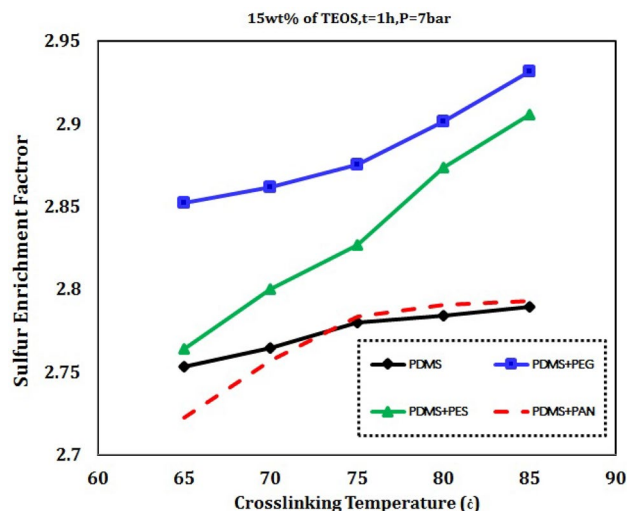


Fig. 12 Sulfur enrichment factor as a function of temperature

ratio of total sulfur content of permeate to total sulfur content of feed samples.

Conclusion

In this work, PDMS, PEG, PES and PAN composite membranes have been prepared to reduce sulfur diesel fuel using cross-linking technique by TEOS cross-linking agent in various mass percentages. According to results it can be seen that most of the total flux is related to composite membranes of PEG + PDMS (0.7732 L/h). In addition, it is observed that the lowest amount of sulfur in the back flow related to the state in which the composite membranes PEG + PDMS had been used (1780 ppm). Increasing use of TEOS reduces the

total flux passing retentate stream, however, the amount of sulfur in the return flow is also reduced. It can be noted that by increasing the amount of TEOS from 8 to 22 wt% in the case of composite membranes PDMS + PAN, PDMS + PES, PDMS + PEG, PDMS, the flux changed from 0.5412 to 0.5217 L/h, 0.6215 to 0.6033 L/h, 0.7583 to 0.6211 L/h and 0.6813 to 0.6314 L/h, respectively; while, the differences between the total flux passing through the composite membranes are too much in the range of 1–8 wt% relative to 15–22 wt%. Also by increasing use of TEOS from 8% to 22 wt% in the case of composite membranes PDMS + PAN, PDMS + PES, PDMS + PEG, PDMS, the amount of sulfur in the back flow is changed from 2035 to 1982 ppm, 1933 to 1921 ppm, 1825 to 1811 ppm, 2011 to 1972 ppm, respectively; while, the differences between the amount of sulfur in the back flow is too much in the range of 1–8 wt% relative to 15–22 wt%.

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