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Studies on the influence of coagulation bath composition on the preparation of PVDF membranes

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ABSTRACT

In recent times membrane processes are virtually supplementing most of the conventional separation processes. Membrane distillation and membrane solvent extraction are two such processes that have high potential in the separation applications. In this context, there is a need to develop membranes with better hydrophobicity and mechanical strength for overall process efficiency. In this paper, we present our studies on developing polyvinylidene fluoride (PVDF) flat sheet membranes with varying concentrations of poly ethylene glycol (PEG) additive 0%–4% by weight, and using n-methyl-2-pyrrolidone as a solvent through phase inversion technique. During this process, effects of different coagulation baths were studied using n-butanol and water with two different volume ratios 0:100 and 45:55. The membrane characteristics such as liquid entry pressure, porosity, tensile strength, elongation-at-break, water contact angle and pure water flux were analysed in detail and results were documented. The structure and morphology of the membranes were studied using Fourier transform infrared spectroscopy and scanning electron microscope. An increase in contact angle indicating more hydrophobic surface was observed with addition of n-butanol as anti-solvent to coagulation bath. The n-butanol-water bath-based membranes having highest PEG proportion (4% by wt.) displayed relatively superior overall performance in comparison with other membranes with respect to the examined characteristics.

Keywords: Polyvinylidene fluoride; Polyethylene glycol; Membrane fabrication; Characterisation; Coagulation bath; Phase inversion

1. Introduction

Polyvinylidene fluoride (PVDF) membranes have many applications in membrane processes such as ultra-filters, membrane bio-reactors and membrane contactors because of good mechanical strength, membrane forming properties, outstanding anti-oxidation [1], excellent chemical resistance, thermal stability [2] and a hydrophobic surface [3]. It was initially perceived that membrane contactors are predominantly inert matrices providing high interfacial contact area for mass transfer and the role of membrane materials was not evident regarding their impact on directly affecting the separation phenomena. However, the development of membrane distillation has begun to unravel the importance of the physico-chemical nature of the membrane in achieving the separation objectives [4,5]. Furthermore, the membrane contactors have the potential to provide an alternative or supplementary solution to many chemical engineering unit operations such as membrane solvent extraction, distillation and crystallization.

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Thereby, it becomes essential to tune the characteristics of the membrane to suit the separation requirements. Some of the significant properties of the membrane contactors include their hydrophilic/hydrophobic nature besides the membrane compatibility with reference to the components of the system. In this context, a large number of experimental studies have been reported for improving the surface morphology and characteristics by varying the dope composition, solvents for preparing the dope, additives and coagulation bath composition. Many studies have been carried out to modify the surface morphology of PVDF membranes and their performance using variety of organic solvents [6–8]. PVDF membranes prepared with well-defined characteristics have found various applications in water treatment in various configurations including flat sheet as well as hollow fiber modules [9–14].

Development of membranes with specific surface characteristics has attracted the attention of researchers in recent years. The interaction between molecules in the feed stream and membrane surface can play a role in enhancing or inhibiting the molecules to pass through the membrane. Hydrophobic membranes are specifically desired in applications that require recovery of small amount of non-aqueous solvents from streams comprising primarily of water. Also, hydrophobic membranes have been used in gas absorption applications that require removal of CO_2 through non-dispersive contact with amine solutions. The non-wetting membrane contactors with gas-filled pores facilitate enhanced mass transfer between gas and liquid phases [15–17]. It is reported that the change in the composition of additive [18] and use of different non-solvents in the coagulation bath [19] changes the surface morphology and increase the permeability of the PVDF membranes. The addition of additive can improve the pore formation, increase the solution viscosity and increase the rate of the phase inversion process [20]. Some of the common additives used in the PVDF membrane formation are water, methyl cellulose, glycerine, poly-(vinyl pyrrolidone), poly ethylene glycol (PEG), lithium chloride and zinc chloride [21–24]. Of these, PEG is widely mainly due for its good solubility, compatibility and non-irritating nature [25].

The phase inversion technique was first introduced by Leob and Sourirajan [26]. The blending characteristics of polymers play a key role in this method [27]. Immersion precipitation is a type of phase inversion in which a polymer solution is cast over a suitable support, and then immersed in a coagulation bath which contains a non-solvent. The diffusion exchange of solvent and anti-solvent results in the phase separation and the formation of membrane take place. One of key controlling factors for the formation of flat sheet membranes is the composition of the coagulation bath. It influences the membrane formation by affecting inter-diffusion of solvent and non-solvent [28]. The interaction between polymer and non-solvent is also found to modify the demixing rate and membrane structure [29]. A few authors have studied water and ethanol as the coagulation medium [19, 30–31]. However, only a limited literature is available on the effect of n-butanol-water coagulation medium for PVDF membranes. Kuo et al. [32] studied the effect of non-aqueous solvents, including methanol, ethanol, propanol and butanol, as the coagulation bath. However, the impact of mixed composition coagulation medium (butanol and water) has not been investigated so far.

Therefore, the present study aims at preparing and characterizing the PVDF flat sheet membranes by altering the coagulation bath using n-butanol-water solution to achieve a hydrophobic surface using n-methyl-2-pyrrolidone (NMP) as a solvent and PEG as an additive. The concentration additive (PEG) was varied from 0%, 1%, 2% and 4% (by weight). The prepared membranes were immersed in the coagulation bath which contains water and n-butanol, with different proportions as 0:100 and 45:55 (water:butanol volume ratios). The PVDF membranes prepared were characterized for their porosity, viscosity, water contact angle, pure water flux and tensile strength. Structural characteristics were analysed using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF) of molecular weight 440,000; NMP (anhydrous 99.5%) solvent; and PEG-400 as additive were purchased from Tech Inc., Chennai, India, and anti-solvent n-butanol (99.9% purity) was purchased from Sisco Research Laboratories Pvt. Ltd., India. These chemicals were used in this study for the preparation of PVDF flat sheet membranes without any further purification.

2.2. Membrane preparation

PVDF flat sheet membranes were fabricated by the immersion precipitation technique as illustrated in Fig. 1. The dope solution was synthesised by dissolving 16% (wt %) PVDF in NMP solvent at 35°C ± 2°C by means of a mechanical stirrer. After a series of trials, the concentration of PVDF was optimized at 16 wt %. PEG (with concentrations of 0, 1, 2 and 4 wt %) was used as the additive. The polymers were fractionally added into the solvent until the entire amount was dissolved to form a solution which was then continuously mechanically stirred for 14 h. The final homogenous dope solution was kept still for 4 h at ambient temperature for degassing. The polymer solution was then cast (0.3 mm thickness) onto the clean glass plates at room temperature, after which the plates were immediately immersed into the coagulation bath. The two different coagulation bath conditions namely DME where the volume ratio of n-butanol and water was (0:100) and DMB for volume ratio (45:55) of n-butanol and water were used in the present study. The nomenclature for membranes of both coagulation baths and various compositions is listed in Table 1. The numbers 1, 2, 3, 4 in the nomenclature of each membrane series indicate the PEG concentration by weight percent. The membranes were immersed and kept in the bath for at least 5 h to allow membrane formation and solvent removal.

2.3. Characterization of membranes

2.3.1. Viscosity and porosity

Viscosity of the dope solution affects the ability to impede the rate of exchange of non-solvent and solvent

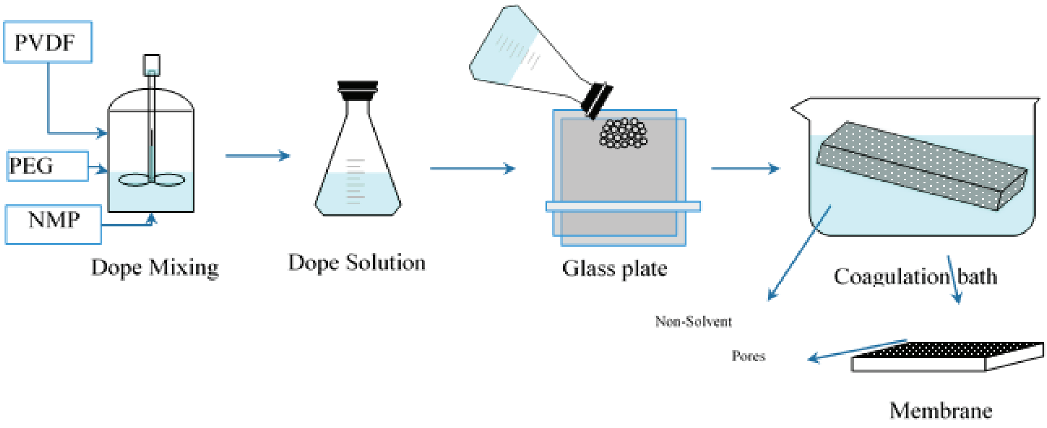

Fig. 1. Schematic representation of PVDF membrane preparation by phase inversion technique.

Table 1
Composition and preparation condition of membranes

Membrane	Polymer concentration (PVDF) wt %	Additive concentration (PEG) wt %	Solvent concentration (NMP) wt %	Coagulation bath conditions
DME 1	16	0	84	Distilled water (100:0)
DME 2	16	1	83	Distilled water (100:0)
DME 3	16	2	82	Distilled water (100:0)
DME 4	16	4	80	Distilled water (100:0)
DMB 1	16	0	84	n-Butanol: water (45:55)
DMB 2	16	1	83	n-Butanol: water (45:55)
DMB 3	16	2	82	n-Butanol: water (45:55)
DMB 4	16	4	80	n-Butanol: water (45:55)

DME – 0:100 (n-butanol:water), DMB – 45:55 (n-butanol:water).

during the process of phase inversion [33]. The viscosity of dope solutions with varying additive concentration was measured before casting the membranes. The measurements were carried out using the DV-II+Pro Brookfield Viscometer at room temperature.

Prior to measuring the porosity, the membranes were kept in water for a minimum of 24 h to ensure complete wettability. The weight of the wet membrane sample was measured before it was dried at 60°C in a drying oven for a minimum of 48 h, after which dry weight was measured. The experiments were repeated three times to get the concordant value. The porosity was calculated by the following relation [34]:

$$\varepsilon = \frac{\left(M_w - M_d\right)/\rho_w}{\left(\left(M_d/\rho_p\right) + \left(M_w - M_d\right)\right)/\rho_w} \times 100\% \qquad (1)$$

where M_w is the weight of the wet membrane and M_d is the weight of the dry membrane, ρ_w and ρ_p are the density of water and the membrane, respectively.

2.3.2. Water contact angle

The hydrophobic nature of the fabricated membranes was studied by the water contact angle method. Before testing, the membrane samples were dried in ambient conditions for at least 24 h. During the analysis, a droplet of water is introduced on the surface of the sample using a micropipette. Digital images of the contour of the water droplet are then captured and analysed in the ImageJ software (NIH, USA). The water contact angles were obtained by taking an average of four measurements on dissimilar locations of the membrane surface.

2.3.3. Mechanical properties

In order to check the flexibility and elongation characteristics, mechanical behaviour of membranes was studied in detail. The specific characteristics including tensile strength and the elongation at break of the developed membranes were evaluated using tensile testing machine, TKG EC-2500N (Krutam Techno Solutions Pvt. Ltd., India). The procedure involves cutting the membranes into rectangular strips (sized 7 mm × 1.5 mm). Once the membrane samples are cut to this size, sand paper of size 3 cm × 1.5 cm is attached to both the ends of the membrane using an epoxy adhesive. Using bolts and nuts, the membrane sample is then fixed between two clamps which are then hung onto the hooks. The equipment is switched on and the material is gradually stretched as the hooks are moved apart. The readings are taken based on the thickness and load till the breaking point is reached.

2.3.4. Fourier transform infrared analysis

The FTIR spectra were investigated using a FTIR-ALPHA Spectrometer, with the measurements in the range from 4,000 to 500 cm^{-1}. The membrane samples were dried at 60°C for 24 h in a drying oven before the analysis. This study was used to verify the presence of functional groups in the fabricated membranes.

2.3.5. SEM analysis

The properties of prepared membranes mainly depend on the rate of the solvent precipitation which can change the structure of the membrane. This was evaluated by using Quanta FEG 200 High Resolution Scanning Electron Microscope (FEI, USA). The membrane sample of dimension 1 cm × 0.5 cm placed vertically on a carbon tape supported by the copper grid to view the morphology of the membrane. The sample was then placed inside the chamber and stage was set towards the electron gun with the distance of 10 mm. Further electron gun was operated at 30 kV. The desired area was focussed and recorded.

2.3.6. Water permeability and liquid entry pressure measurement

The membranes were pre-wet for 24 h in pure water, after which the pure water flux was measured by using a test cell (Tech Inc, India) (Fig. 2). The set up comprises of a rectangular membrane module unit with an effective area of 100 mm × 125 mm. The pump is connected in the piping line from feed tank to the module unit along with a pressure gauge. The pressure operating range is 0–1 bar (gauge pressure). The membrane performance was evaluated for each membrane using the test cell by conducting flux study experiments. The permeate flux was calculated with respect to the time taken to collect permeated water. All flux measurement experiments were carried out at constant pressure of 0.8 bar (gauge pressure). The permeate flux is defined by the following formula:

$$J = \frac{V}{A \times t} \qquad (2)$$

where J denotes the permeation flux of membrane of pure water (L/(m^{2}h), V denotes the permeate volume of pure water (L), A is the effective area of the membrane (m^2) and t is the collection time (h). Flux data were determined by averaging the values observed in three independent measurements for each membrane under identical conditions.

The liquid entry pressure (LEP) was evaluated with the same test cell. Briefly, the procedure for LEP measurement is described here. The fabricated membrane is fixed in the test cell. The feed pump connected to the inlet is started with minimum operating pressure. Initially, no permeate flow takes place and all reject is recirculated to the feed tank. The pressure is slowly increased in steps of 0.1 bar till the first droplets of permeate are observed. It corresponds to the LEP for specific membrane being tested.

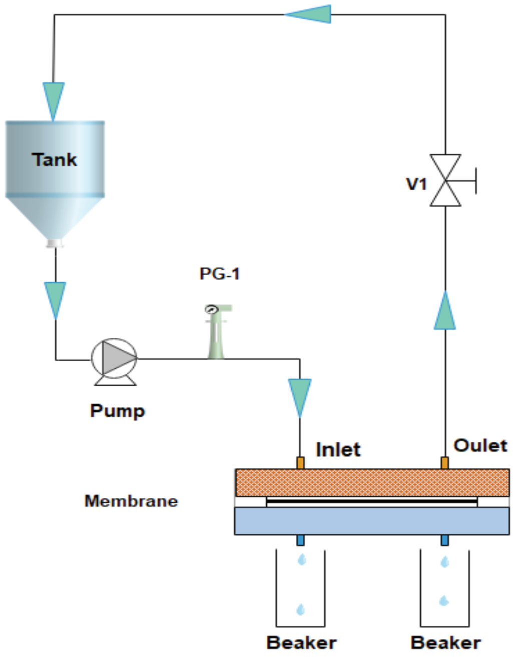

Fig. 2. Schematic representation of membrane test cell.

3. Results and discussion

3.1. Viscosity and porosity

The viscosity values for various PEG concentrations used in the present study are shown in Fig. 3. The dope solutions prepared with 0–4 wt % additive range exhibited different viscosities. From the figure, it is seen that a significant increase in viscosity was apparent as the concentration of the additive increased from 0, 1, 2 and 4 wt %. The manual casting operations performed with more viscous solutions in this range allowed more uniformly controlled thickness of the fabricated membranes. The change in viscosity can also influence the precipitation process in the coagulation bath pore forming characteristics and eventually the membrane structure and its performance.

The obtained porosity values for varying coagulation bath condition are presented in Fig. 4. The porosity of the DME membranes that used water as the coagulation bath was

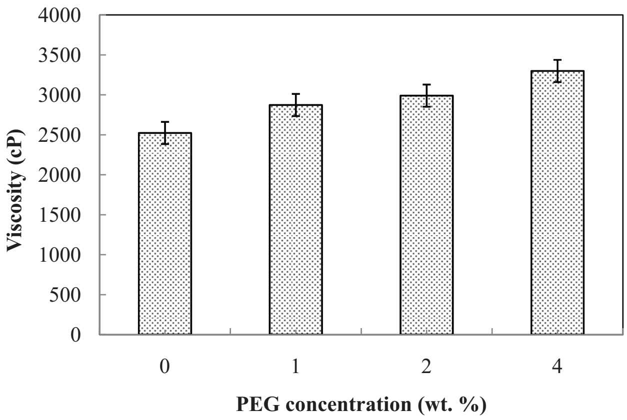

Fig. 3. Effect of PEG concentration on viscosity.

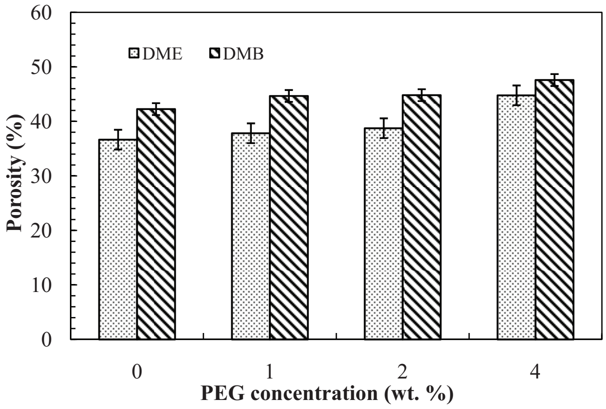

Fig. 4. Effect of PEG concentration on porosity.

found to be lower than that of the DMB membranes which used a mixture of n-butanol and water. It was observed from the results, the difference in porosity can be attributed to the variation of the coagulation bath mixtures used in both cases that affects the phase inversion phenomena and hence the pore formation [32]. This may be due to the altered interactions that occur between the membrane polymer and the coagulation medium.

3.2. Water contact angle

The water contact angle measurement for different conditions is shown in Fig. 5. The n-butanol-water medium based membrane samples show lower water wettability than the water medium based samples. Therefore, it can be inferred that the contact angle for membranes formed by the n-butanol-water coagulation bath are significantly higher, that is, the DMB membranes are more hydrophobic in nature as compared with the DME membranes formed by the water coagulation bath. The hydrophobicity can be related with the surface porosity for PVDF membrane [35]. In this study, as the concentration of PEG (wt %) increases, a significant increase in porosity is observed, accompanied by a decrease in the contact angle. Therefore, from the results, it is noticed that DMB membranes with lower PEG additive composition exhibit more hydrophobic surface.

3.3. Mechanical properties

The stress–strain data for each fabricated membrane was acquired by applying a tensile force at a uniform rate to the sample at a constant temperature. Figs. 6(a) and (b) show stress–strain curves for membranes in water coagulation medium and n-butanol-water coagulation medium, respectively. The slope at origin increases with increase in polymer additive suggesting increase in modulus. Similar trend is observed for DME and DMB series of membranes. The tensile strength and elongation-at-break data of fabricated membrane in respective coagulation medium were obtained and represented in Figs. 7(a) and (b). It is observed that there is an increase in tensile strength with the increase in the weight% of additive used. Similar conditions are observed in the n-butanol-water medium also. The values show that the additive 4% by weight yields fairly good tensile strength in both the coagulation mediums. The tensile strength for DME4 is 0.69 N/mm^2 as compared with 0.53 N/mm^2 shown by DMB 4.

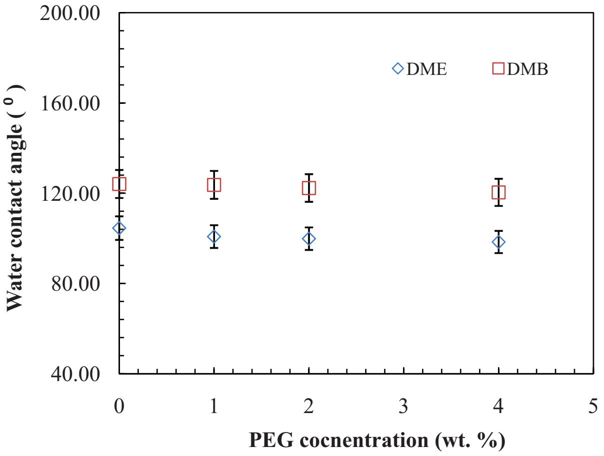

Fig. 5. Effect of PEG concentration on water contact angle.

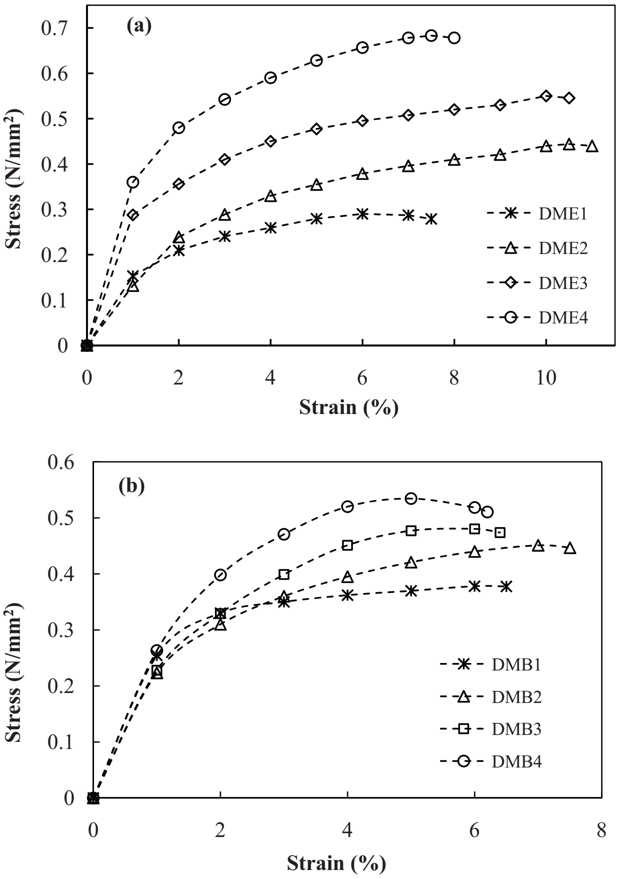

Fig. 6. Stress vs. strain curves for (a) DME membranes and (b) DMB membranes.

Fig. 7(a) shows that the increase in additive concentration of the membrane leads to an increase in its tensile strength. This may be attributed to the significant increase in viscosity caused by the addition of the PEG polymer, which causes a subsequent change in the mechanical properties.

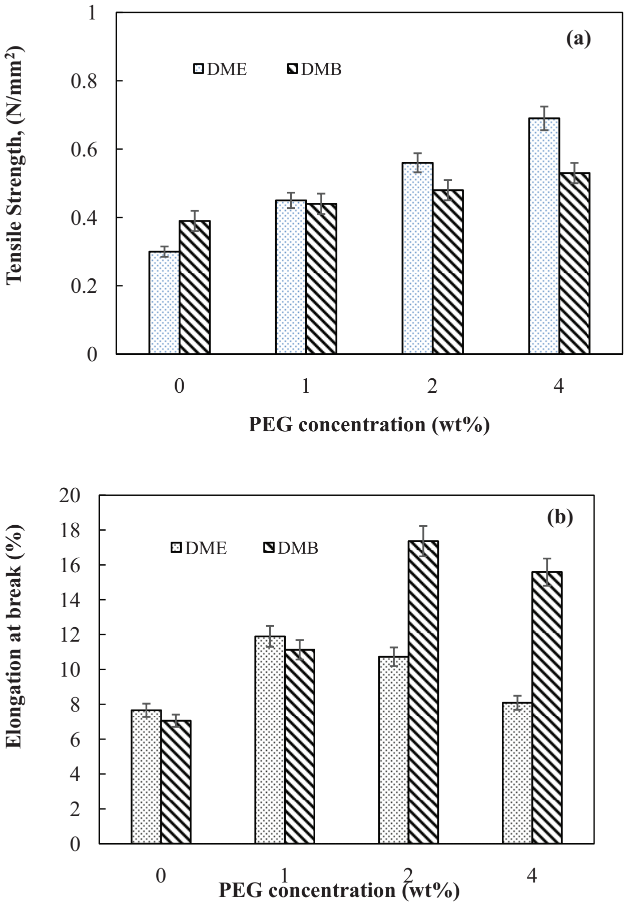

Fig. 7. Effect of PEG concentration on (a) tensile strength and (b) elongation-at-break of membranes.

A comparison of elongation-at-break data also suggests the influence of additives and coagulation medium on flexibility of membranes (Fig. 7(b)) possibly resulting from interactions of polymer matrix components. The data indicates that the mechanical properties of the membranes can be tailored by introducing an appropriate amount of additive.

3.4. Fourier transform infrared analysis

The FTIR spectrum of the membranes is shown in the Fig. 8. The peaks at 3,310–3,320 cm^{-1} and 2,854–2,924 cm^{-1} represent the CH_2 asymmetric and symmetric vibration of PVDF and are identical to the spectrum and the peaks at 1,450–1,460 cm^{-1} are related to the CH_2 wagging vibration reported by Bai et al. [36]. The peaks at 838–840 cm^{-1} and 873–874 cm^{-1} correspond to the C–F stretching vibration and the C–C–C asymmetrical stretching of PVDF [37]. DMB samples (n-butanol-water medium) show longer peaks in all the above graphs than DME membranes obtained using water medium. Both the mediums prove to have all the characteristic functional groups of PVDF components [38]. The two characteristic absorption peaks of PEG (O–H: 2,885 cm^{-1}) and (C–O: 1,110 cm^{-1}) were either very small or not manifested. This suggests that all PEG in the membrane top layer had been leached out after membranes were soaked in the coagulation bath as suggested by Zuo et al. [18] and Alamery et al. [33]. The presence of O–H group generally shows broad peaks at 3,550–3,200 cm^{-1}, this is attributed to the interaction of O–H present in n-butanol and water coagulation mediums. The other bonds show narrow peaks such as the C–F bond which varies from 1,180 to 1,190 cm^{-1} and shows the presence of CF_2 stretching by Deng et al. [39]. The wavelength of 1,640–1,643 cm^{-1} was attributed to the bending vibration of absorbing H–O–H groups, and is significantly more prominent in the DMB series.

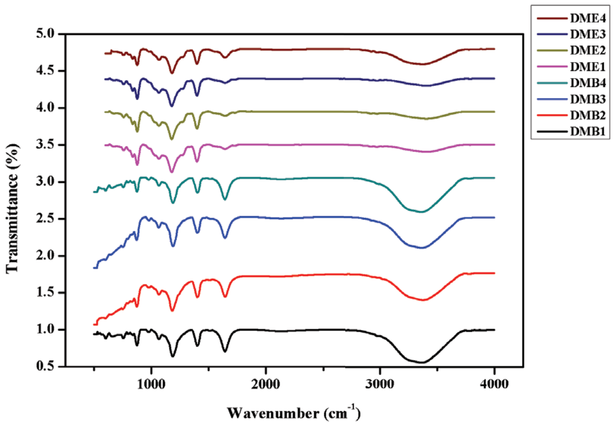

Fig. 8. Fourier transform infrared spectroscopy (FTIR) spectrum for PVDF membranes.

3.5. SEM analysis

The SEM was used to analyse the cross-sectional surface morphology of the PVDF membranes. Fig. 9 shows the skin layer of the membranes used in the present study. Eight different samples were analysed based on the varying coagulation mediums and concentration of additive used. Images show cloud-like features suggesting differences in surface roughness. The surface of the membranes appears rough. This is due to the fact that the solutions cast on a glass plate are free to shrink during immersion in the coagulation bath and do not maintain completely flat surfaces [40]. The structural changes in membranes are likely due to differences in phase separation phenomena in different types of coagulation mediums. Delayed demixing causes cloud-like feature formation. However, faster exchange between solvent and non-solvent results in denser membranes morphologies.

3.6. Water permeability and liquid entry pressure

The water flux was studied for DME and DMB membranes. The flux was found to decrease in the membranes with n-butanol-water mixture as the coagulant. This is attributed to its hydrophobic characteristic behaviour of the membranes. The DME membranes have a higher flux compared with that of DMB membranes as shown in Fig. 10. The highest water flux for DMB membranes was 268 L/(m^2 h) (lmh) (for membrane without PEG) and it reduced to 240 lmh on increasing the PEG additive concentration to 4 wt %. The corresponding change in the water flux was from 454 to 357 lmh for same change in the PEG additive concentration for DME membranes. The liquid entry pressure for DMB 4 was found to be 0.4 bar

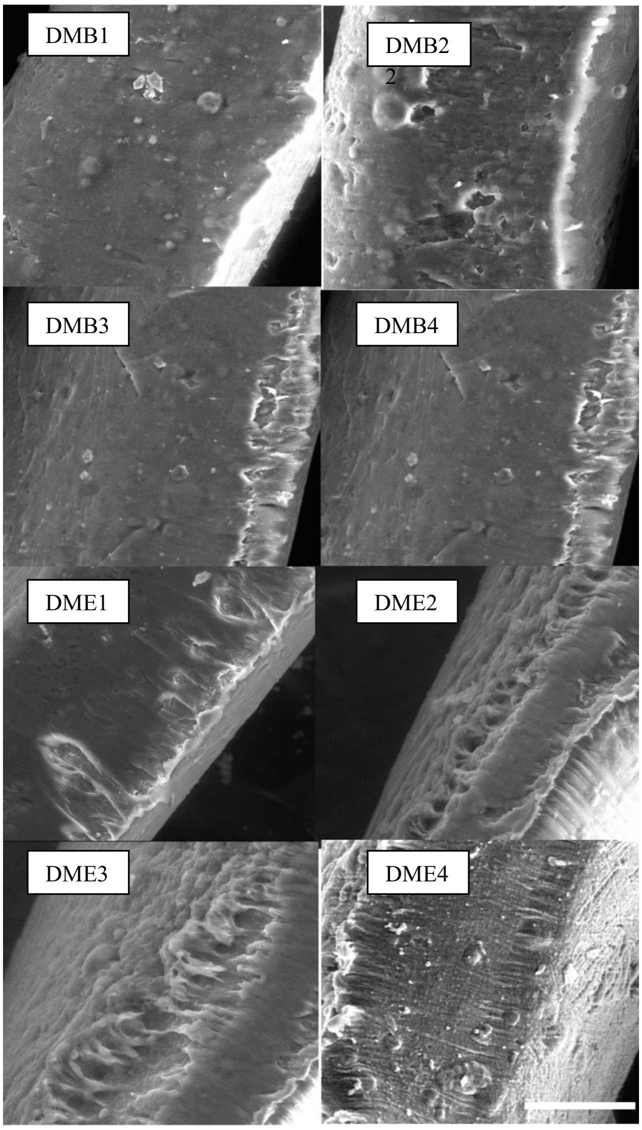

Fig. 9. Scanning electron microscope (SEM) images of PVDF membranes. Scale bar represents 200 μm.

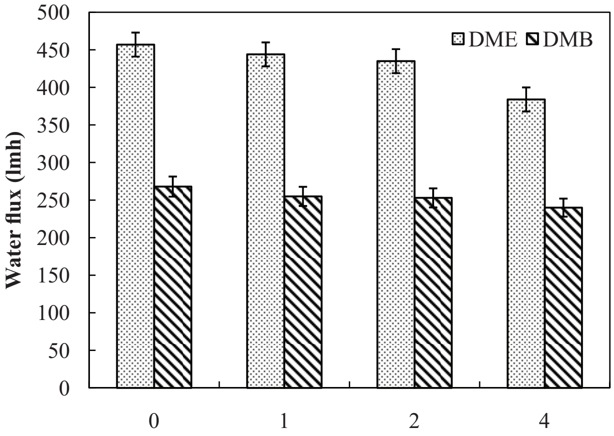

Fig. 10. Effect of PEG concentration on water flux for PVDF membranes.

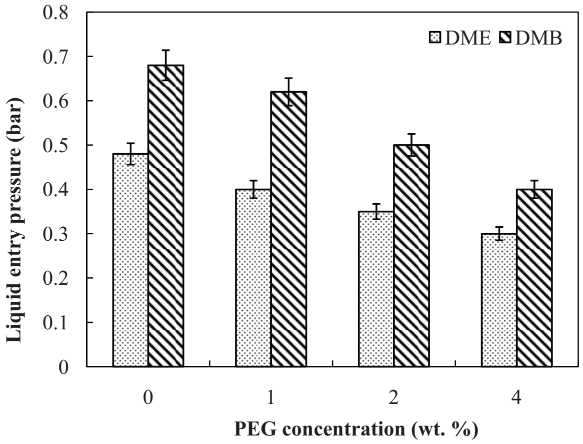

Fig. 11. Effect of PEG concentration on liquid entry pressure (LEP) for PVDF membranes.

which was higher than the liquid entry pressure for DME4 that was 0.3 bar (Fig. 11). The observations correlate with the higher hydrophobic nature of DMB membrane series compared with DME series. The observations concord with the reported data [11,12,41].

4. Conclusion

In this study, PVDF flat sheet membranes were prepared using the immersion precipitation phase inversion method with two different coagulation baths, namely water and n-butanol-water mixture, named here as DME and DMB series, respectively. The contact angle of the fabricated PVDF membranes increased with the usage of n-butanol-water bath suggesting an increase in hydrophobicity of the membranes. On increasing the proportion of PEG additive from 0% to 4% by weight, a relative decrease in hydrophobicity was observed for membranes prepared with either of the coagulation bath. Tensile strength of the membranes increased with the addition of PEG. The flux of DMB membranes exhibited a minimum and the liquid entry pressure showed a maximum value that is attributed to its hydrophobic behaviour compared with the DME membranes. The results provide an insight into understanding of the effect of introducing n-butanol into the coagulation bath and the effect of PEG additive concentration on membrane properties and structure. Our experiments have inferred that coagulation medium composition can play a role in determining membrane characteristics, in improving hydrophobicity. The outcome reported here would pave way for development of tailored membranes for applications in separation phenomena.

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