Preparation and characterisation of Nylon/PEG/PAN composite membrane for liquid filtration

Gobi Nallathambi[a], M Abinaya, S Ragavee, R Sivaranjani, S Arunkarthick, S Nisha & B Devi

Department of Textile Technology, Anna University, Chennai 600 025, India

A novel method has been proposed to prepare a Nylon/PEG/PAN composite membrane for the improvement of electrospun PAN fibre properties and filtration efficiency. Polyacrylonitrile fibre has been prepared by electrospinning technique. Different proportions of blended mixture of Nylon and PEG are prepared separately. Blended mixture of Nylon and PEG is poured over the electrospun PAN to prepare a Nylon/PEG/PAN composite membrane. The prepared Nylon/PEG/PAN composite membrane and Nylon/PEG membrane are characterized by using optical microscope, porosimeter, X-ray diffractometer and thermogravimetric analysis. Filtration efficiency of the prepared Nylon/PEG/PAN composite membrane is studied using pure water flux and oil water emulsion methods. The 50/50 proportion of Nylon and PEG has been identified for getting uniform and evenly distributed pores and also it shows around 80% of solute rejection, whereas 60/40 proportion shows little bit higher percentage due to higher proportion of Nylon. Thus, the pure water flux of 60/40 and 50/50 PAN/PEG/Nylon membranes met with the recommended pure water flux.

Keywords: Nanofibres, Nylon/PEG composite, Oil/water separation, Polymeric composite membrane, Ultra filtration, Water filtration

1 Introduction

The dissolved and dispersed components of chemical and biological systems in water are called pollutants which cause various health care issues in human beings. These pollutants are to be removed from water before being consumed. Different methods are being used to purify the water such as sedimentation, separation, absorption and adsorption by using different materials e.g. activated carbon.

Utilization of membranes is one of the well-knowntechniques for the separation of pollutants from water. The developments in membranes replace various water treatment processes, such as ion exchange system, filters, clarifiers and waste water bio reactors. Based on the separation of particles, the membranes are classified as micro filtration membranes (0.1 - 5 μm), ultra filtration membrane (0.1 - 0.5 μm) and nano filtration membrane (0.01 - 0.0001 μm) along with the reverse osmosis for the separation of dissolved salts and other ionic solutes from the solution[1].

The membrane preparation methods are classified as immersion precipitation[2-5], vapour induced phase separation[6,7], thermally induced phase separation[3, 8] and dry casting[9]. Phase separation is a common method for the preparation of polymeric membranes, blending of two or more different polymers or additives offer developments of membranes with functional properties[10-13], and dry phase inversion is suitable for the formation of macro voids[14,15].

Separation performance of membrane was enhanced by membrane surface chemistry. The hydrophilicity/ hydrophobicity property of the membrane was decided by the surface property of the membrane and it is based on the interactions between solid and liquid[16]. The hydrophilicity of the membrane is an important property for water filtration and this can be enhanced by blending of hydrophilic polymers[17, 18], coating of hydrophilic materials[19] and surface grafting[20-23].

The addition of pore forming additives such as non-solvent additives and their proportion in the polymer casting solution improves the hydrophilicity of the membranes and also induces the formation of macro voids[10,24]. Use of PEG/DME combination in a polymer gives finger like cross-section in a membrane[10]. In polyetherimide (PEI)/ polybenzimidozole (PBI) and polyethyleneglycol (PEG) polymer membrane, PEG improves the hydrophilicity of PEI, blend miscibility and antifouling property of the membrane[10,23,25].

The proportion of PEG in casting solution decides the formation of micro and macro pores. This is due to the demixing of casting solution, such as nucleation and growth of rich polymer phase[10,26-28]. This also

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[a]Corresponding author.
E-mail: gobsnn@gmail.com

enlarges the pores in phase inversion process due to its water soluble nature[29]. The formation of macro and micro voids with the intact flow path of the membrane results in high pure water flux and permeates flux, but it decreases the rejection percentage. Nano fibrous membranes are developed for liquid filtration with enhanced micro pores and solute rejection percentage due to its high specific surface area, nano scale pore size and controlled porosity[30]. The layers of nano fibres capture very small particles in the flow of liquid. The smaller diameter nano fibres offer high surface area, resulting in adsorption and better retention of smaller particles[30,31]. By nature, high surface area and surface energy electrospun nano fibres exhibit a very high contact angle as compared to a polymer film made by the same polymer[30].

In order to overcome the problems of casted polymeric membrane and nano fibrous polymeric membrane, various techniques are developed. One of the techniques was the development of three tier arrangement of composite membrane such as the electro spinning of PVA nano fibres on nonwoven micro fibres support and chemically cross-linked with glutraldehyde to enhance the mechanical and water resistance properties[31]. The nonwoven fabric/electrospunnano fibre web was used as a three tier membrane for ultra filtration[32-34], nano filtration[35] and forward osmosis[36].

In another study, polyethersulfone (PES) nano fibres are placed on nonwoven PET which acts as a backing layer to enhance the pressure related and strength properties[30, 37]. Interfacial polymerization and coating of hydrophilic polymer such as ultra-thin coating of cellulose on the surface of membrane enhances the hydrophilicity and rejection percentage[30, 38, 39]. Cross linking of hydrogel PVA on PVA electrospun scaffold results in the formation of fully inter connected submicron pores with three dimensional networks. The thickness of the coating layer influences the permeability and permeates rejection of the membrane[38]. The chemical stability of polyacrylonitrile (PAN) helps to select the preparation of fibrous filter media[40-43]. It also has moderate hydrophilicity but poor compatibility and high brittleness[44].

In this study, a novel technique has been used to construct a composite membrane with Nylon/PEG/PAN. Nylon was used as membrane polymer, PEG was used as additive for pore formation (formation of macro voids) and also to enhance the hydrophilicity of the membrane, and PAN electrospun web was used as middle layer of the membrane. Different properties were analysed for constructed membranes and the influence of various factors was also discussed.

2 Materials and Methods

2.1 Materials

Nylon 6 $[HN(CH)_5CO]_n$ with the density of 1.14 g/cm^3 was used for membrane preparation. Polyethylene glycol (PEG 1000) was procured from Alfa Aesar and used as pore forming additive. Polyacrilonitrile $(CH_2CHCN)_n$(PAN) from sigma was used for producing electrospun web. Analytical grade N,N'-dimethyl formamide (DMF) and formic acid (85%) were procured from SRL Ltd. India. Soya bean oil, deionised & distilled water, and sodium lauryl sulphate (SLS) were used for preparing emulsion for filtration.

2.2 Methods

2.2.1 Electrospinning

Polyacrylonitrilepolymer was dissolved (8% w/w) in N,N'-dimethyl formamide (DMF) with magnetic stirrer by mild string. After viscous solution was formed, it was loaded in 5mL syringe with 18 gauge needle and mounted in electro spinning machine. A DC voltage of 18 kV (Gamma High Voltage Apparatus, USA) was applied between the syringe needle tip and the collector covered with the aluminium foil. The droplet emerged from the tip of the needle was split due to repulsive force set at the needle. During the process, the solution evaporated and polymeric fibres are deposited on the aluminium foil in the form of nonwoven fibrous mat[45-47].

2.2.2 Characterisation of Electrospun Web

The morphology of nano fibres was analysed using scanning electron microscope (HITACHI S-3400 SEM) at a voltage of 10-15 kV.

2.2.3 Preparation of Blended Membrane

Different proportions of polymer casting solutions of Nylon and PEG were prepared as per the experimental plan given in Table 1. Initially, the total polymer concentration was taken as 25% and the observations were made with respect to pore formation and permeability. It was observed that in this case the pores were randomly formed. Hence, 20% concentration was then tried with 50/50 proportion of Nylon and PEG and the uniform pore formation was observed, based on which the experimental plan was designed (Table 1). As per the experimental plan, the Nylon and PEG mixture was dissolved in formic acid and the prepared homogenous polymer solution was

Table 1 — Proportion of Nylon/PEG and thickness of samples

Sample ID	Proportion of Nylon/PEG	Thickness, mm
S_1	60/40	0.062
S_2	50/50	0.040
S_3	40/60	0.032
SW_1	60/40W*	0.104
SW_2	50/50W*	0.080
SW_3	40/60W*	0.076

*Constant mass (3 g/m²) of PAN electrospun web.

kept as such for 5 h to eliminate air bubbles. In this study, the membranes S1, S2 and S3 were prepared by dry phase inversion technique using different Nylon/PEG proportions. Each Nylon and PEG mixture (5mL) casting solution was prepared and poured over a glass plate. By using a glass rod the solution was spread on the glass plate and allowed to evaporate the solvent for 24 h at 27° C with 50% RH. The dry film was removed from the glass plate and washed with cold water followed by drying in hot air oven at 70°C to remove residual solvent. For samples S4, S5 and S6, PAN web was placed on the glass plate and similar procedure was followed to prepare the membrane. Three layer structure of membrane was formed, such as internal core layer with PAN electrospun web and external surface layers by Nylon and PEG; the outer layers are highly permeable due to the macro voids present in it[25]. The schematic representation of the Nylon/PEG/PAN and Nylon/PEG membranes are shown in Fig. 1. The membrane sheets were inspected under light box to detect defects as thin spots and pin holes; defective membranes were discarded and good membranes were taken for further studies.

2.3 Membrane Characterisation

2.3.1 Morphological Studies

The morphological characteristics of blended membranes were studied using optical microscope (Leica DM2700M). The prepared membranes were placed between the glass plate and glass slit, the images of the membrane were captured with the magnification of ×100. The thickness of the samples was also measured with the precision thickness gauge.

2.3.2 Pore Size Analysis

The pore parameters such as mean flow pore diameter and bubble point of the membranes were determined for produced membranes by capillary flow pore meter (CFP-1200 AEL., PMI Inc.).

2.3.3 XRD Studies

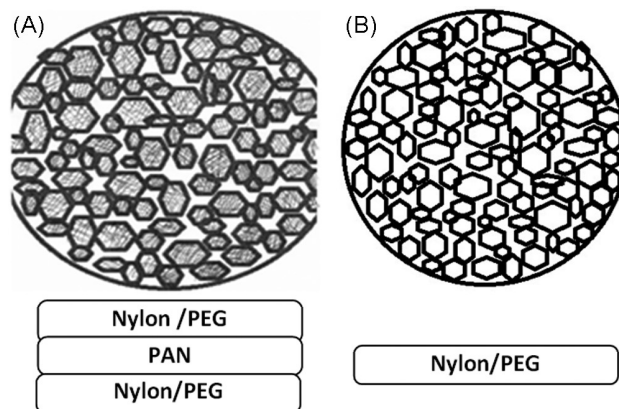X-ray diffraction patterns of pure PAN and PAN/PEG/Nylon membranes were analysed by a

Fig. 1 — Schematic diagrams of (A) Nylon/PEG/PAN(electrospun web) membrane, and (B) Nylon/PEG membrane

Ragaku Rota Flex D/Max – C x-ray diffractometer using Cu Kα radiation (λ = 0.154 nm). The x-ray diffractograms were measured at diffraction angle (2θ) range of 5 - 80° with a constant operating voltage of 40 kV and a tube current of 30mA. From the diffractograms, the crystallinitypercentages were calculated for pure PAN and with PAN membranes by the following equation.

$$C_r I \ (\%) = \frac{I_{002} - I_{am}}{I_{am}} \times 100 \qquad ... (1)$$

where I_{002} is the peak intensity from the (002) lattice plane; and I_{am}, the peak intensity of amorphous plane[48].

2.3.4 Thermal Analysis

The thermal degradation studies of the Nylon/PEG and Nylon/PEG/PAN blended membranes were carried out on a TGA Q 50 analyser in nitrogen atmosphere. The samples were tested from room temperature (27°C) to 700°C at a heating rate of 20° C/min. From the thermograms, the thermal degradation characteristics were studied.

2.3.5 Pure Water Flux

The prepared membranes were subjected to pure water flux studies. The pure water flux is a measure of the hydraulic permeability of the membrane and the most extensively used parameter in micro and ultra filtration. Flux is a measure of interplay of pore size (distribution), tortuosity and thickness of the active part of the membrane and will be influenced very much by fouling and concentration of minor components present in pure water. Pure water flux was calculated by the following formula:

$$J_W = \frac{Q}{A \, \Delta T} \qquad ... (2)$$

where Q is the permeated pure water (L); A, the effective membrane area (m^2), and ΔT, the testing duration (h).

2.3.6 Determination of Filtration Efficiency

The filtration efficiency of the membranes can be evaluated by oil/water emulsion separation process[38]. Oil/water emulsion was prepared for measuring the cross flow measurements of the membranes by mixing of soya bean oil (1350 ppm), non-ionic surfactant (150ppm) and water. Initially, 5% oil/surfactant emulsion was prepared. The oil/water blend was prepared by adding water to oil slowly under constant rate of agitation. There was change in viscosity initially, and a decrease in viscosity by addition of water continuously causes formation of oil-in-water emulsion at inversion point. The pressure applied during filtrations was10PSI and the experiment was carried out in room temperature (27° C). The area exposed for filtration was 20 cm^2. The quality of emulsion and filtered solute was evaluated by UV- vis spectrophotometers (absorbance at 230 nm). The permeate flux and the total organic content (TOC) were calculated by using Eq. (2). The total organic concentration (TOC) and rejection percentage (R%) were calculated using the following equation:

$$R\% = \left(1 - \frac{TOC\ in\ permeate}{TOC\ in\ feed}\right) \times 100 \qquad \ldots (3)$$

3 Results and Discussion

3.1 Properties of Electrospun Web

PAN electrospun web has been produced in submicron range and its mass per unit area is found 3 g/m^2. Scanning electron microscopic image of electrospun pure PAN is given in Fig. 2. The fibre size has been optimised by optimising the parameters of electrospinning process. The image shows that the electrospun fibres are randomly oriented which helps to ensnare different sizes of particles and their uniformity in size. Electrospun membranes give high porosity due to the entanglement of nano fibres and all the pores are interconnected. Electrospun nano fibres are extremely susceptible to fouling because of the very large intrinsic surface area[38,49-51]. Hence, it is very difficult to use it alone as water filtration membrane.

Table 1 shows details of Nylon/PEG samples and their thickness. Thickness of the prepared membrane gradually decreases when the proportion of PEG increases due the water soluble nature of PEG and also its density (1.0927 g/cm^3).
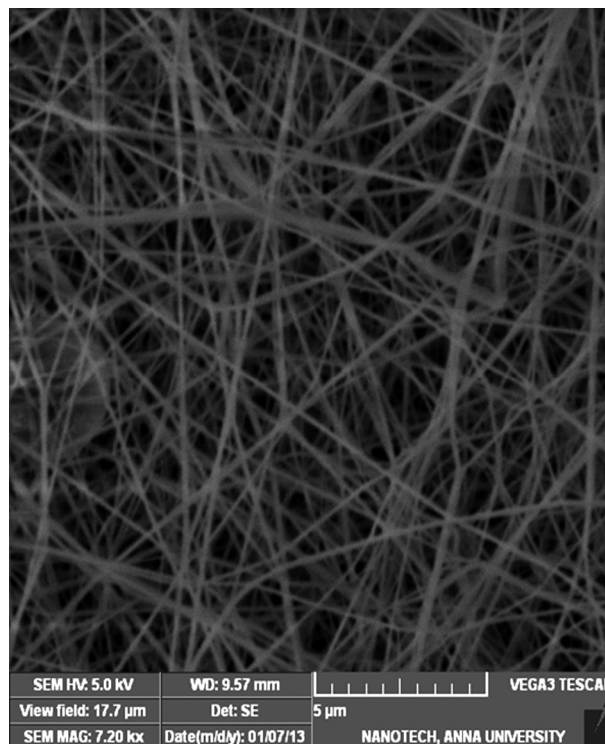

Fig. 2 — SEM image of PAN electrospun web

3.2 Morphological Studies

The proportion of Nylon, PEG & solvents and processing conditions influence the structure of membrane and its properties. Pore formation and its uniformity are significantly influenced by the additive PEG. By blending of hydrophilic polymer with hydrophobic polymer, the hydrophilic property can be improved for casting membranes. Both Nylon and acrylic are moderate hydrophobic and their hydrophilic property has been enhanced by PEG. Overall polymer concentration has been maintained as 20% and the proportion of the Nylon and PEG have been varied. Higher proportion of Nylon results lower pure water flux and random pore formation. Hence, 50% proportion of Nylon has been taken as reference to prepare membrane and analysis of its influence on other properties. Hexagonal shape of macro voids are formed (Fig. 1) when solvent/additive combination as formic acid/PEG is used.

A novel idea has been used in this study to enhance the properties of membrane by surmount the disadvantages of polymeric membrane and nano fibrous membrane. Lower mechanical and thermal properties are claimed as disadvantages of the nano fibrous membrane and the intact flow path of the polymeric membrane will also deduce the filtration efficiency.

3.2.1 Optical Microscope Images

The optical microscopic images are given in Fig. 3. S1 and SW1 show poor pore formation, S2 & SW2 show more uniform and well distributed pore formation, and S3 & SW3 show more open structure than other samples. Membranes without PAN web and made by Nylon/PEG are more transparent. Membrane S1 shows lesser pores and also the pores are not uniform. When the proportion of PEG is increased as 50% in S2, more uniform pores are formed as shown in Fig. 3. By increasing the proportion of PEG as 60%, larger and more transparent pores are appeared in S3.

Similarity of pore formation is also observed in composite membranes (SW1, SW2 and SW3). The pore formation property has not been influenced by the PAN nano fibrous layer which is formed as a core layer.

3.2.2 Pore Size and its Distribution

Mean flow pore diameter and bubble point pore diameter are presented in Table 2. It is evident from the results that the lesser additive proportion of PEG shows smaller mean flow pore diameter and higher bubble point than S2. This shows that the variation in pores are higher in S1. The mean flow pore diameter increases from 6.3 to 12.7 for membranes S1 and S3 due to the proportion of PEG in the casting solution. Bubble point is the biggest pore in the membrane which is an indication of uniformity of pores. For membrane S1, mean flow pore diameter is 6.3 but the bubble point diameter is 37.1, showing that it contains more variation in pores. The increase in PEG content do favour for more pore formation with different size. Increase in pore size and bubble point leads to increase in permeate flux of the membrane. Due to electrospun

PAN as a middle layer, the mean flow pore diameter and bubble point diameter are reduced for blended membrane; similar trend has also been observed for the increase in proportion of PEG in composite membranes.

3.3 X-ray Diffraction (XRD) Studies

The structures of Nylon/PEG and Nylon/PEG/PAN have been analysed by X-ray diffraction analysis and the diffraction patterns are shown in Fig. 4. A sharp crystalline peak at $2\theta = 17°$ is observed in XRD spectrogram due to the hexagonal packing of rod like chains of polyacrylonitrile. There are two characteristic peaks as α format, $\alpha_1 = 20.2°$ and $\alpha_2 = 23.8°$, corresponding to the reflection of the crystalline phase of Nylon 6. In general, Nylon 6 shows that α form of crystalline structure in case of extended chain conformation or γ form when the chains are twisted. The high flexibility of PEG facilitates the increase in crystallization of the Nylon as more perfect α modification. The observed value of $2\theta = 19\text{-}20°$ is due to polyethylene glycol and it enhances the hydrophilicity of the membrane[52]. Table 2 shows that the crystallinity index decrease while increasing the proportions of PEG and it induces formation of α crystalline structure in Nylon polymer[53].

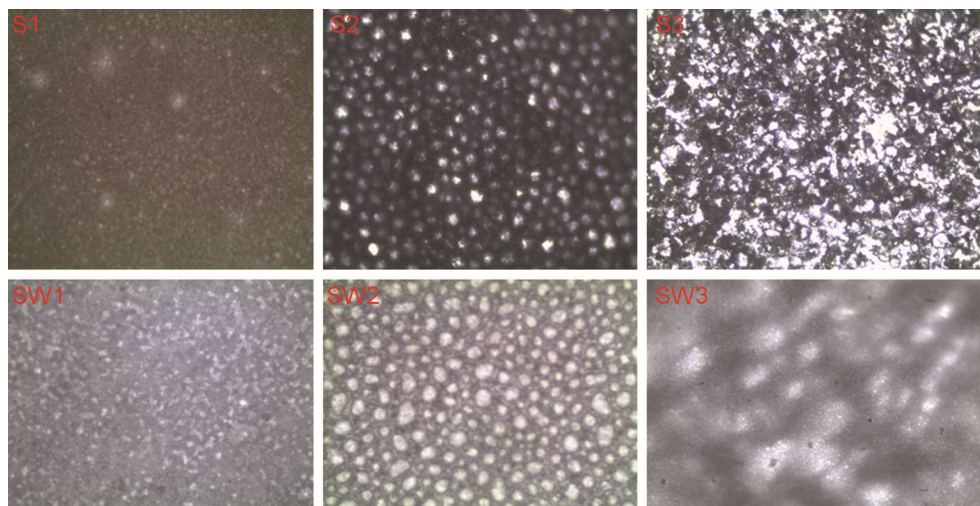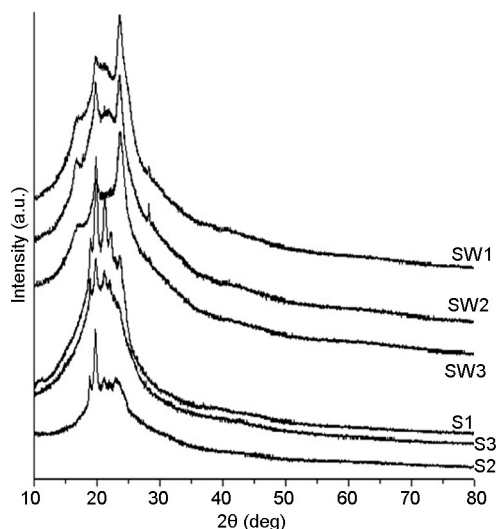| Table 2 — Pore properties and crystallinity index of membranes		
Sample ID	Mean flow pore diameter, μm	Bubble point pore diameter, μm	Crystallinity %
S_1	6.3	37.1	38.5
S_2	8.9	26.5	36.7
S_3	12.7	48.25	24.2
SW_1	0.29	6.14	55.9
SW_2	0.57	5.58	45.8
SW_3	0.83	4.21	32.6

Fig. 3 — Optical microscopic images of membranes

Fig. 4 — XRD pattern of Nylon/PEG and Nylon/PEG/PAN membranes

By adding Nylon/PEG solution on PAN web, the crystallinity of the composite membranes is increased. Hence, the handling property of the membrane is improved. Both hard and soft segments are important to enhance the properties of membrane and these properties are improved by blending of Nylon and PEG proportionally.

3.4 Thermo Gravimetric Analysis

The thermal behaviour of composite membrane has been analysed for identifying the influence of blends and the proportions. The proportion of Nylon/PEG blend changes crystallinity of the membrane and also it changes the thermal behaviour. The differential thermogrames of all the membranes are obtained by TGA by increasing the temperature at a heating rate of 20° C/ min from room temperature (27° C) to 700°C, under nitrogen atmosphere (Fig. 5). The temperature required for minimal degradation of Nylon is 310°C. The principal gaseous products of decomposition of Nylon are carbon dioxide and water. Nylon 6 produces small amount of various simple hydro carbons. The decomposition begins at 340°C in air and at 420° C in nitrogen. At temperature range 350 - 420°C, random chain scission leads to oligomers. The C-N bonds are the weakest in the chain, but the CO-CH$_2$ bond is also quite weak. However, both are involved in decomposition. At low temperatures, most of the decomposition products are non-volatile, but above 385°C main chain scissions lead to monomer and some dimer and trimer production[54]. PAN begins to decompose exothermally between 250°C a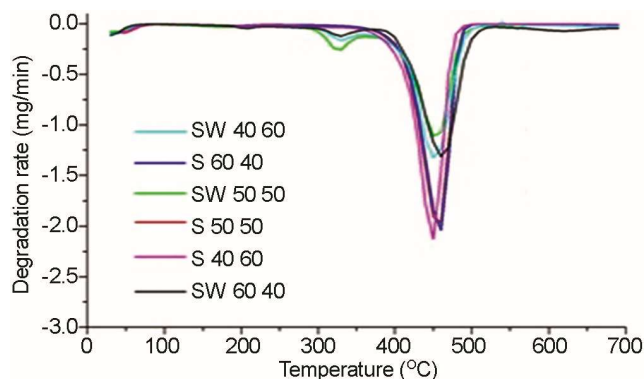nd 350°C with evolution of small amounts of ammonia and hydrogen cyanide. The crystalline melting temperature of PAN is 317°C. Ammonia is derived principally from terminal amine groups (NH) of acrylic. At temperature range 350°- 700°C, hydrogen is evolved as a cyclic structure carbonizes.

By the presence of PAN in membranes SW1, SW2 and SW3, the percentage of weight loss is lower than in Nylon/PEG membranes under the same temperature. PAN tends to form crosslinks when it reaches the decomposition temperature and also it reduces the rate of degradation. It enhances the stability of the membranes even at high temperatures.

Fig. 5 — Thermograms of Nylon/PEG and Nylon/PEG/PAN membranes

Table 3 — Filtration performance of membranes

Sample No.	Pure water flux, L/m^2/h	Rejection, %	Permeate flux L/m^2/h
S$_1$	411.04	26.22	323.15
S$_2$	529.79	14.09	396.75
S$_3$	740.34	2.95	648.32
SW$_1$	234.63	82.29	186.52
SW$_2$	347.10	79.67	275.36
SW$_3$	592.04	54.75	310.58

3.5 Pure Water Flux

The recommended pure water flux (PWF) for an ultra filtration membrane is 153 - 347 Lm^{-2}h^{-1}. Known volume of deionised and distilled water was taken and the rate of cross flow was measured. The area exposed for water flow and quantity of water was kept constant. Time taken for cross flow of liquid was observed and pure water flux was calculated for all membranes by using the Eq. (4) (Table 3). The pure water flux is found to increase from 411.04 L m^{-2}h^{-1} to 529.79 L m^{-2}h^{-1} when pore forming PEG is increased from 40% to 50%.

Further increase in PEG from 50% to 60% shows an increasing trend of pure water flux from 529.79 Lm^{-2}h^{-1} to 740.37 Lm^{-2}h^{-1}. This is due to more random pore

formation by PEG. The formation of macro voids formed as a result of PEG addition tends to increase the pure water flux. When the PAN electrospun web is placed as core layer, the pure water flux is found to be 234.63 $Lm^{-2}h^{-1}$ for 60/40 Nylon/PEG membrane which is 75% lower than that of without PAN web membrane with same proportion of Nylon and PEG. The increasing trend of PWF is observed even for composite membrane (Nylon/PEG/PAN) with the increase in PEG proportion. It increases from 234.63 $Lm^{-2}h^{-1}$ to 347.1 $Lm^{-2}h^{-1}$ and reaches up to 592.04 $Lm^{-2}h^{-1}$ while increasing the proportion of PEG from 40% to 60%. The increasing trend of PWF is observed, while comparing the samples S1, S2 and SW3 (SW3>S2>S1).

3.6 Filtration Properties

Ultra filtration performance of the composite membranes has been analysed by cross flow measurements of emulsion solution. Oil/water emulsion with surfactant is prepared for evaluating the ultra filtration performance of the membranes. The emulsion contains soya bean oil, water and non ionic surfactant. The experiment is carried out at room temperature (27° C) and UV spectrophotometer was used to characterize the in-feed and out-flow emulsions and also the permeate flux was calculated from the Eq. (2).

Sample S3 shows very less rejection % (2.95%) due to macro voids formed by the higher proportion of additives. The solute rejection percentage gradually increases by reducing the proportion of additive (PEG). The Nylon/PEG membrane shows lesser rejection % than the composite membrane due to undisturbed pores of the membranes. The core layer of membranes of SW1, SW2 and SW3 plays an important role to increase the solute rejection percentage. The PAN electrospun web contains layer of nano fibres in its cross section, the top and bottom surfaces of the membranes are covered by macro pores of Nylon/PEG polymer which helps to maintain the flux and also it gives excellent support for nano membranes to withstand the pressure given by the solute.

In this study, the membranes of Nylon/PEG show uniform and evenly distributed pores at 50/50 proportion and it gives higher pure water flux. When electrospun PAN web is placed between the layers of Nylon/PEG, it enhances drastically its performance in case of thermal stability, permeate flux and solute rejection percentage. The increase in proportion of PEG results in high permeate flux and the solute rejection will drastically fall. This happens in the membranes S1, S2 & S3. The permeate flux increases and rejection % decreases when the proportion of PEG increases.

Composite of Nylon/PEG/PAN membrane acts as a surface and depth filtration membrane, Nylon/PEG layer acts as a surface filtration membrane and PAN electrospun layer acts as a depth filtration membrane due to its layers of nano fibres[38]. More number of pores with smaller size results in better retention and higher number of smallerpores, favouring higher permeate flux[10]. This has been achieved by blending of appropriate proportion of Nylon and PEG with PAN electrospun web as a core layer.

4 Conclusion

Different proportions of Nylon/PEG mixture with PAN composite membrane have been prepared successfully for functional properties. The proportions of PEG in the composite membrane influences various parameters such as mean flow pore diameter, crystallinity, pure water flux, percentage of rejection of solute and permeate flux. Crystallinity and rejection percentage of composite membrane decreases when the concentration of PEG is increased, whereas pure water flux and permeate flux increase with increasing concentration of PEG. TGA result shows that the rate of decomposition of composite membrane is low, since the PAN is placed between the blend mixtures. Hence, polymeric membrane between the PAN improves thermal property of the electrospun PAN. In this study, the proportion of PEG and Nylon as 50/50 has been identified for uniform and evenly distributed pores, as compared to 60/40 and 40/60 proportions. The 50/50 proportion of Nylon/PEG with PAN electrospun web membrane shows around 80% of solute rejection (oil/water separation) and 60/40 shows little bit higher percentage due to higher proportion of Nylon. The recommended pure water flux have been met by 60/40 and 50/50 PAN/PEG/Nylon membranes. Thus, a novel technique of membrane preparation is used to prepare Nylon/PEG/PAN composite polymeric fibrous membrane with improved properties and filtration efficiencies for wastewater treatment.

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