International Journal of Membrane Science and Technology, **2015**, *2*, **39-46**

Recycling of Polysulfone: Study Properties of Membranes

Mayank Saxena[1], Saroj Sharma[2] and A. Bhattacharya[1,*]

[1]Reverse Osmosis Division, [2]Electro-Membrane Process Division, CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar- 364 002, (Gujarat), INDIA.

Abstract: Many significant developments regarding membranes have been taken place in past few decades. The wet phase inversion is a simple method to prepare asymmetric polysulfone membranes. Membranes were fabricated from polysulfone using N,N dimethyl formamide (solvent) and water (non-solvent) and permeation properties were investigated. We have explored the differences in performances of the membranes prepared from consecutive phase inversion of polysulfone. The effect of addition of sodium lauryl sulphate and their multi stage phase inversion were also studied. Functional group ruination/formation, Morphology, hydrophobicity, MWCO were analysed from different analytical instruments (viz. SEM, FTIR-ATR, TGA, contact angle, GPC). Fourier Transform Infrared (FTIR-ATR) spectra of polysulfone membranes were analysed to identify the variations of the bonds. The results obtained from water permeation experiments showed that consecutive phase separation of polysulfone increased the water permeability of the membranes. The polysulfone membranes resulted from multistage phase separation showed decreasing trend in separation for polyethylene oxide (PEO, 200kDa) as well as Bovine Serum Albumin (BSA, 66 kDa).

Keywords: Polysulfone, N,N dimethyl formamide, Wet phase separation, Bovine Serum Albumin.

INTRODUCTION

Polysulfones (PSf) are well-known high temperature amorphous engineering thermoplastic materials. The PSf has attracted the polymer scientists for its excellent characteristics, such as good solubility in a wide range of aprotic polar solvents, high thermal resistance (150-170°C), good chemical resistance over a wide range of pH, good oxidative resistivity, high mechanical resistance of the films (fracture, flexure, torsion), moderate reactivity in aromatic electrophilic substitutions reactions (sulfonation, nitration, chloromethylation, acylation, etc.) [1, 2]. The PSf can be molded, extruded, and thermoformed into a wide variety of shapes for different applications. Due to all these features, PSf and it derivatives have been widely used as new functional materials in various fields such as; biochemical, industrial and medical applications, as a high performance technological/biomedical material, but mostly in membranes for separation technologies (ultra filtration, reverse osmosis, or gas separation) [3-10].

It has been found that mostly the modification of polysulfone has been achieved chemically (by chloromethylation, suphonation, grafting of suitable monomers on to membrane surface etc.) to get the polymer of desired properties for its specific applications viz. fuel cell, pH responsive membrane etc. [11-16]. Apart from its functionality, the formation of controlled pores is another criterion to form better membranes. There are many techniques to form pores on the membranes such as incorporation of porogens in the membrane which can be destructed thermally, leached after particular reaction [17-20]. The porosity in PSf was introduced by embedding calcium carbonate nanoparticles in the bulk polymer [21].

Here in this particular study we have approached simple wet phase inversion technique. The demixing of solvent–non-solvent is the basic mechanism of the formation of pores in polymer membrane. In the present study phase inversion steps are enhanced to study the property profiles of PS membranes from different steps. The present study is conceptualised focusing the justification of reusability of polysulfone, once phase-inversion has done.

MATERIALS AND METHODS

Materials

Polysulfone (PSf) pellet (Udel P-3500, Solvey Advanced Polymers, USA), Non-Woven polyester fabric (Filtration Sciences Corp., USA), N,N dimethyl formamide (Merck, India), Sodium lauryl sulphate (SLS, SD fine chemicals, India) were used for the preparation of membranes. Polyethylene Oxide (Mw 200kDa) (Sigma-Aldrich) was used as markers for the characterization of membranes in terms of separation abilities. Bovine serum albumin (BSA) (Mw 66kDa) (Sigma-Aldrich, USA) was used to study the separation performances of the membrane. Milli-Q water was used in the experiment.

---

[*] Address correspondence to this author at the Reverse Osmosis Division CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific & Industrial Research (CSIR), G. B. Marg, Bhavnagar- 364 002, (Gujarat), INDIA; Tel: 91-0278-2567760-7610; Fax: 91-0278-2567762; E-mail: bhattacharyaamit1@rediffmail.com

E-ISSN: 2410-1869/15

Preparation of Polysulfone (PS) Membrane

Polysulfone (PS) solution (15% w/w) in DMF was prepared through dissolution in heating under stirring condition over a period of 3h until the solution become homogenous. Then the solution was brought to RT (27°C).

The milli-Q water (with and without adding sodium lauryl sulfate) was added dropwise in prepared PSf solution under stirring condition. The concentration of sodium lauryl sulfate was kept at 2.1g/ l. The PS was solidified into non-solvent (water) in the mentioned two systems. The PS collected from the two systems was designated as PS-I-w and PS-I-s from water and SLS-water system. PS-I-w and PS-I-s both (15% w/w in DMF) were taken into the DMF solutions as mentioned before. The milli-Q water (with and without adding sodium lauryl sulfate) again poured drop-wise and solidified into water and SLS-water respectively. The PS collected from the two systems and designated as PS-II-w and PS-II-s. In similar approach PS-III-w, PS-III-s, PS-IV-w and PS-IV-s were collected from 3rd and 4th stage respectively.

PS membranes were prepared from all the PS samples (PS-0-w (initial), PS-I-w, PS-II-w, PS-III-w, PS-IV-w, PS-0-s (initial), PS-I-s, PS-II-s, PS-III-s, PS-IV-s). PS solutions were taken in DMF solvent and casted on non-woven Polyester fabric fitted on glass plate and then immediately immersed in gelation bath. The solution was cast on the support under controlled conditions of temperature (27°C), relative humidity (37%). PS membranes (w and s-series) were prepared from water and SLS-water system respectively. The whole system is depicted in Scheme **1**.

Analytical Tools

FTIR-ATR (Cary 680, Agilent Technologies), SEM (Leo, 1430UP, Oxford Instruments), Thermal Gravimetric Analyser GA (TG-209 F1 Libra, NETZSCH, Germany), X-ray Diffractometer (PAN alytical Empyrean using Cu K α radiation as monochromator), Contact angle measurements were done by sessile drop method (DSA 100, KRUSS, Germany) were used for the characterization study of Polysulfone asymmetric membranes. Thermal studies are carried out at heating rate 10°C/min in nitrogen atmosphere. The viscosities of PSf solutions were measured by viscometer (DVII+ Pro Brookfield Viscometer, USA) at 29°C using LV-3 spindle and 80rpm speed. UV-Vis absorption spectrophotometer (UV-2700, Shimadzu) was used for BSA concentration measurements.

Permeability Measurements

Water permeability study was carried out using cross-flow filtration system at temperature 30°C and 0.34MPa. The macromolecule (PEO Mw 200kDa) and BSA (66kDa) separation experiments were carried out using cross-flow and dead-end filtration system at 0.34 and 0.17MPa respectively. In cross-flow filtration the membrane area is kept at 0.00152 m^2, where as in dead-end filtration it is kept at 0.00385 m^2). The separation was determined by HPLC-GPC Waters, 2695 module 2414 RI detector) using the following equation

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) x100 \tag{1}$$

Where C_f is the feed and C_p is the permeate concentration

Porosity Measurements

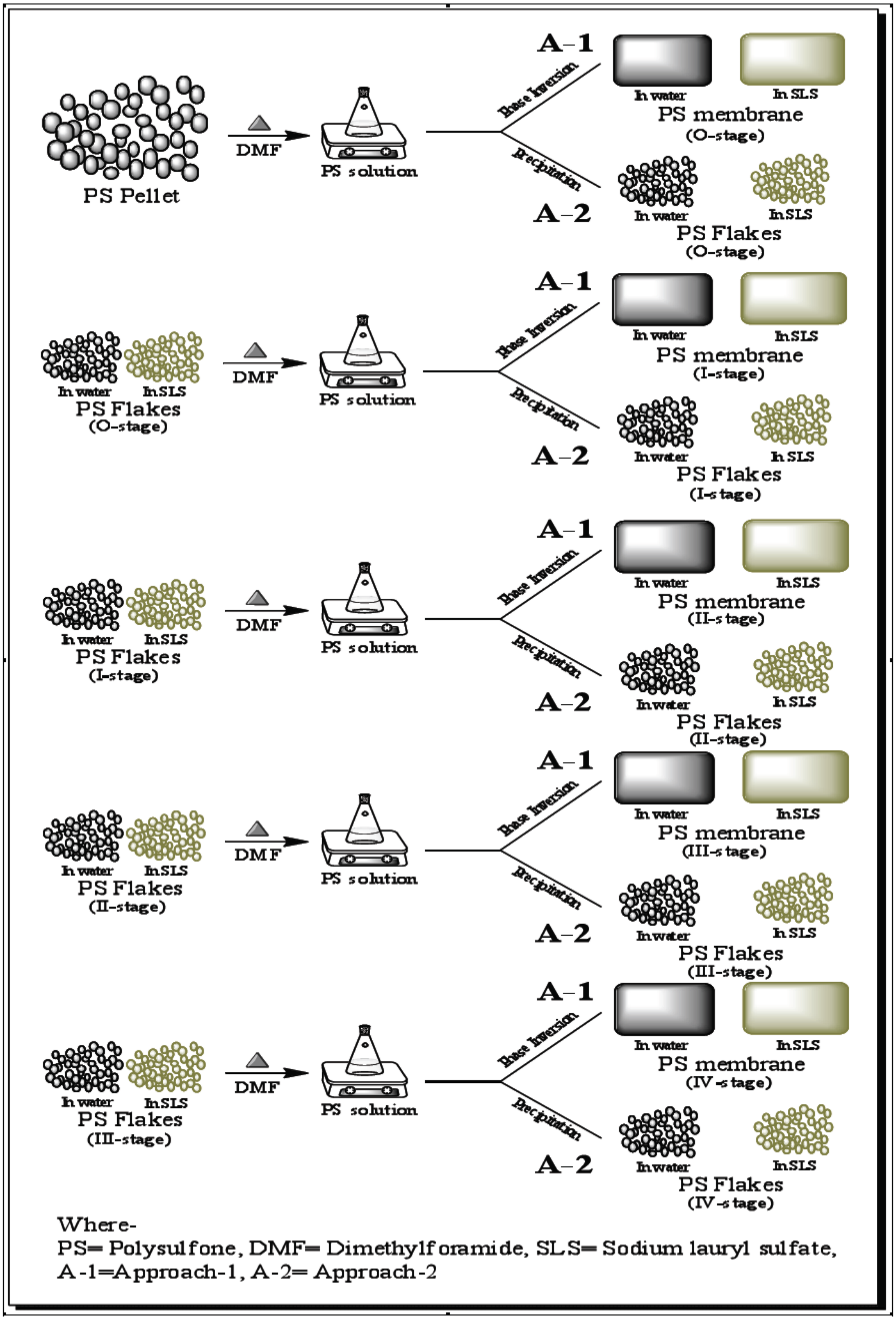
The porosity measurements were done using Polysulfone membranes having area of 3 x 3 cm^2. First membranes were dipped in water for 16h and then they were sorbed with tissue paper and weight was taken. After drying at 70°C weights of the membranes were rechecked. The porosities were determined using the following equation

$$Porosity\ (\%) = \frac{W_{wet} - W_{dry}}{A \times d \times p} \times 100 \tag{2}$$

where W_{wet} and W_{dry} are the weight of the membranes in wet and dry conditions respectively, A (membrane area), d (density of water) and ρ (thickness of the membranes) are used.

RESULTS AND DISCUSSION

Polysulfone membranes are prepared by wet phase separation technique. In the phase separation process there is diffusional exchange between N, N dimethyl formamide (solvent) and water (non-solvent). This results the polymer rich and lean phases and it is better described asymmetric with a top skin layer supported by porous layer. The phase separation results in order to minimize the free energy of the polymer-solvent-nonsolvent mixture [22]. It is one of the kinds of ternary system and diagram is divided into a homogeneous region and an area representing liquid-liquid demixing gap. [23] The diffusion exchange between solvent-non-solvent of polysulfone polymer results the solution to be thermodynamically unstable and demixing occurs [24,



Scheme 1: Schematic diagram of the whole process.

25]. This mechanistic pathway designs the asymmetric nature as well as porosities of the membranes. The membranes from the consecutive stages are prepared following the same mechanistic pathways.

FTIR-ATR studies (Figure **1**) prove the existence of Polysulfone on the non-woven polyester fabric. It shows the strong reflectance benzene ring stretching mode at 1583-1502 cm^{-1}. Aromatic C-H bending, rocking vibrations (871, 850, 831cm^{-1}) are seen in the spectra. The band at 1149 cm^{-1} (symmetric stretching of sulfone (C-SO_2-C)) and at 1319 and 1292 cm^{-1} (asymmetric C-SO_2-C stretching) are observed. Asymmetric C-O stretching frequencies are also seen at 1238 and 1012 cm^{-1}. FTIR spectra of the membranes from consecutive stages are closely observed and there is no difference reflected. The spectra of the membranes from 1st and 4th stage from both the series (water and surfactant-water) are in ensemble. It suggests the functionalities are remaining same in the consecutive stages of membrane preparation.

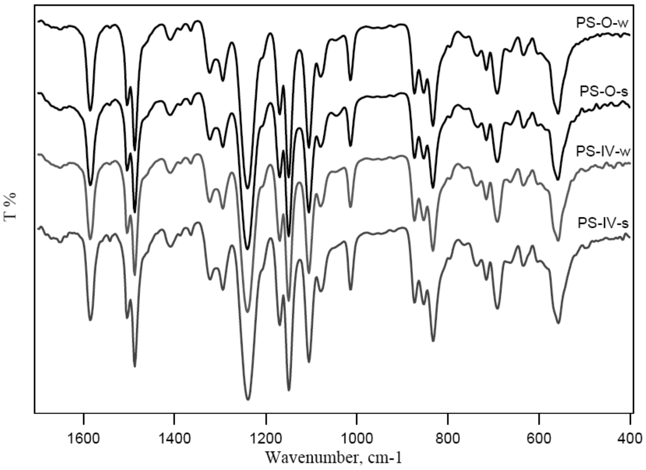


Figure 1: FTIR-ATR spectra of Polysulfone membranes.

Thermal studies of polysulfone membranes from the consecutive phase separation stages are performed. The thermal stabilities of Polysulfone in both the series is excellent up to 350°C, after that the degradation starts and mass change is little above 75% at 500 °C. It is reported that the chain scission at the temperature range 400-500°C at the carbon-sulphur bond, the weakest link in the polysulfone repeat unit between the aromatic ring and sulfone [26]. There are no changes in thermo gravimetric studies of polysulfone membranes of different stages. The thermograms of membranes from 1st and 4th stages of both the series water and surfactant-water series are in ensemble (Figure **2A, B**). It suggests that there is no bond breaking and formation in the consecutive stages of polysulfone membrane preparation.

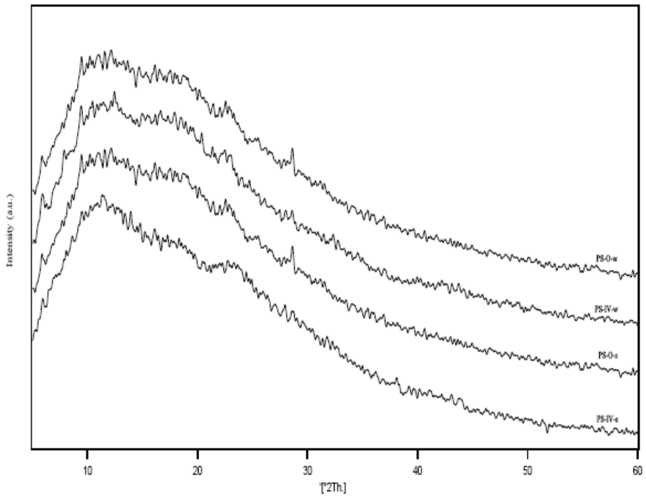


Figure 3: XRD pattern of Polysulfone membranes from PS-w and PS-s series.

The X-ray diffraction studies of polysulfone membranes show that they are in general amorphous. It shows in the Figure **3**. It also suggests that there are no major changes in the amorphous character in the consecutive stages of preparation of membranes. The

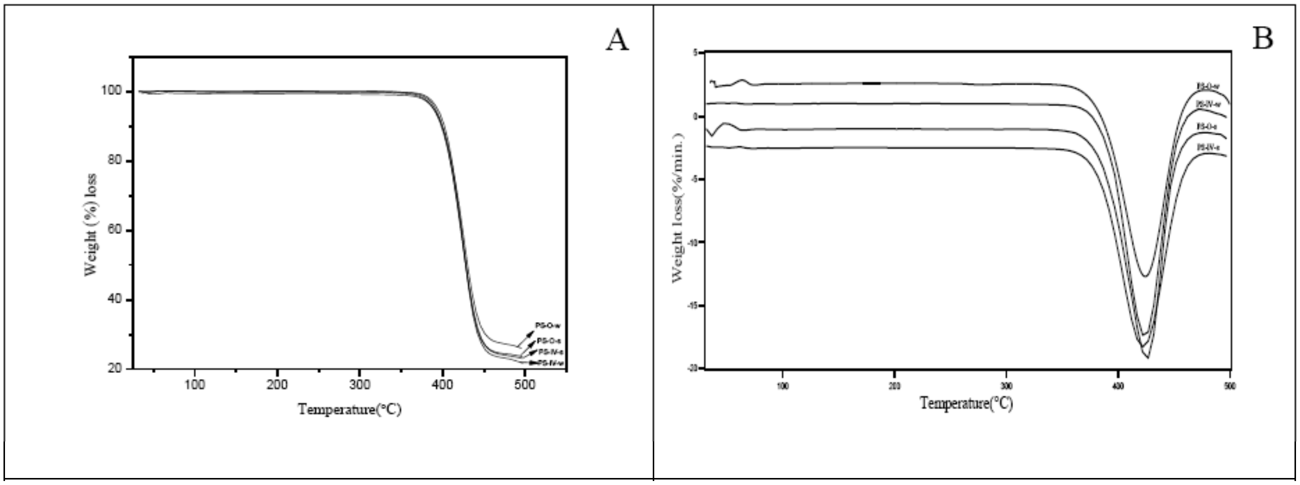


Figure 2: A. Thermogravimetric **B.** Differential Thermal pattern of Polysulfone membranes from PS-w and PS-s series.

phase inversion step couldn't bring any influence in the amorphous character in the polysulfone membrane. But contact angle studies show that contact angles of the membranes for the consecutive stages are in decreasing trend. It suggests that the relative hydrophobic character decreases for the membranes prepared in consecutive stages and Figure **4** shows similar trend for both the series (water and sodium lauryl sulfate-water).

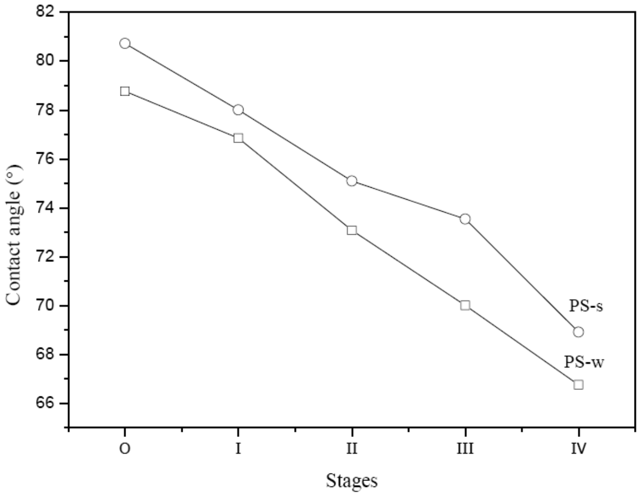


Figure 4: Variation of contact angle of Polysulfone membranes of different stages.

The micrographs of the top surface of membranes from first and fourth stages of polysulfone membranes are depicted in Figure **5**. There is distinct difference with respect to polysulfone membrane matrix. It shows that the porous networks in fourth stages are more compared to initial stage. In the surfactant series the porous network is also well marked.

The property profiles in terms of water permeability show systematic increase with the consecutive stages. The percentage increase in water permeability for different stages compared to initial stage (95.23 LMH (water only) and 264.47 LMH (water- surfactant)) are shown in Figure **6**. It indicates that with stages the asymmetric character of the membranes is increasing. The successive solidification of the phase separated solution leads to a porous, asymmetric structure. Table **1** shows that the decreasing trend in viscosities for polysulfone solutions, prepared from different stages suggest that the diffusion exchange with water is comparatively better. Thus the growth of asymmetric nature is better with the consecutive stages of preparation. This is reflected from porosity studies. The % porosity, obtained from equation 2 shows the increasing trend with the consecutive stages (Figure **7**).

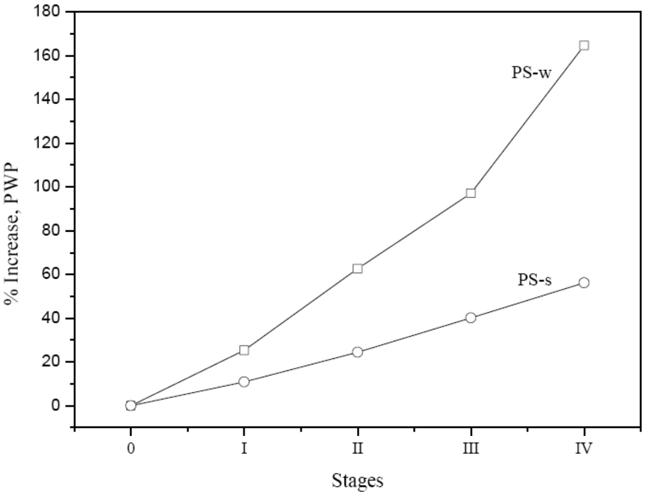


Figure 6: Variation of percentage increase in pure water permeability of the membranes for different stages.

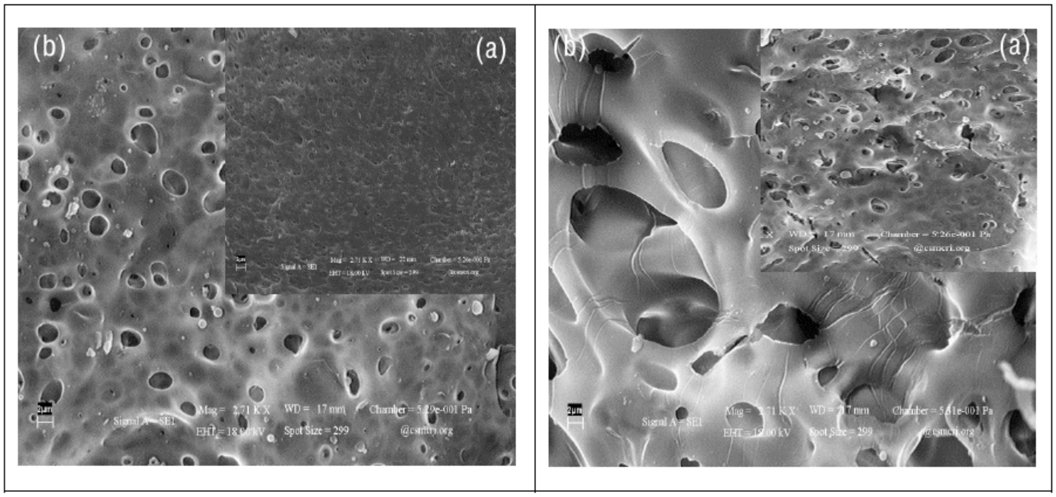


Figure 5: Scanning electron micrograph of Polysulfone samples for Ps-w series (LHS) and Ps-s (RHS), Inset **(a)** is for initial and **(b)** for fourth stage.

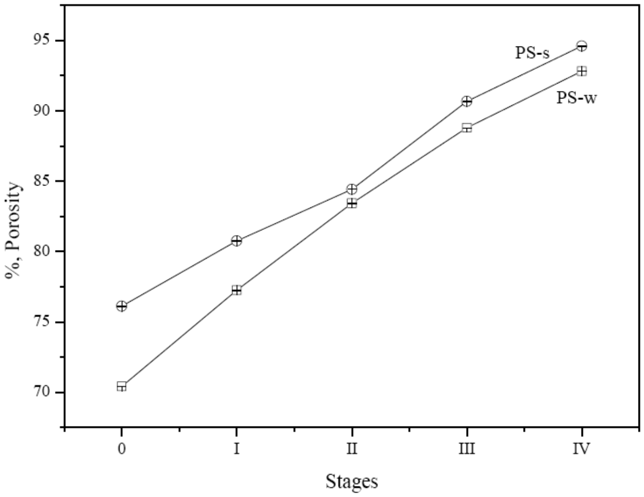


Figure 7: Variation of porosity (%) of membranes (PS-w and PS-s) for different stages.

Table 1: Viscosities of Polysulfone Solutions of Different Stages

Stages	PS-w (cP)	PS-s (cP)
0	302.9	289.2
I	231	218.2
II	201.2	181.4
III	175	157
IV	131.9	111.8

The macromolecule separation abilities of membranes are also co-related with the different stages. The initial stage (termed as ‘0’ stage) shows >90% separation where as for the consecutive stages it is in decreasing trend (Figure **8**). It suggests that porosities are increasing with the consecutive stages. It supports the increase in water permeability as well as porosities with the stages. The trend is similar for the membranes from both the series.

SEPARATION PERFORMANCES OF BSA THROUGH MEMBRANES

The performances of membranes in terms of biomacromolecule Bovine Serum albumin (BSA) separation are performed. The results are shown in Figure **9**. It shows that the separation performances of membranes with the stages are decreasing with the increasing flux data. The extent of separation of the membranes from surfactant-water mixtures is little higher. It may be the effect of surfactant which influences uniform pores. The flux data of the membranes are also increased with the membranes prepared from different stages.

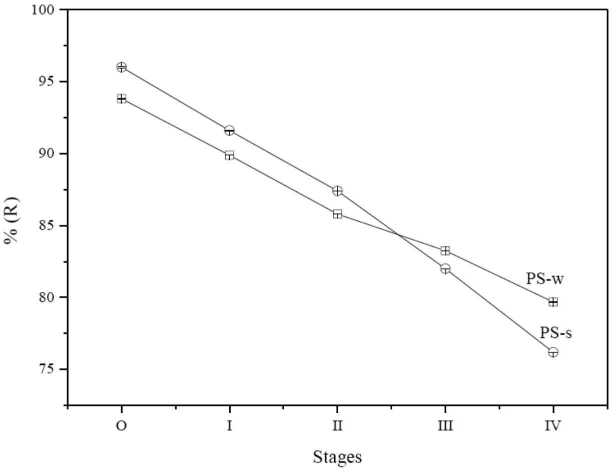


Figure 8: Separation performance of polyethylene oxide (MW-200 kD) through membranes for different stages (Feed concentration 500 mg/L), (pressure 0.34MPa).

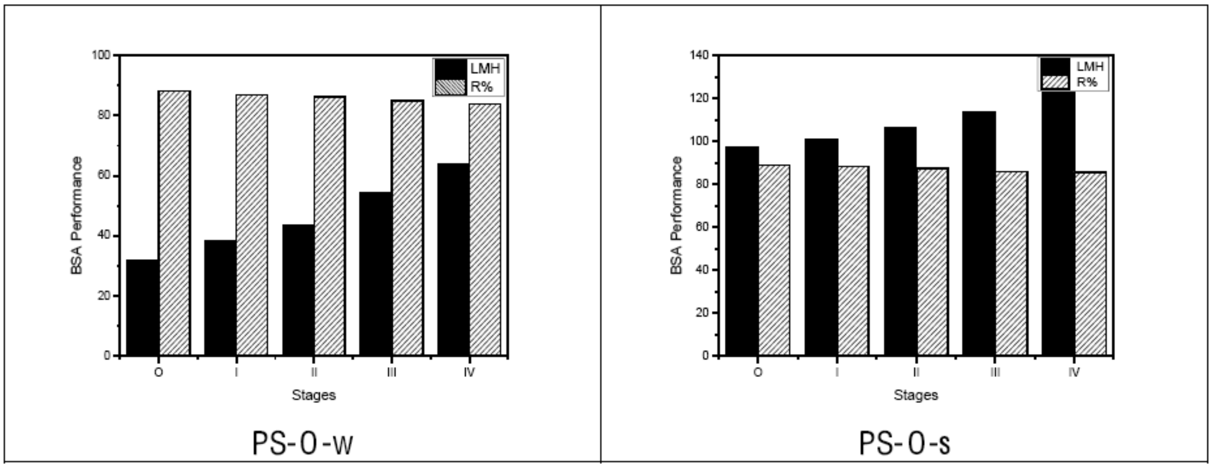


Figure 9: Separation performance of BSA (MW-66 kD) through membranes for different stages (Feed concentration 500 mg/L), (pressure 0.17MPa).

CONCLUSIONS

In this study an improved scheme multi- wet phase separation has been used successfully. The addition of sodium lauryl sulphate into the non-solvent water bath was used to investigate the performances of the membranes. Results clearly demonstrate that membrane performance is quite sensitive to the multi-phase separation with significant membrane property changes expected. There is no functional group formation/ruination in the multi-phase separation of polysulfone. The water permeabilities of the membranes are increased for the membranes result from consecutive stages of preparation. The polysulfone membranes result from multistage phase separation show decreasing trend in separation for polyethylene oxide (PEO, 200kDa) as well as Bovine Serum Albumin (66kDa). Our approach offers a powerful means both for correlating membrane performance with the repetitive phase separation.

ACKNOWLEDGEMENT

Authors are grateful to SERB, Department of Science and Technology, India for research funding.

REFERENCES

[1] Johnson RN. Polysulfones. Plastics, Resins, Rubbers, Fibers In Herman FM, Norman GG Bikales MN editors. Encyclopedia of Polymer Science and Technology, John Wiley & Sons, New York, London, Sydney and Toronto, 1969; 11: 447-63.

[2] Drioli E, Giorno L. Comprehensive Membrane Science and Engineering, Elsevier, The Boulevard Langford Lane, Kidlington OX51GB, United Kingdom, First edition 2010; 1

[3] Albu RM, Avram E, Stoica I, Ioanid E G, Popovici D, Ioan S, Surface Properties and Compatibility with Blood of New Quaternized Polysulfones. J. Biomat. Nanobiotech 2011; 2: 114-24.
http://dx.doi.org/10.4236/jbnb.2011.22015

[4] Hayama M, Yamamoto KI, Kohori F, Sakai K, How polysulfone dialysis membranes containing polyvinylpyrrolidone achieve excellent biocompatibility? J. Membr. Sci. 2004; 234 (1-2): 41-49.
http://dx.doi.org/10.1016/j.memsci.2004.01.020

[5] Zodrow K, Brunet L, Mahendra S, Li D, Zhang A, Li Q, Alvarez PJJ. Polysulfone ultrafiltration membranes impregnated with silver nanoparticles show improved biofouling resistance and virus removal. Water Res. 2009; 43(3): 715-23.
http://dx.doi.org/10.1016/j.watres.2008.11.014

[6] Tweddle TA, Kutowy O, Thayer W L, Sourirajan S. Polysulfone ultrafiltration membranes Ind. Eng. Chem. Prod. Res. Dev 1983; 22 (2): 320-26.
http://dx.doi.org/10.1021/i300010a030

[7] Mehta R, Brahmbhatt H, Saha NK, Bhattacharya A. Removal of substituted phenyl urea pesticides by reverse osmosis membranes: Laboratory scale study for field water application. Desalination 2015; 358: 69-75.
http://dx.doi.org/10.1016/j.desal.2014.12.019

[8] Saxena M, Jain RM. Brahmbhatt H, Mody K, Bhattacharya A. Biosurfactant in membrane separation of atrazine from water. Water, air, soil Pollution 2014; 225(5): 1942-49.
http://dx.doi.org/10.1007/s11270-014-1942-9

[9] Reid BD, Ruiz-Trevino FA, Musselman IH, Balkus KJ, Ferraris JP. Gas Permeability Properties of Polysulfone Membranes Containing the Mesoporous Molecular Sieve MCM-41. Chem. Mater 2001; 13 (7): 2366-73.
http://dx.doi.org/10.1021/cm000931

[10] Julian H, Wenten IG. Polysulfone membranes for CO_2/CH_4 separation: State of the art, IOSR J. Eng. Mar 2012; 2(3): 484-95.
http://dx.doi.org/10.9790/3021-0203484495

[11] Fu YZ, Manthiram A. Synthesis and characterization of sulfonated polysulfone membranes for direct methanol fuel cells. J. Power Sources 2006; 157: 222-25.
http://dx.doi.org/10.1016/j.jpowsour.2005.08.007

[12] Chen MH, Chiao TC, Tseng T. Preparation of sulfonated polysulfone/polysulfone and aminated polysulfone/polysulfone blend membranes. J. Appl. Polym. Sci 1996; 61: 1205-09.
http://dx.doi.org/10.1002/(SICI)1097-4628(19960815)61:7<1205::AID-APP16>3.0.CO;2-W

[13] Gupta S, Yogesh, Singh K, Bhattacharya A. Studies on permeation of Bovine serum albumin (BSA) through photo-modified functionalized asymmetric membrane. Macromol. Sci.: Pure Appl. Chem 2009; 46: 90-96.
http://dx.doi.org/10.1080/10601320802515506

[14] Yogesh, Gupta S, Javiya S, Paul P, Basu S, Singh K, Bhattacharya A. Natural colors through modified synthetic membranes: Separation performances of floral pigments from the extract of rose petals. J. Ind. Chem. Soc.2008; 85:1134-59.

[15] Xie D, Wang, Weng Y, Chu D, Chen R, ECS Transactions, Polysulfone-composed alkaline anion exchange membrane for improved ionic conductivity 2010; 25(13): 3-14.

[16] Liu G, Lu Z, Duncan S, Macromolecules, Porous membranes of Polysulfone-graft-poly (tert-butyl acrylate) and Polysulfone-graft-poly(acrylic acid) : Morphology, pH gated water flow, size selectivity and ion selectivity 2004; 37:4218-26.

[17] Eyal AM, Hazan B, Hazdu K, Edelstein D. Premembranes for porogen derived membranes and thermal decomposition of porogens. J. Appl. Polym. Sci 1992; 45(6): 1065-74.
http://dx.doi.org/10.1002/app.1992.070450616

[18] Lopatin G, Yen LY. Microporous membranes of ultrahigh molecular weight polyethylene. US 4778601A 1950.

[19] Stanley LR, John DA. Process of producing porous materials US 2,504,208A 1950.

[20] Dermody WF, Meltzer TH, Method of producing a microporous polymeric resin. US3062760A 1962.

[21] Sivaraman KM, Kellenberger C, Pané S, Ergeneman O, Lühmann T, Luechinger NA, Hall H, Stark WJ, Nelson BJ. Porous polysulfone coatings for enhanced drug delivery. Biomed. Microdevices 2012; 14(3): 603-12.
http://dx.doi.org/10.1007/s10544-012-9639-6

[22] Di Luccio M, Nobrega R, Borges C P (2000) Microporous anisotropic phase inversion membranes from bisphenol-A polycarbonate: study of a ternary system. Polymer 41(11): 4309-4315.
http://dx.doi.org/10.1016/S0032-3861(99)00653-9

[23] Shimizu H, Kawakami H, Nagaoka S, Polym. Adv. Tech., Membrane formation mechanism and permeation properties of a novel porous polyimide membrane 2002; 13: 370-380.

[24] Zhao W, Su Y, Li C, Shi Q, Ning X, Jiang Z. Fabrication of antifouling polyethersulfone ultrafiltration membranes using Pluronic F127 as both surface modifier and pore-forming agent. J. Membr. Sci 2008; 318: 405-412.
http://dx.doi.org/10.1016/j.memsci.2008.03.013

[25] Sharma S, Dhandhala N, Bhattacharya A, Studies on the effects of salt and surfactant in wet phase separation of Polysulfone - Macromol. Sci.: Pure Appl. Chem 2012; A 49(11): 918-25.

[26] Pielichowski K, Njuguna J. Thermal Degradation of Polymeric Materials, Shawbury, Rapra Technology Limited, Crewe UK, 2005: 120.

Received on 02-03-2015 Accepted on 18-03-2015 Published on 15-05-2015

http://dx.doi.org/10.15379/2410-1869.2015.02.01.7