

Special Issue: Microfiltration and Ultrafiltration
Membrane Science and Technology

Guest Editors: Prof. Isabel C. Escobar (University of Toledo) and
Prof. Bart Van der Bruggen (University of Leuven)

EDITORIAL

Microfiltration and Ultrafiltration Membrane Science and Technology

I. C. Escobar and B. Van der Bruggen, *J. Appl. Polym. Sci.* 2015,
DOI: 10.1002/app.42002

REVIEWS

Nanoporous membranes generated from self-assembled block polymer precursors: *Quo Vadis?*

Y. Zhang, J. L. Sargent, B. W. Boudouris and W. A. Phillip, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41683

Making polymeric membranes anti-fouling via "grafting from" polymerization of zwitterions

Q. Li, J. Imbrogno, G. Belfort and X.-L. Wang, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41781

Fouling control on MF/ UF membranes: Effect of morphology, hydrophilicity and charge

R. Kumar and A. F. Ismail, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.42042

EMERGING MATERIALS AND FABRICATION

Preparation of a poly(phthalazine ether sulfone ketone) membrane with propanedioic acid as an additive and the prediction of its structure

P. Qin, A. Liu and C. Chen, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41621

Preparation and characterization of MOF-PES ultrafiltration membranes

L. Zhai, G. Li, Y. Xu, M. Xiao, S. Wang and Y. Meng, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41663

Tailoring of structures and permeation properties of asymmetric nanocomposite cellulose acetate/silver membranes

A. S. Figueiredo, M. G. Sánchez-Loredo, A. Mauricio, M. F. C. Pereira, M. Minhalma and M. N. de Pinho, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41796

LOW-FOULING POLYMERS

Low fouling polysulfone ultrafiltration membrane via click chemistry

Y. Xie, R. Tayouo and S. P. Nunes, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41549

Elucidating membrane surface properties for preventing fouling of bioreactor membranes by surfactin

N. Behary, D. Lecouturier, A. Perwuelz and P. Dhulster, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41622

PVC and PES-g-PEGMA blend membranes with improved ultrafiltration performance and fouling resistance

S. Jiang, J. Wang, J. Wu and Y. Chen, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41726

Improved antifouling properties of TiO₂/PVDF nanocomposite membranes in UV coupled ultrafiltration

M. T. Moghadam, G. Lesage, T. Mohammadi, J.-P. Mericq, J. Mendret, M. Heran, C. Faur, S. Brosillon, M. Hemmati and F. Naeimpoor, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41731

Development of functionalized doped carbon nanotube/polysulfone nanofiltration membranes for fouling control

P. Xie, Y. Li and J. Qiu, *J. Appl. Polym. Sci.* 2015, DOI: 10.1002/app.41835



**Special Issue: Microfiltration and Ultrafiltration
Membrane Science and Technology**

Guest Editors: Prof. Isabel C. Escobar (University of Toledo) and
Prof. Bart Van der Bruggen (University of Leuven)

SURFACE MODIFICATION OF POLYMER MEMBRANES

Highly chlorine and oily fouling tolerant membrane surface modifications by *in situ* polymerization of dopamine and poly(ethylene glycol) diacrylate for water treatment

K. Yokwana, N. Gumbi, F. Adams, S. Mhlanga, E. Nxumalo and B. Mamba, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41661](https://doi.org/10.1002/app.41661)

Fouling control through the hydrophilic surface modification of poly(vinylidene fluoride) membranes

H. Jang, D.-H. Song, I.-C. Kim, and Y.-N. Kwon, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41712](https://doi.org/10.1002/app.41712)

Hydroxyl functionalized PVDF-TiO₂ ultrafiltration membrane and its antifouling properties

Y. H. Teow, A. A. Latif, J. K. Lim, H. P. Ngang, L. Y. Susan and B. S. Ooi, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41844](https://doi.org/10.1002/app.41844)

Enhancing the antifouling properties of polysulfone ultrafiltration membranes by the grafting of poly(ethylene glycol) derivatives via surface amidation reactions

H. Yu, Y. Cao, G. Kang, Z. Liu, W. Kuang, J. Liu and M. Zhou, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41870](https://doi.org/10.1002/app.41870)

SEPARATION APPLICATIONS

Experiment and simulation of the simultaneous removal of organic and inorganic contaminants by micellar enhanced ultrafiltration with mixed micelles

A. D. Vibhandik, S. Pawar and K. V. Marathe, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41435](https://doi.org/10.1002/app.41435)

Polymeric membrane modification using SPEEK and bentonite for ultrafiltration of dairy wastewater

A. Pagidi, Y. Lukka Thuyavan, G. Arthanareeswaran, A. F. Ismail, J. Jaafar and D. Paul, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41651](https://doi.org/10.1002/app.41651)

Forensic analysis of degraded polypropylene hollow fibers utilized in microfiltration

X. Lu, P. Shah, S. Maruf, S. Ortiz, T. Hoffard and J. Pellegrino, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41553](https://doi.org/10.1002/app.41553)

A surface-renewal model for constant flux cross-flow microfiltration

S. Jiang and S. G. Chatterjee, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41778](https://doi.org/10.1002/app.41778)

Ultrafiltration of aquatic humic substances through magnetically responsive polysulfone membranes

N. A. Azmi, Q. H. Ng and S. C. Low, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41874](https://doi.org/10.1002/app.41874)

BIOSEPARATIONS APPLICATIONS

Analysis of the effects of electrostatic interactions on protein transport through zwitterionic ultrafiltration membranes using protein charge ladders

M. Hadidi and A. L. Zydney, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41540](https://doi.org/10.1002/app.41540)

Modification of microfiltration membranes by hydrogel impregnation for pDNA purification

P. H. Castilho, T. R. Correia, M. T. Pessoa de Amorim, I. C. Escobar, J. A. Queiroz, I. J. Correia and A. M. Morão, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41610](https://doi.org/10.1002/app.41610)

Hemodialysis membrane surface chemistry as a barrier to lipopolysaccharide transfer

B. Madsen, D. W. Britt, C.-H. Ho, M. Henrie, C. Ford, E. Stroup, B. Maltby, D. Olmstead and M. Andersen, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41550](https://doi.org/10.1002/app.41550)

Membrane adsorbers comprising grafted glycopolymers for targeted lectin binding

H. C. S. Chenette and S. M. Husson, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.41437](https://doi.org/10.1002/app.41437)



Polymeric membrane modification using SPEEK and bentonite for ultrafiltration of dairy wastewater

Aruna Pagidi,¹ Y. Lukka Thuyavan,¹ G. Arthanareeswaran,¹ A. F. Ismail,² Juhana Jaafar,² Diby Paul³

¹Membrane Research Laboratory, Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli 620015, India

²Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

³Department of Environmental Engineering, Konkuk University, Seoul, Republic of Korea

Correspondence to: G. Arthanareeswaran (E-mail: arthanaree10@yahoo.com)

ABSTRACT: The different polymeric membrane materials were fabricated using modifiers such as sulfonated poly(ether ether ketone) (SPEEK) and bentonite for effective ultrafiltration of proteins from dairy effluent. Polyvinylidene fluoride (PVDF), polyethersulfone (PES), polyetherimide (PEI), polyamide-imides (PAI), cellulose acetate (CA), and polyphenylsulfone (PPSU) were selected for modification. Membrane morphology and functional group analysis were characterized using scanning electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FTIR). Pure water permeability (64.66×10^{-9} m/s kPa) was higher for the PES/SPEEK/bentonite membrane when compared with other polymeric membranes. Contact angle (54.05°) value was lower for CA/SPEEK/bentonite membranes and which indicates that hydrophilicity has got enhanced. The membrane performance was tested using model dairy wastewater by ultrafiltration under longer run mode. Further it was evaluated using resistance in series model. This study infers that modification of membranes using charged SPEEK polymer and nanofiller as bentonite can be used to alleviate the fouling in the treatment of dairy wastewater. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41651.

KEYWORDS: bentonite; model dairy effluent; polymeric membranes; resistance in series model; SPEEK

Received 31 July 2014; accepted 20 October 2014

DOI: 10.1002/app.41651

INTRODUCTION

Dairy industry discharges large volume of wastewater, which is mainly of carbohydrates, proteins, fats, and other nutrients. These components enhance the growth of algal blooms and other microbial population thereby, which leading to deterioration of water quality.^{1,2} Therefore, the treatment of dairy wastewater is a major prerequisite to maintain the water quality. To meet out the regulations of environmental agencies for the reclamation of dairy effluent; membrane technology is vastly employed at present.³ Ultrafiltration is used widely in various stages in dairy industries for the fractionation of valuable products such as cheese and whey proteins etc.^{4,5} However, major limitation of aforementioned membrane process is fouling. As it results in reduction of both flux and membrane performance.^{6,7}

In last few decades, studies on membrane modification methods are focused to minimize fouling. SPEEK has the characteristics of high hydrophilicity and good conductivity. Bowen *et al.*⁸ observed that water permeability and salt retention was improved with the addition of SPEEK as modifier on synthesis

of polyetherimide (PEI) membrane. Moreover, Arthanareeswaran *et al.*^{9,10} confirmed that SPEEK plays a significant role in alteration of morphology of membrane by reducing the possibility of formation of macrovoids on cellulose acetate (CA)/SPEEK and CA/PSf/SPEEK membrane. This in turn increases porosity on the membrane surface and that enhances the water permeability. Lately, various hydrophilic nanofillers have gained more consideration in the synthesis of mixed matrix membranes (MMMs). The main role of incorporation of nanofillers was to an interaction between both bulk (polymer) and dispersed (inorganic particle) phase in polymer matrix. The improved interaction largely improves flux and mitigates fouling, which are the desired properties for an ideal membrane.¹¹

Studies on synthesis of ultrafiltration membrane with clay material are limited. Hence, in this study developing cheap and effective nanofiller to improve the membrane performance is attempted. Nanoclays such as halloysite,¹² montmorillonite,¹³ kaolinite,¹⁴ cloisite,¹⁵ etc. are used in the development of MMMs as it exhibits a unique characteristics of layered structures. It

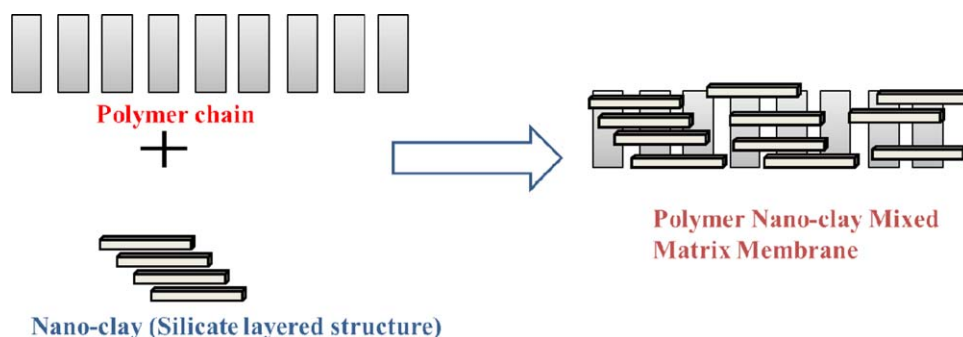


Figure 1. Schematic illustration of polymer-nanoclay mixed matrix membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

includes the (i) higher hydrophilicity, (ii) higher surface area and aspect ratio, (iii) good compatibility with polymer material, and (iv) requires a low amount of loading to attain the desired properties.¹⁶ Inorganic clay particles act as a host for the polymer to form a hybrid polymer-clay mixed matrix membranes (PCMMs). In these PCMMs, polymer materials can effectively bind with sheets layered clay structures and it results in improvement of desired property such as hydrophilicity, mechanical, and thermal stability.¹⁷ The description of clay on polymer matrix is illustrated in Figure 1. Recently, nanoclays and its modification have attracted more researchers for the modification of membrane to arrive the aforementioned desired properties. Chen *et al.*¹⁸ observed that the antifouling and biofouling properties were improved significantly in polyethersulfone (PES) membrane with the addition of Ag immobilized chitosan grafted halloysite nanocomposites. Wang *et al.*¹⁹ studied the adsorption of BSA on modified PES membrane with halloysite grafted 2-methacryloyloxyethyl phosphorylcholine. The hybrid membrane showed better antifouling properties with better flux rate. The major advantage of such nanoclay material over other material was cheaper and it offers good compatibility with polymer for further modification.²⁰

Literature shows that only few studies have used the bentonite as nanofillers in ultrafiltration membrane fabrication. Bentonite clay belongs to the smectite group, which has an arrangement of aluminium-phylosilicate ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) with two layers

of tetrahedral silica sheets and an octahedral alumina sheet.²¹ Extensively used in the ion exchange process and as an adsorbent material. It is an impure ore of clay, which constitutes mainly of montmorillonite.²² Anadão *et al.*²³ observed that membrane hydrophilicity was improved while with the blending of montmorillonite on polysulfone membrane. Moreover, functionalized bentonite-SPEEK membrane favored fuel cell application due to its good conductivity.²⁴ The above properties of bentonite is expected to improve membrane performance.

In this study, six different polymers such as polyvinylidene fluoride (PVDF), PES, PEI, polyamide-imides (PAI), CA, and polyphenylsulfone (PPSU) with as SPEEK and bentonite modifiers are used for treatment of model dairy effluent. Hydrophilicity, membrane morphology and surface functionality studies for the membranes are studied. Filtration performance of membranes is evaluated by water permeability and treatment of model dairy effluent.

EXPERIMENTAL

Materials

Table I presents the detail of chemicals used in this study.

Synthesis of Sulfonated Poly Ether Ether Ketone (SPEEK)

Sulfonation reactions are conducted by using sulfuric acid as the sulfonating agent and method was suggested by Jaafar

Table I. List of Materials

| Chemicals | Molecular weight (Mw) (Dalton) | Suppliers |
|---------------------------------------------------------|--------------------------------|-----------------------------------------|
| Polyvinylidene fluoride (Kynar® 740) (PVDF) | 156,000 | M/s. Arkema, Philadelphia |
| Polyethersulfone (PES) (Veradale 3000P) | - | M/s. Solvay process India |
| Polyetherimide (PEI) | Repeating unit -529 | M/s. Sigma Aldrich |
| Polyamide-imides (PAI) Torlon® | - | M/s. Solvay Advanced Polymers, L.L.C. |
| Cellulose acetate (CA) | 115,000 | M/s. Mysore Acetate and Chemical, India |
| Polyphenylsulfone (PPSU) | 53,000-59,000 | M/s. Sigma Aldrich |
| 1-Methyl-2-pyrrolidone (N-methyl-2-pyrrolidone, NMP) | | M/s. Merck chemical, India limited |
| Sulfuric acid | | M/s. Merck chemical, India limited |
| Poly ether ether ketone (PEEK) | | M/s. Vitrex |
| Bentonite | | M/s. Sigma Aldrich |
| Sodium dodecyl sulfate (SDS) | | M/s. Merck chemical, India limited |

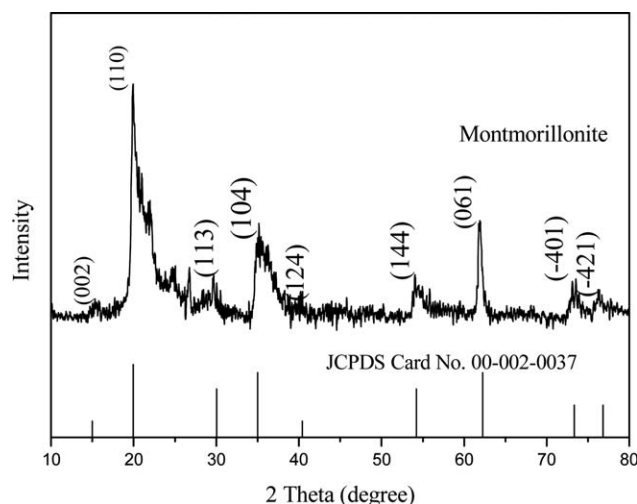


Figure 2. XRD pattern of bentonite.

*et al.*²⁵ A mixture of 50 g of poly(ether ether ketone) (PEEK) and 1000 mL of sulfuric acid was magnetically stirred at room temperature for 1 h. Then, the solution is continuously stirred at 65°C for 3 h. The sulfonated polymer is recovered by precipitating the acid polymer solution into a large excess of ice water. The obtained SPEEK polymer is filtrated and thoroughly washed with deionized water until the pH falls in the range of 6–7. Finally, the sulfonated PEEK was dried in the drying oven at 80°C for 24 h. The resultant SPEEK polymer was then characterized using Hydrogen-nuclear magnetic resonance (^1H NMR) spectroscopy to obtain the degree of sulfonation (DS). The DS is found to be 77%. It is observed that the contact angle value of SPEEK at DS of 77% is 69.02 ± 1.06 . The proton conductivity test is conducted using the impedance spectroscopy over a frequency range of 1– 10^7 Hz with 50–500 mV oscillating voltage; model Solartron 1260 Gain Phase Analyzer, AMETEK, UK. The proton conductivity value of the SPEEK is found to be $7.57 \times 10^{-3} \text{ S cm}^{-1}$.

Table II. Composition of Dope Solution and Hydrophilicity Characteristics

| Membrane type | Polymer composition | Modifiers | | Contact angle value | Pore radius (nm) | Water permeability (10^{-9} m/s kPa) |
|---------------|---------------------|-----------|-----------|---------------------|------------------|--------------------------------------------------|
| | | SPEEK | Bentonite | | | |
| Z1 | PVDF (99%) | (1.0%) | - | 68.36 ± 3.2 | 8.86 | 17.36 |
| Z2 | PVDF (98.5%) | (1.0%) | (0.5%) | 65.12 ± 1.8 | 29.28 | 33.33 |
| Z3 | PEI (99%) | (1.0%) | - | 69.60 ± 2.9 | 9.59 | 13.19 |
| Z4 | PEI (98.5%) | (1.0%) | (0.5%) | 67.23 ± 3.8 | 21.6 | 25.08 |
| Z5 | PES (99%) | (1.0%) | - | 64.95 ± 2.5 | 34.5 | 33.33 |
| Z6 | PES (98.5%) | (1.0%) | (0.5%) | 61.20 ± 1.6 | 48.6 | 66.66 |
| Z7 | PAI (99%) | (1.0%) | - | 73.41 ± 2.8 | 6.89 | 10.41 |
| Z8 | PAI (98.5%) | (1.0%) | (0.5%) | 70.22 ± 3.8 | 17.71 | 22.22 |
| Z9 | PPSU (99%) | (1.0%) | - | 74.90 ± 1.5 | 0.95 | 2.08 |
| Z10 | PPSU (98.5%) | (1.0%) | (0.5%) | 73.11 ± 2.5 | 2.03 | 4.86 |
| Z11 | CA (99%) | (1.0%) | - | 60.80 ± 2.2 | 23.5 | 26.39 |
| Z12 | CA (98.5%) | (1.0%) | (0.5%) | 54.05 ± 3.3 | 36.7 | 50.00 |

Membrane Preparation

In this study, PVDF, PES, PEI, PAI, CA, and PPSU are used as base polymers. Membranes were synthesized using SPEEK and bentonite as modifier and NMP as solvent under wet phase inversion technique. The detailed composition of each prepared membranes and its labeling is provided in Table II. Primarily, the polymers are dried in an hot air oven kept at 80°C for 8 h. Casting dope solution is prepared by dissolving SPEEK in NMP for 3 h. It is then followed with the addition of dried polymer to dope solution. Subsequently, the solution is mixed at the condition of 60°C for 12 h. Homogeneous solution is then allowed for deaeration to remove the air bubbles. Consequently, dope solution is poured and cast on to a glass plate using doctor blade to a desired thickness of 150 μm . The resultant thin film from the casting solution was allowed for a time period of 30 s. Then, glass plate is immersed in a deionized (DI) water bath at a temperature of 10°C for 24 h. Finally, the prepared membrane is stored in 0.1% formalin solution to prevent the microbial growth. Whereas in case of bentonite modified MMMs, bentonite is primarily dissolved in NMP solvent for 2 h and followed by sonication for 1 h. Next, SPEEK is added onto the bentonite solution and the aforementioned procedure is followed for the preparation of membranes. Prior to casting the dope solution, solution was sonicated again and left undisturbed for 6 h.

Dairy Effluent

Dairy effluent is synthesized as suggested by Luo *et al.*²⁶ and the milk used in this study is procured from M/s. Sakthi milk, Tamil Nadu, India. The milk is skimmed using a cooling centrifuge (M/s Remi C-24BL) kept at 10,000 rpm for 4°C and 20 min. Feed solution is then prepared by diluting the skim milk to a ratio of 1 : 9 and then, it is used for the filtration experiments.

Characterization of Bentonite

The morphology and elemental composition of bentonite sample is analyzed by scanning electron microscopy (SEM VEGA 3 TESCAN) coupled Energy Dispersive X-ray detector (Bruker).

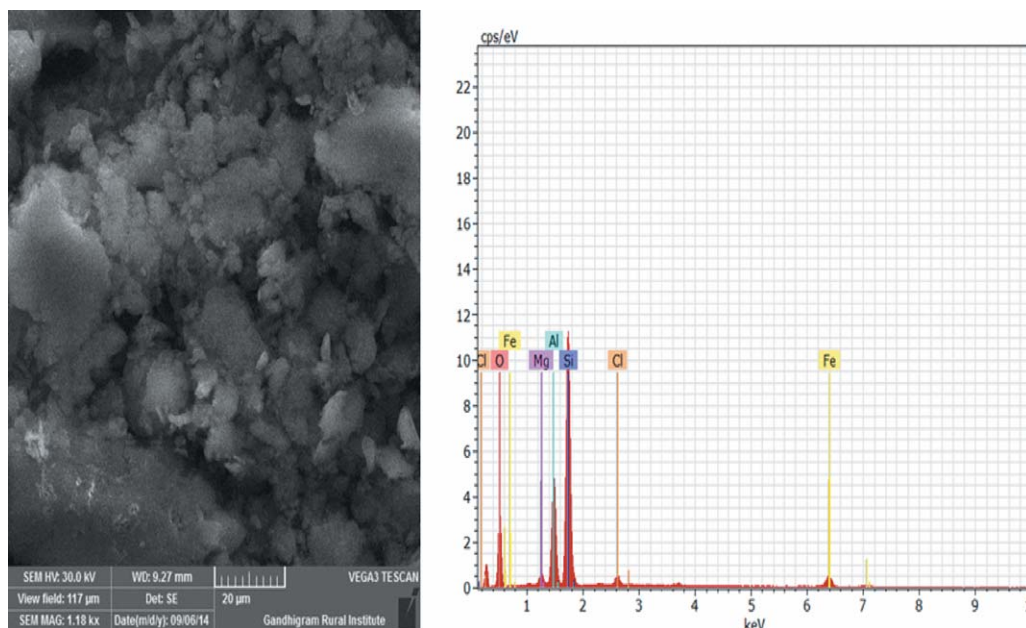


Figure 3. SEM micrographs and EDX analysis of bentonite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The crystalline size and structure of bentonite is studied using X-ray diffractometer (Model Rigaku Ultima III) equipped with monochromator Cu K α radiation ($\lambda = 1.541 \text{ \AA}$) for 2θ value ranging from 10° to 80° under 40 kV.

Characterization of Modified Membranes

Sessile drop method is used to determine the wettability of membrane using goniometer (model 250-F1 Rame Hart Instruments, Succasunna, NJ). The reported values are collected from the five various regions on the membrane surface. Membrane chemical surface functionality is studied using attenuated-total-reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Thermo Scientific Nicolet iS5 FTIR spectrometer). The spectra for all the dried membranes are observed from the range between 4000 to 550 cm^{-1} wavelength. Prior to SEM analysis, membranes were dried and immersed in liquid nitrogen to obtain frozen state. Then, membrane samples are initially coated with gold ion and scanning is done at a voltage of 15 kV. Both top surface and cross-section morphology of membranes were visualized using SEM (JEOL JSM -5600 SEM).

Water Permeability

Dead-end stirred cell filtration unit (Ultrafiltration cell-S76-400-Model, Spectrum, USA) was used to assess the performance of membranes. The performance study includes both pure water permeability and synthetic dairy effluent filtration analysis. Synthesized membranes are subjected to compaction in filtration module at a transmembrane pressure of 400 kPa until it reaches constant flux value. The water flux corresponding to each membrane is calculated by the following eq. (1).

$$J_w = \frac{V}{A \cdot \Delta t} \quad (1)$$

where $V(L)$ is the volume of filtrate, $A \text{ (m}^2\text{)}$ is the membrane effective cross-sectional area and $\Delta t \text{ (h)}$ is the sampling time. The membrane permeability (L_p) is calculated from the pure

water flux value and applied transmembrane pressure (ΔP) using below eq. (2).

$$L_w = \frac{J_w}{\Delta p} \quad (2)$$

The average pore radius (r_m) of membranes were calculated using the below modified Guerout-Elford Ferry equation.²⁷

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8L_p l \eta}{\varepsilon}} \quad (3)$$

where ε is the porosity, L_p is the pure water permeability (m/Pa s), l is the thickness of membrane (m), and η is the dynamic viscosity of the water (Pa s).

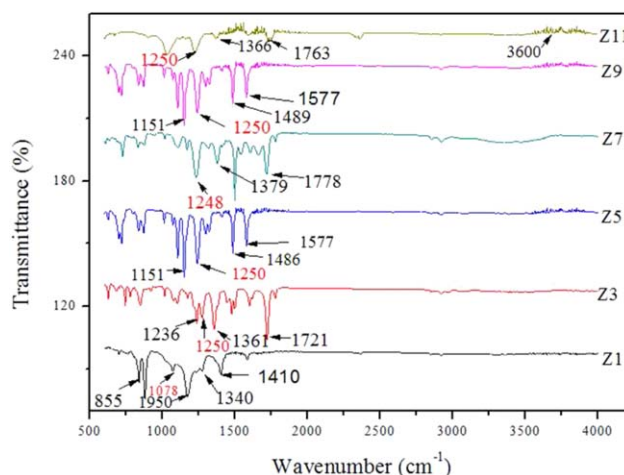


Figure 4. FTIR spectra of SPEEK modified various polymeric membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

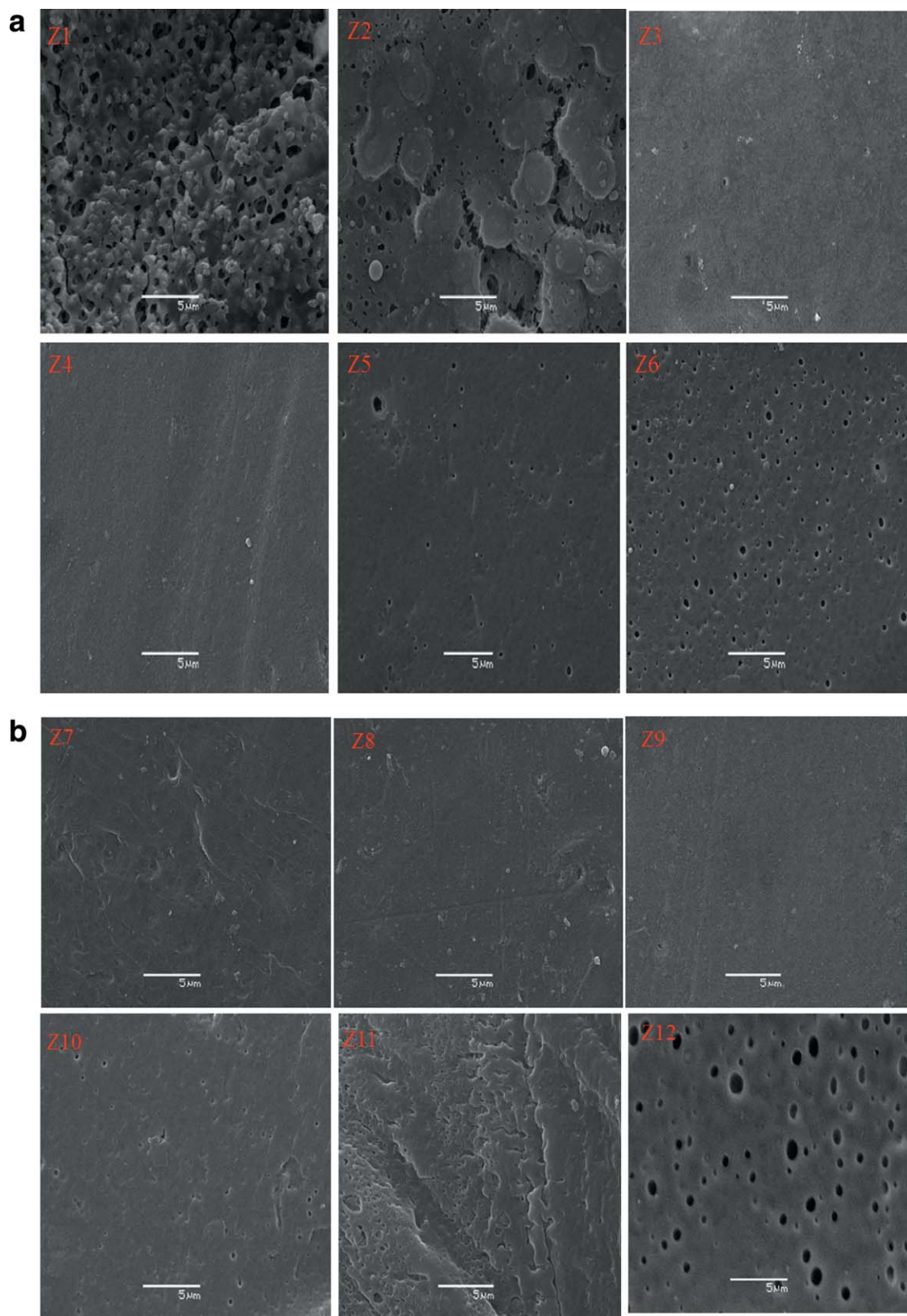


Figure 5. (a) Top surface images of membranes (Z1–Z6). (b) Top surface images of membranes (Z7–Z12). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

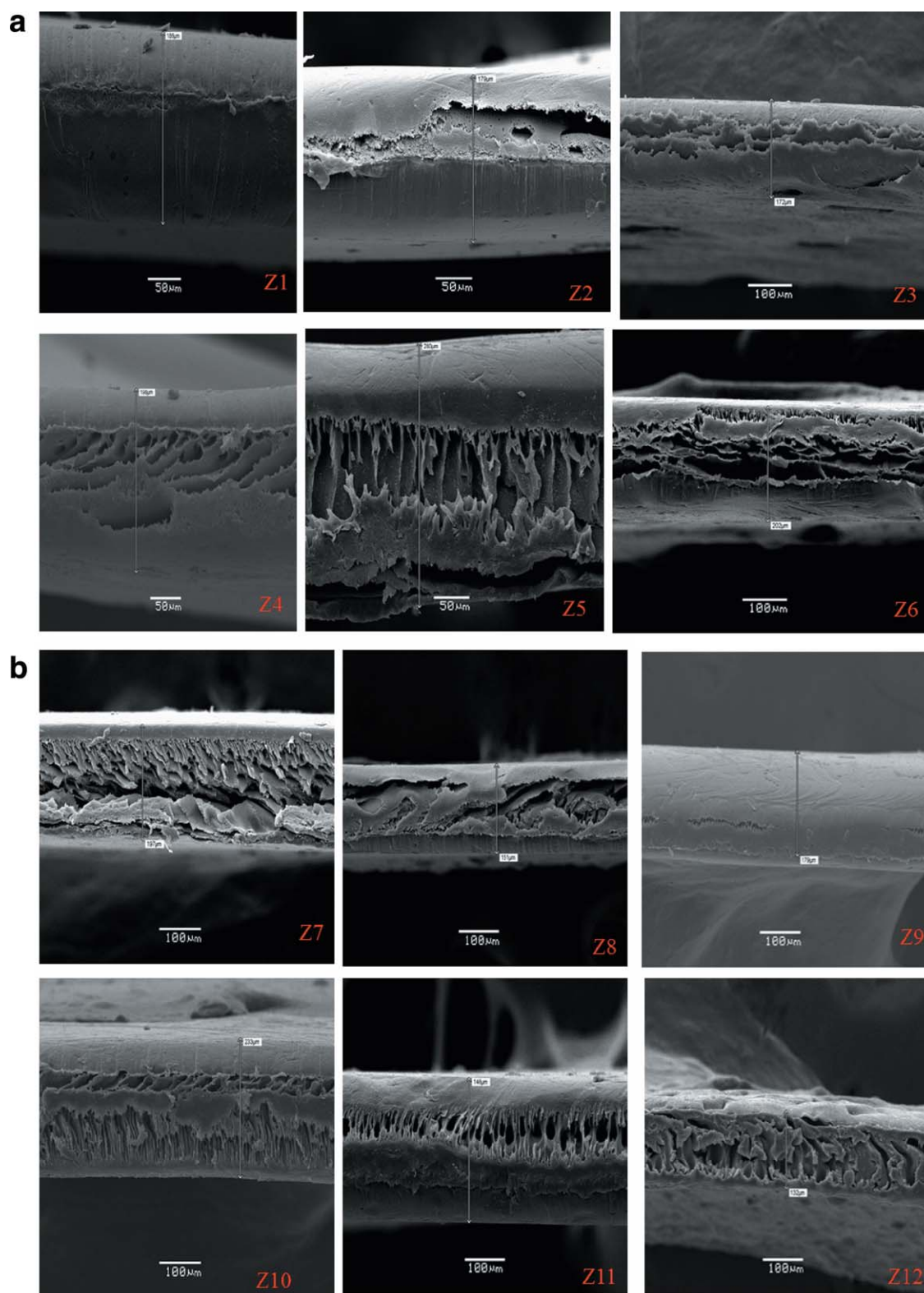


Figure 6. (a) Cross-section images of membranes (Z1–Z6). (b) Cross-section images of membranes (Z7–Z12). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. FTIR Peak Analysis of SPEEK Modified Polymeric Membranes

| Base polymeric membrane | Wave number | Functional group |
|-------------------------------------------|---------------|----------------------------------------------|
| PVDF (Z1) ^{29,30} | 855 | α -Crystal of PVDF |
| | 1078 | Sulfonic acid group |
| | 1950 | CF ₂ bending |
| | 1340 | C–H deformation |
| | 1410 | CF ₂ stretching |
| PEI(Z3) ³¹ | 1236 | Aromatic ether C–O–C |
| | 1250 | Sulfonic acid group |
| | 1361 | C–N stretching |
| | 1721 | Imide carbonyl group |
| PES(Z5) ^{32,33} and PPSU (Z9) | 1151 | Sulfonic acid group |
| | 1250 | Sulfonic acid group |
| | 1486 | C=C stretching |
| | 1950 | Aromatic benzene ring band |
| PAI(Z7) ³⁴ | 1248 | Sulfonic acid group |
| | 1379 | C–N–C stretching |
| | 1778 | Imide transmission bands (C–O stretching) |
| CA(Z11) ³⁵ | 1250 | Sulfonic acid group |
| | 1366 | Acetyl group |
| | 1763 | Acetyl group |
| | 3200– 3600 | O–H bond stretching, |

Filtration Performance of Model Dairy Effluent Using Modified Membranes

The model dairy effluent filtration experiments are carried out under longer run mode. Prior to passing of synthetic dairy effluent, initial pure water flux (J_{wi}) was measured. Subsequently, model dairy effluent is ultrafiltered at a transmembrane pressure of 400 kPa for 150 min and the feed flux (J_v) is sampled at a time interval of 15 min. Again the pure water flux (J_{wf}) is measured to calculate both the fouling and concentration polarization. Then membrane is further cleaned by passing 0.2% sodium dodecyl sulfate (SDS) solution for about 20 min. Finally, the pure water flux is again measured to check the membrane flux recovery. Besides, membranes efficacy is tested again using filtration of dairy effluent by repeating the above-mentioned procedure. The experiments are performed twice and the values are reported. It was also evaluated using resistance in series model by the following eq. (4).

$$J_w = \left[\frac{\Delta P}{\eta(R_m + R_f + R_{cp})} \right] \quad (4)$$

where η is the viscosity of the permeate solution, R_m is the intrinsic membrane resistance, and R_f is the fouling resistance, and R_{cp} is the polarizable layer resistance. Fouling and concentration polarization are the major phenomenon for flux decline in membrane filtration process.²⁸ Fouling adsorption or blockage of

solute particles on membrane pores is generally referred as fouling and its resistance can estimate by using eq. (7). On the other side, concentration polarization is the buildup of solute particle on the membrane surface and its resistance can calculate by substitution of R_f and R_m in eq. (6).

$$R_w = \left[\frac{\Delta P}{\eta J_{wi}} = \frac{1}{\eta L_p} \right] \quad (5)$$

$$R_m + R_f + R_{cp} = \frac{\Delta P - \sigma \Delta \Pi}{\eta J_v} \quad (6)$$

$$R_m + R_f = \frac{\Delta P}{\eta J_{wf}} \quad (7)$$

where σ is the reflection coefficient and $\Delta \Pi$ the osmotic pressure, which is assumed to be negligible. Moreover, total protein is estimated by using Lowry's method in UV-visible spectrophotometer (Spectroquant[®] Pharo 300, Merck India Limited) at 600 nm. Protein rejection was calculated from the concentration of permeate (C_p) and retentate (C_r) using the equation below.

$$\text{Rejection}(\%) = \left(1 - \left(\frac{C_p}{C_r} \right) \right) \times 100 \quad (8)$$

RESULT AND DISCUSSION

Bentonite Characterization

Figure 2 shows a powder X-ray diffraction pattern of received bentonite material. The diffraction lines are exactly matched with montmorillonite (JCPDS card no. 00-002-0037) and their lattice parameters were found to be $a = 5.1900$, $b = 9.0000$, $c = 11.9000$ Å and $\beta = 90.00^\circ$ (by using least square method). Further, the crystalline size of bentonite is estimated as 25.7 using the Debye Scherrer equation followed the most intense plane (110) and given by eq. (9) as:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (9)$$

where K represents the dimensionless shape factor and its value is 0.9, λ the X-ray wavelength, and β is the full width at half maximum intensity of peak corresponding to 2θ . Moreover,

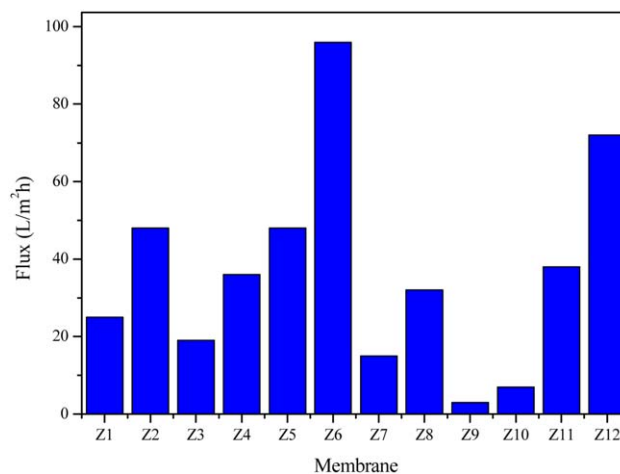


Figure 7. Comparison of pure water flux for SPEEK and SPEEK/bentonite modified membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

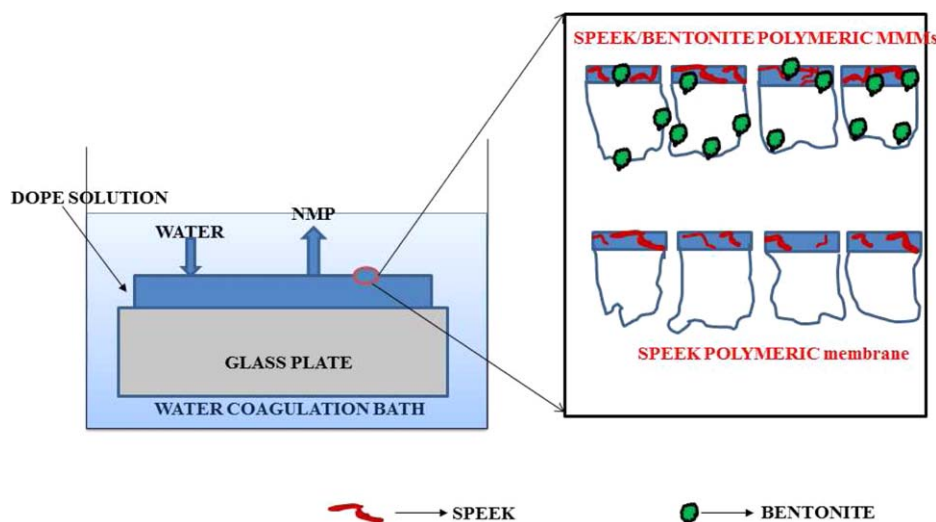


Figure 8. Schematic representation of the role of SPEEK and bentonite on membrane formation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface morphology and elemental composition of received bentonite are illustrated in Figure 3. Here, the particles are aggregate in the forms of flake like structure. In addition EDX spectrum, were confirmed the presence of characteristic montmorillonite elements such as Al, Fe, Si, Mg, and Oxygen.

Membrane Surface Functionality

Figure 4 shows the FTIR spectra of polymeric membranes modified with SPEEK. The characteristic peaks of the base polymeric membranes (PVDF, PEI, PAI, PES, PPSU, and CA) are clearly presented in Table III. The spectral band of 1250 cm^{-1} for sulfonic group is clearly visible in all the SPEEK modified membranes. It reveals that SPEEK has good compatibility with the base polymers. Moreover, the imide carbonyl group at 1778 and 1721 cm^{-1} along with C–N stretching band of 1361 and 1379 cm^{-1} are observed in both PEI/SPEEK and PAI/SPEEK membranes. The hydroxyl group (O–H bands) of CA is

distinctly seen at the spectral wavelength of $3200\text{--}3600\text{ cm}^{-1}$ in Figure 4.

Membrane Morphology

Figures 5 and 6 show the top surface and cross-section morphology of both SPEEK and SPEEK/bentonite modified membranes. The synthesized membranes exhibited an asymmetric structure with skin top layer and support layer [Figure 6(a,b)]. Figure 5 clearly shows that modifiers modified by PVDF (Z1 and Z2), PES (Z5 and Z6), and CA (Z11 and Z12) membranes have loose porous structure with distinct larger pores. These results were in good agreement with average pore radius data which is listed in Table II. Highest pore size of 48.6 nm was observed for PES/SPEEK/bentonite MMMs. In case of other membranes, dense porous structure is observed in PEI (Z3 and Z4), PAI (Z7 and Z8), and PPSU (Z9 and Z10). SPEEK and bentonite added MMMs showed increased average pore radius than SPEEK modified membranes. It indicates that hydrophilic

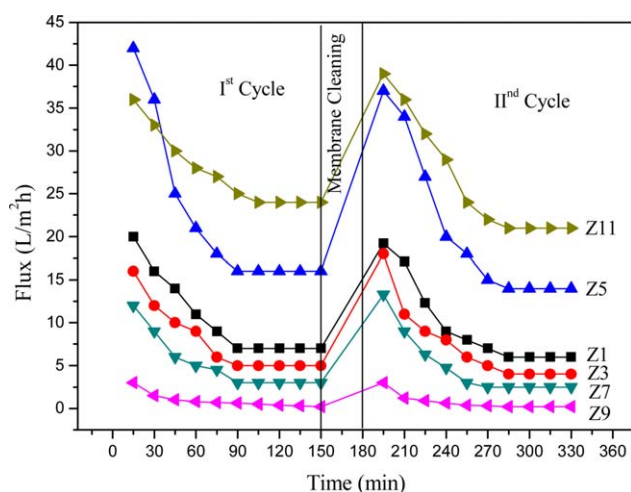


Figure 9. Flux profile of polymeric membranes modified with SPEEK on model dairy effluent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

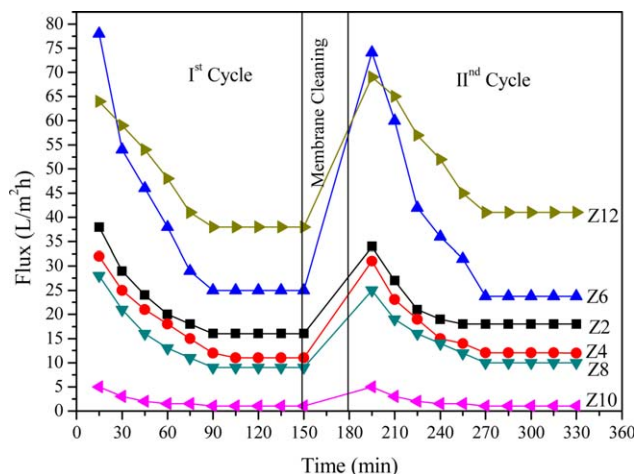


Figure 10. Flux profile of polymeric membranes modified with SPEEK and bentonite on model dairy effluent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Fouling and Concentration Polarization Resistances for Model Dairy Protein Solution

| Membrane type | R_f ($\times 10^{13} \text{ m}^{-1}$) | R_{cp} ($\times 10^{13} \text{ m}^{-1}$) | Total protein rejection (%) |
|---------------|----------------------------------------------|-------------------------------------------------|-----------------------------|
| Z1 | 6.67 | 7.88 | 89 |
| Z2 | 3.81 | 9.63 | 87 |
| Z3 | 5.27 | 11.34 | 95 |
| Z4 | 3.11 | 9.86 | 96 |
| Z5 | 8.25 | 4.65 | 91 |
| Z6 | 5.23 | 5.16 | 87 |
| Z7 | 5.59 | 12.68 | 95 |
| Z8 | 4.16 | 10.27 | 91 |
| Z9 | 6.32 | 14.55 | 97 |
| Z10 | 4.11 | 11.39 | 97 |
| Z11 | 3.16 | 5.78 | 88 |
| Z12 | 3.08 | 6.77 | 84 |

inorganic bentonite has possible to form an incompatibility with organic polymer matrix. Thus it leads to demixing of the casting dope solution and resulted in improvement in pore formation.³⁶ It is clear that addition of both modifiers such as bentonite and SPEEK to the casting dope solution has resulted in the formation of porous membrane matrix. As presented in Figure 6(a,b), cross-section image of the Z5, Z6, Z11, and Z12 membrane displayed thin skin layer and fine interconnected porous structure. It is generally well known that thin skin layer and spongy support layer are responsible for the better permeation rate. The addition of SPEEK on casting polymer dope solution causes the increase in exchange rate of solvent during coagulant process, which results in the formation of macrovoids.³⁷ Moreover, with further incorporation of bentonite on polymer dope solution, faster exchange process converted to slower release of solvent (NMP) in nonsolvent water bath.³⁸ It causes formation of slight spongy structures, which is necessary for the desired separation process. This result displays that the pore sizes of PVDF, PES, and CA membranes are larger.

Hydrophilicity and Water Permeability

Contact angle value and pure water permeability of the membranes are listed in Table II. From Table II, it can be seen that contact angle value is lesser of 56° for CA/SPEEK/bentonite membrane. It is well known that decrease in contact angle value is a measure of increase in hydrophilicity on surface. Hydrophilicity is an important determining membrane characteristic for fouling minimization and separation process. It involves the reduction of interaction between the both solute particles and membrane surface thus results in enhancing the filtration performance.³⁹ The contact angle value of both CA/SPEEK and CA/SPEEK/bentonite membranes are 60.8° and 54.5° and they were lower contact angles as compared to other polymeric membranes. It is mainly due to the fact that CA belongs to hydrophilic groups. As a comparison of different polymeric materials, hydrophilicity is in the order of CA > PES > PVDF > PEI > PAI > PPSU. In case of

SPEEK and bentonite made MMMs, contact angle was reduced when compared with SPEEK analogs. The main cause for enhancing the hydrophilicity was due to the major constituents of bentonite. Bentonite contains mainly of both alumina and silica, which are widely used as hydrophilic modifier to improve the fouling propensity in membrane separation process.^{40,41} These constituents make the membrane surface with higher hydrophilic property and resulting in improved wettability.

Figure 7 shows the water flux data for membranes. The higher flux of $96 \text{ L/m}^2\text{h}$ is observed for PES/SPEEK/bentonite MMMs. Next to that, for CA/SPEEK/bentonite MMMs a flux value of $72 \text{ L/m}^2\text{h}$ is observed. The water permeability (Table I) results also depicted that SPEEK and bentonite added MMMs have higher values than SPEEK analogs. The modifier SPEEK has a hydrophilic characteristic and this could enhance the attraction of water in the polymer matrix. Further with the addition of bentonite, it dispersed into two layers and thereby resulting in the formation of bigger pores and leading to higher water flux, which is schematically represented in Figure 8.

Membrane Performance on Filtration of Model Dairy Effluent

Efficacy of synthesized membranes is tested by passing model dairy effluent at the transmembrane pressure of 400 kPa for 150 min. Filtration experiment is repeated in two cycles and their flux patterns are shown in Figures 9 and 10. From Figures 9 and 10, it can be observed that the flux profile displaying three regions i.e., (i) sharp declining phase of up to 45 min, (ii) slow decline phase of 90 min, (iii) steady state phase of up to 150 min. Flux reduction in filtration operation is mainly because of blocking of pores by solute particles.^{42,43} It infers that rate of blockage is higher in the array of sharp declining phase, followed by second phase and steady state phase. The interaction of solute particle with membrane is mainly based on the property of pore size and hydrophilicity.⁴⁴ Among SPEEK incorporated membranes, CA holds the higher average flux of $27.5 \text{ L/m}^2\text{h}$ followed by PES membrane. It clearly displays that hydrophilicity has a significant role in enhancement of flux. However, PES membrane holds the higher water permeability but the flux decline rate was very high as compared to other membranes. It could be due to solute particles adsorption on the membrane surface eventually leading to reduction in flux.⁴² In second cycle filtration, flux value is consistent in all the membranes when compared to the first cycle. It indicates that synthesized membrane has higher filtration efficiency for longer run also. In case of both PEI and PAI membranes, flux drop rate is minimal and it was mainly because of lower pore size. Finally, PPSU has the lower flux value of $1 \text{ L/m}^2\text{h}$. On the other side, SPEEK and bentonite added MMMs showed higher performance than SPEEK blended membranes. Overall, the highest average flux value of $45.6 \text{ L/m}^2\text{h}$ is observed for CA/SPEEK/bentonite membranes. The membrane flux performance of synthesized polymeric membranes is in the order of CA > PES > PVDF > PEI > PAI > PPSU.

Protein Rejection

The major proteins present in milk are casein ($M_w = 28\text{--}30 \text{ kDa}$), whey proteins as α -Lactalbumin ($M_w = 14.4 \text{ kDa}$), and

β -Lactoglobulin ($M_w = 18.4$ kDa), and other minor constituents are BSA ($M_w = 66$ kDa) Immunoglobulin ($M_w = 150$ kDa).^{45,46} The total protein in model dairy effluent is found to be ~ 0.6 mg/mL and separation by membranes are listed in Table IV. In PPSU modified membranes, both Z9 and Z10 shows the higher protein rejection of up to 97%. The reason for enhancement in protein rejection is due to smaller pore size. Among synthesized membranes, protein rejection is lower for CA (Z11 and Z12) membranes. This is mainly because of both hydrophilic modifiers (SPEEK and bentonite) resulted in alteration of membrane morphology and the formation of larger pores. Hence, it allows the transport of protein molecules inside the polymer matrix. The membrane performance is also evaluated by resistance in series model and the resistance owing to fouling and concentration polarization value is presented in Table IV. Fouling resistance is higher for the PES/SPEEK (Z5) membrane. This is mainly because of solute particles can easily adsorb and block the large pores on the membrane surface. Fouling resistance (R_f) is decreased with the incorporation of bentonite on SPEEK/polymer resulting hybrid MMMs (Table IV). In bentonite modified MMMs, antifouling resistance property is improved because of the enhancement of hydrophilicity on the membrane surface. It may be due to reduce the interaction between feed and membrane surface and prevents the blockage of solutes. Moreover, fouling resistance is lower for CA membranes (Z11 and Z12), which also have the higher pore size than other membranes. The results shown in Table IV indicate that concentration polarization resistance (R_{cp}) is dominant for PPSU/SPEEK, PEI/SPEEK, and PAI/SPEEK membranes. These results clearly depict that the above membranes are lower in pore size thus the protein molecules were not able to enter through the matrix. Hence, it has resulted in formation of solute particles on membrane surface. When resistance is compared, concentration polarization was higher than fouling. It reveals that proteins are of higher molecular weight. Therefore, this result (Table IV) shows CA/SPEEK/bentonite MMMs has good flux performance with fouling minimization property. Further, this study will provide insight to other researchers for selection of polymeric materials and utilization of both SPEEK and bentonite modifiers for the antifouling properties.

CONCLUSION

In this study, results indicate that different polymeric materials of PVDF, PEI, PES, PAI, PPSU, and CA showed good compatibility in membrane formation with modifiers of both SPEEK and bentonite. The following conclusion could be drawn from the above study.

Hydrophilicity was increased while with incorporation of bentonite on SPEEK/polymeric resultant membrane. Bentonite and SPEEK has a mutual influence on alteration of membrane morphology.

Among polymeric materials, water permeability was higher for PES/SPEEK/bentonite MMMs. However, fouling resistance was higher for PES/SPEEK membrane and it was found that it

reduced with the incorporation of bentonite on PES/SPEEK resultant hybrid MMMs.

CA/SPEEK/bentonite MMMs has shown better permeation rate for model dairy effluent with lesser fouling property. This result revealed that hydrophilicity was increased with the both modifiers.

ACKNOWLEDGMENT

The author (Juhana Jaafar) would like to thanks to the Universiti Teknologi Malaysia and Ministry of Science, Technology and Innovation (MOSTI) for the Research University Grant vote number Q.J130000.2509.05H52 and R.J130000.7942.4S057 for the financial support.

REFERENCES

1. Luo, J.; Cao, W.; Ding, L.; Zhu, Z.; Wan, Y.; Jaffrin, M. Y. *Sep. Purif. Technol.* **2012**, *96*, 194.
2. Gottschall, N.; Boutin, C.; Crolla, A.; Kinsley, C.; Champagne, P. *Ecol. Eng.* **2006**, *9*, 154.
3. Sarkar, B.; Chakrabarti, P. P.; Vijaykumar, A.; Kale, V. *Desalination* **2006**, *195*, 141.
4. Cheryan, M. *Ultrafiltration and Microfiltration Handbook*, 2nd ed.; Technomic Publishing: Lancaster, PA, **1998**; Chapter 20, pp 345–494.
5. Baldasso, C.; Barros, T. C.; Tessaro, I. C. *Desalination* **2011**, *278*, 381.
6. Jeantet, R.; Rodriguez, J.; Garem, A. *LAIT* **2000**, *80*, 155.
7. Van der Bruggen, B.; Kim, J. H.; DiGiano, F. A.; Geens, J.; Vandecasteele, C. *Sep. Purif. Technol.* **2004**, *36*, 203.
8. Bowen, W.; Cheng, S.; Doneva, T.; Oatley, D. J. *J. Membr. Sci.* **2005**, *250*, 1.
9. Arthanareeswaran, G.; Srinivasan, K.; Mahendran, R.; Mohan, D.; Rajendran, M.; Mohan, V. *Eur. Polym. J.* **2004**, *40*, 751.
10. Arthanareeswaran, G.; Thanikaivelan, P.; Raajenthiren, M. *Ind. Eng. Chem. Res.* **2008**, *47*, 1488.
11. Kim, J.; Van der Bruggen, B. *Environ. Pollut.* **2010**, *158*, 2335.
12. Chen, Y.; Zhang, Y.; Liu, J.; Zhang, H.; Wang, K. *Chem. Eng. J.* **2012**, *210*, 298.
13. Wang, P.; Ma, J.; Wang, Z.; Shi, F.; Liu, Q. *Langmuir* **2012**, *28*, 4776.
14. Saranya, R.; Arthanareeswaran, G.; Sakthivelu, S.; Manohar, P. *Ind. Eng. Chem. Res.* **2012**, *51*, 4942.
15. Zulkhairun, A. K.; Ismail, A. F. J. *J. Membr. Sci.* **2014**, *468*, 20.
16. Singhal, R.; Datta, M. *J. Appl. Polym. Sci.* **2006**, *103*, 3299.
17. Ghaemi, N.; Madaeni, S. S.; Alizadeh, A.; Rajabi, H.; Daraei, P. *J. Membr. Sci.* **2011**, *382*, 135.
18. Chen, Y.; Zhang, Y.; Zhang, H.; Liu, J.; Song, C. *Chem. Eng. J.* **2013**, *228*, 12.
19. Wang, Z.; Wang, H.; Liu, J.; Zhang, Y. *Desalination* **2014**, *344*, 313.

20. Zhang, J.; Zhang, Y.; Chen, Y.; Du, L.; Zhang, B.; Zhang, H.; Wang, K. *Ind. Eng. Chem. Res.* **2012**, *51*, 3081.
21. Hu, Q. H.; Qiao, S. Z.; Haghseresht, F.; Wilson, M. A.; Lu, G. *Ind. Eng. Chem. Res.* **2006**, *45*, 733.
22. Chen, Z.; Jin, Q.; Guo, Z.; Montavon, G.; Wu, W. *Chem. Eng. J.* **2014**, *256*, 61.
23. Anadão, P.; Sato, L. F.; Wiebeck, H.; Valenzuela-Díaz, F. R. *Appl. Clay Sci.* **2010**, *48*, 127.
24. Sasikala, S.; Meenakshi, S.; Bhat, S. D.; Sahu, A. K. *Electrochim. Acta* **2014**, *135*, 232.
25. Jaafar, J.; Ismail, A. F.; Matsuura, T. *J. Membr. Sci.* **2009**, *345*, 119.
26. Luo, J.; Ding, L.; Qi, B.; Jaffrin, M. Y.; Wan, Y. *Bioresour. Technol.* **2011**, *102*, 7437.
27. Lukka Thuyavan, Y.; Anantharaman, N.; Arthanareeswaran, G.; Ismail, A. F. *Desalin. Water Treat.* under press (doi:10.1080/19443994.2014.934738).
28. Tansel, B.; Bao, W. Y.; Tansel, I. N. *J. Colloid Interface Sci.* **2000**, *129*, 7.
29. Shahgaldi, S.; Ghasemi, M.; Ramli, W.; Daud, W.; Yaakob, Z.; Sedighi, M. *Fuel Process. Technol.* **2014**, *124*, 290.
30. Yu, L.; Xu, Z.; Shen, H.; Yang, H. *J. Membr. Sci.* **2009**, *337*, 257.
31. Kim, K.; Ingole, P. G.; Kim, J.; Lee, H. *Chem. Eng. J.* **2013**, *233*, 242.
32. Saha, N. K.; Joshi, S. V. *J. Membr. Sci.* **2009**, *342*, 60.
33. Ananth, A.; Arthanareeswaran, G.; Wang, H. *Desalination* **2012**, *287*, 61.
34. Dutczak, S. M.; Cuperus, F. P.; Wessling, M.; Stamatialis, D. *F. Sep. Purif. Technol.* **2013**, *102*, 142.
35. Yu, S.; Cheng, Q.; Huang, C.; Liu, J.; Peng, X.; Liu, M. *J. Membr. Sci.* **2013**, *434*, 44.
36. Arthanareeswaran, G.; Thanikaivelan, P.; Raajenthiren, M. *J. Appl. Polym. Sci.* **2009**, *116*, 995.
37. Lau, W.; Ismail, A. F. *Desalination* **2014**, *249*, 996.
38. Kesting, R. E. *Synthetic Polymeric Membrane*, 2nd ed.; Wiley: New York, **1985**.
39. Wavhal, D. S.; Fisher, E. R. *Langmuir* **2003**, *19*, 79.
40. Mukherjee, R.; De, S. *J. Hazard. Mater.* **2014**, *265*, 8.
41. Huang, J.; Zhang, K.; Wang, K.; Xie, Z.; Ladewig, B.; Wang, H. *J. Membr. Sci.* **2012**, *423–424*, 362.
42. Rai, P.; Rai, C.; Majumdar, G. C.; DasGupta, S.; De, S. *J. Membr. Sci.* **2006**, *283*, 116.
43. Sarkar, B. *J. Food Eng.* **2013**, *116*, 333.
44. Palencia, M.; Rivas, B. L.; Valle, H. *J. Membr. Sci.* **2014**, *455*, 7.
45. Wong, D. W.; Camirand, W. M.; Pavlath, A. E. *Crit. Rev. Food Sci. Nutr.* **1996**, *36*, 807.
46. Arunkumar, A.; Etzel, M. R. *J. Membr. Sci.* **2014**, *454*, 488.