RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Journal Name

ARTICLE

Nanoscale homogeneity of silica-poly (vinyl alcohol) membranes by controlled cross-linking *via* sol-gel reaction in acidified and hydrated ethanol

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Organic-inorganic hybrid membrane in which nanoscale hybrid domains creating preferential pathways for selective permeation exhibits excellent performance in separation processes. Herein, a synthesis route of sol-gel reaction in acidified and hydrated ethanol to prepare silica-poly (vinyl alcohol) hybrid membrane of nanoscale homogeneity is reported. ^{29}Si NMR study was performed on the membrane samples to probe the connectivity of SiO_4 tetrahedra in the cross-linking hybrid networks while the small-angle scattering study revealed nanostructure of the silica-polymer hybrid. TEM, DSC, IR, TGA, XRD and swelling studies were performed to study other physico-chemical properties of the membrane. The hybrid membrane exhibited superior water permeability 96 L m^{-2} h^{-1} µm than the other reported membranes in pervaporation desalination of saline water of 2000 ppm NaCl.

Introduction

Mixed matrix membrane based on organic-inorganic hybrid formed by interaction between organic and inorganic components through weak hydrogen bonds or van der Wall electrostatic forces or strong chemical bonding, is considered as the potential “new generation” membrane due to its excellent performance in separation applications.[1-4] Among the various hybrid membranes, silica-poly (vinyl alcohol) membrane prepared from sol-gel reaction using tetraethoxysilane as precursor for silica,[5-7] is of much interest as such hybrid membranes exhibited enhanced performance in pervaporation separation applications. At the same time, the membrane maintained excellent flexibility that thin membrane film of high permeation rate could be made.

Enhancements of membrane performance was observed in pervaporation dehydration of alcohol for the membrane prepared from a cross-linking reaction between poly(vinyl alcohol) and aminopropyltriethoxysilane, in which amino propyl groups of the membrane simultaneously enhanced the water permselectivity and permeation flux. [8,9] Furthermore, in order to control the swelling of poly (vinyl alcohol) membranes, mixtures of poly (vinyl alcohol) and an inorganic oligosilane (Compoceran 1000 from Arakawa Chemical Industry Co. Ltd.) a tetramer of dimethoxysiloxane having terminal epoxy propane groups were prepared using sol-gel reactions to yield the hybrid membranes. [10] The silica-poly (vinyl alcohol) hybrid membrane was also prepared using γ-glycidyloxypropyltrimethoxysilane as initial precursor for silica. γ-Glycidyloxypropyltrimethoxysilane has an organically modified alkoxide moiety containing a reactive epoxy ring which strengthens interaction between organic and inorganic phases, producing membrane of larger free volume with suitable pore sizes (free volume cavities) and increased the pore number density; and such membranes were tested for application in separation of benzene-cyclohexane mixture *via* pervaporation.[11] The annealing temperature and time strongly affected the separation properties of this membrane type. With increasing in annealing temperature and time, the free volume cavity size and number decreased resulting to increase in the benzene separation efficiency but decrease in the flux. [12] Therefore, control of silica-poly (vinyl alcohol) cross-linked network is required to produce a membrane with adjustable free volume cavity size and density. However, in the case where the hydrolysis reaction rate of alkoxysilane is faster than the cross-linking reaction, it leads to micro-phase separation due to formation of large silicate networks in the polymer matrix through self-condensation reaction. The undesired micro-phase separation then results into the poor membrane quality. One way of controlling the cross-linking density of the hybrid membrane was by co-hydrolysis and co-condensation of γ-glycidyloxypropyltrimethoxysilane[13] or γ-mercaptopropyltrimethoxysilane[14] and tetraethoxysilane in poly (vinyl alcohol) aqueous solution. The results showed (i) increased compatibility between the organic phase and inorganic phase, (ii) formation of well-dispersed silica particles and (iii) influence of swelling and pervaporation properties of hybrid membranes. Likewise, preparation of the hybrid membrane using simultaneous cross-linking of poly (vinyl alcohol) with maleic acid and tetraerthoxysilane for pervaporation desalination applications had been reported. [15- 17] In another studies, poly (vinyl alcohol) blended with poly (ethylene glycol) [18] or a copolymer of poly (vinyl alcohol-co-acrylic acid) [19] was cross-linked with tetraethoxysilane to prepare the hybrid membranes. The cross-linking density of the membrane was found to be increased with increase in the tetraethoxysilane content, annealing temperature and time, which

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resulted in increment of water permselectivity for pervaporation dehydration of ethanol. Generally, a micro-phase separation of silica in the membrane was resulted when the tetraethoxysilane content of the membrane was over 15-20 wt. %, which led to decrement in the water permselectivity.

Herein, preparation of silica-poly (vinyl alcohol) membranes without micro-phase separation by controlled cross-linking *via* sol-gel reaction in acidified and hydrated ethanol is reported. High ethanol amount used in the preparation is to slow down the hydrolysis rate of tetraethoxysilane and to provide solvation of hydrolysed tetraethoxysilane for effective cross-linking between –Si-OH and -CH=CHOH at a highly acidic condition (pH < 2) for the formation of silica-poly (vinyl alcohol) membranes. The cross-linking network of silica-poly (vinyl alcohol) hybrid membrane prepared from different synthesis solution compositions of the acidified and hydrated ethanol system as well as influence of temperature on the membrane structure were studied; and their separation properties in pervaporation desalination of saline water of 2000 ppm NaCl were explored.

Experimental

Materials

Hydrophilic polymer, poly (vinyl alcohol) (85000-125000 molecular weight) and tetraethylorthosilicate (TEOS) were purchased from Sigma-Aldrich Co. LLC. Other chemicals were of analytical grade and purchased form S.D Fine-Chem. Ltd., India. All the purchased chemicals were used as received.

Preparation of membrane

Figure 1 shows the schematic representation of membrane preparation method. The solution compositions used for the preparation of the silica-poly (vinyl alcohol) hybrid membranes are given in Table 1. The procedure for preparation of the membranes is described as below. A required amount of poly (vinyl alcohol) was dissolved in deionised water at 80 °C under stirring condition to prepare a desired solution concentration. The solution was allowed to cool down to room temperature followed by microfiltration to remove any suspended impurities. This solution was acidified by adding concentrated HCl solution and stirred for 1 h at room temperature. The TEOS solution was prepared separately by mixing required amounts of TEOS and ethanol with stirring for 1 h. The TEOS solution was added to the polymer solution drop-wise under stirring condition. The resultant homogenous mixed solution was further stirred for 1 h at room temperature. A required amount of the solution was poured in a petridish and the solution was allowed to evaporate completely at room temperature for 72 h. This resulted to a transparent membrane film. The room temperature casted membrane films were cured at 60 °C and degassed for removing trapped solvent and acid to a complete dryness

Characterization and performance evaluation of membranes

X-Ray diffraction (XRD) experiments of the samples were carried out on a PANalytical EMPYREAN over the 2θ range from 2 to 70° with a scanning rate of 0.039°/min. Infrared spectroscopy studies were carried out on PERKIN ELMER GX-FTIR. Differential scanning calorimetric (DSC) studies were carried out by using NETZSCH DSC 204F1 at a heating rate of 10 °C/min from 25 to 400 °C.

Table 1 Solution compositions for preparation of the membranes

Sample	Mole Ratio				
	C_2H_5OH / TEOS	TEOS / $C_2H_4O^a$	H_2O / C_2H_5OH	H_2O / C_2H_4O	HCl / (H_2O+C_2H_5OH)
M1	238.58	0.22	6.47	334.07	0.002849
M2	238.58	0.22	3.23	167.03	0.005025
M3	238.58	0.22	2.16	125.27	0.006211
M4	238.58	0.43	3.23	334.07	0.002513

[a] vinyl alcohol

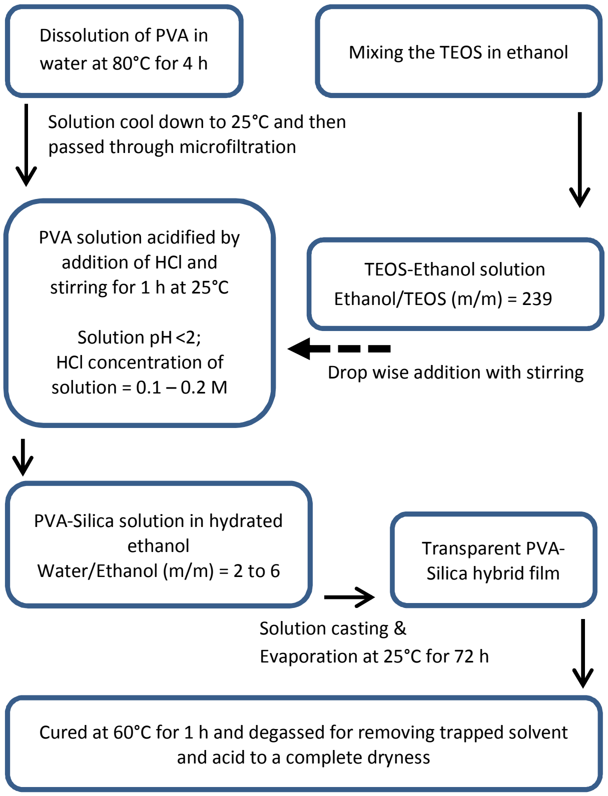

Fig 1 Membrane preparation scheme

Thermo-gravimetric-analysis (TGA) of the samples was measured on TGA/SDTA 851e Mettler Toledo. The solid state ^{29}Si Nuclear magnetic resonance measurements were carried out on a Bruker AVANCE-II 500MHz instrument. Small-angle scattering experiments were carried out using Bruker X-ray scattering instrument. The desalination performance of the hybrid membranes was evaluated on a pervaporation test kit. An aqueous feed containing 2000 ppm NaCl was used as feed for the desalination experiment at room temperature. Conductance of feed and permeate were measured by a conductivity meter of a conductivity bridge model Con 700. The % salt rejection efficiency (% S/R) was determined based on the conductance values of feed and permeate**.**

Results and Discussion

Preparation of the silica-poly (vinyl alcohol) hybrid membrane

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The sol-gel reaction to prepare the silica-poly (vinyl alcohol) hybrid membrane was carried out in acidified and hydrated ethanol. Amount of water content in the hydrated ethanol was varied from 2.4 to 6.5 moles per 1 mole of ethanol. Further reduction in water content of the solution system is not desirable. Because in that case, where the water content in ethanol is below 2 moles per 1 mole of ethanol, poly (vinyl alcohol) is precipitated out due to the phenomenon of phase inversion process in which the poly (vinyl alcohol) is no longer soluble in the ethanol-water mixture and hence, membrane formation is not possible. Comparison of silica-poly (vinyl alcohol) hybrid of the present work with other reported hybrids from different preparations and their application in separation processes [5, 6, 8-11, 14] are given in Table 2. It indicated the hybrid membrane reported here was prepared in a different condition.

Table 2: Comparison of silica-poly (vinyl alcohol) hybrid membranes from different preparations

Solvent	Silica source	Molar Composition of synthesis solution	HCl conc. in solution (mol/L)	Curing Condition	Separation	Ref.
DMSO	TEOS[a]	C_2H_4O:12.4$C_2H_6OS^e$: (1.1-3.7)×$10^{-2}SiO_2$	Not specified	Evaporation at 80˚C for 24 h followed by heat treatment at 130 - 160 ˚C for 6 - 24 h	Ethanol-water	5
Water	TEOS[a]	C_2H_4O:61H_2O: (5.3-42.3)×$10^{-2}SiO_2$	0.12	Room temperature drying for 2-3 days	Isopropanol-water	6
Water	APTEOS[b]	C_2H_4O:61H_2O: (0.5-2.2)×$10^{-2}SiO_2$	0.02	Room temperature evaporation followed by heating at 80 ˚C under vacuum for 24 h	Isopropanol-water	8
Water	APTEOS[b]	C_2H_4O:61H_2O: (0.5-2.2)×$10^{-2}SiO_2$	0.02	Room temperature evaporation followed by stepwise heating at 80 ˚C for 24 h and 80 - 160 ˚C for 6-24 h under vacuum	Ethanol-water	9
DMSO	Oligosilane	C_2H_4O:31 C_2H_6OS: (0.9- 3.4)×$10^{-2}SiO_2$	0.15	Evaporation at 80 ˚C for 30 h followed by heating at 100 ˚C for 12 h	Ethanol-water	10
Water	GPTMS[c]	C_2H_4O:49H_2O: (2.1-15.3)×$10^{-2}SiO_2$	Not specified	Overnight room temperature drying followed by heating at 120 ˚C for 2 h	Benzene-cyclohexane	11
Water	MPTMS[d]	C_2H_4O:35H_2O: (2.5-45.5)×$10^{-2}SiO_2$	Not specified	Room temperature for 2 -3 days followed by stepwise heating at 80 ˚C for 2 h and 150 ˚C for 8 h	Ethylene glycol-water	14
Hydrated ethanol	TEOS[a]	C_2H_4O:108-333H_2O: 50.3C_2H_5OH: (21.5 – 42.2)×$10^{-2}SiO_2$	0.12 - 0.22	Room temperature evaporation followed by heating at 60˚C under vacuum until complete dryness	Desalination	This study

a)tetraethoxysilane, b)aminopropyltriethoxysilane, c) γ -glycidyloxypropyltrimethoxysilane, d)γ-mercaptopropyltrimethoxysilane, e)dimethylsulfoxide (DMSO)

As given in Table 1, the membrane M1, M2 and M3 having same silica content were prepared at room temperature from different polymer solution concentration in which the acid (HCl) amount in the solution for the membrane was in increasing order of M1 < M2 < M3. In case of sample M4, the solution concentration was same with that of M1 but the amount of silica in M4 was twice of the silica in M1. Sample M3-T1 and M3-T2 were cured at different conditions while the other condition was same as that of M3 to check the effect of temperature. In case of M3-T1, the sample was first cured at 60 °C for 1 h, which was then degassed for complete dryness and free from any solvent trapped inside the sample and finally the sample was heated at 150 °C for 2 h, while the M3-T2 was directly cured at 150 °C for 2 h without degassing step.

Figure 2 shows the ^{29}Si NMR spectra of the silica-poly (vinyl alcohol) hybrid membranes films prepared from different compositions and conditions. The ^{29}Si NMR measurement was performed to measure the types of cross-linking networks of silica structures since ^{29}Si NMR is capable of distinguishing SiO_4 tetrahedra of connectivity ranging from 0 to 4, represented by the symbol Q_n. Q_n signals correspond to silicon atoms bonded to four oxygen atoms while ‘n’ represents number of silicon atom bonded with this oxygen atom which varies between 1 to 4.[20] Area of ^{29}Si NMR chemical shift bands was calculated based on Gaussian peak distribution using Origin Pro software.

Analysis of the spectra indicated that all the membranes exhibited bands at -110 and -112 ppm, which are assigned as Q_3 and Q_4 signals respectively. The Q_4/Q_3 ratio for the M1, M2 and M3 membranes were found to be respectively 1, 1.2 and 1.6. This is attributed to increased catalytic activity of acid in the self-condensation of TEOS in the sample solution containing more amount of acid. The acid content was increased for the samples in the order of M1 < M2 < M3. It can be seen from the spectra that significant amounts of Q_4 signal were present in these samples which indicated a large amount of the -O-Si-O- network connectivity from the silica domains. The Q_4/Q_3 ratio was 1.1 for the sample M4 which were again similar with that of the M1.

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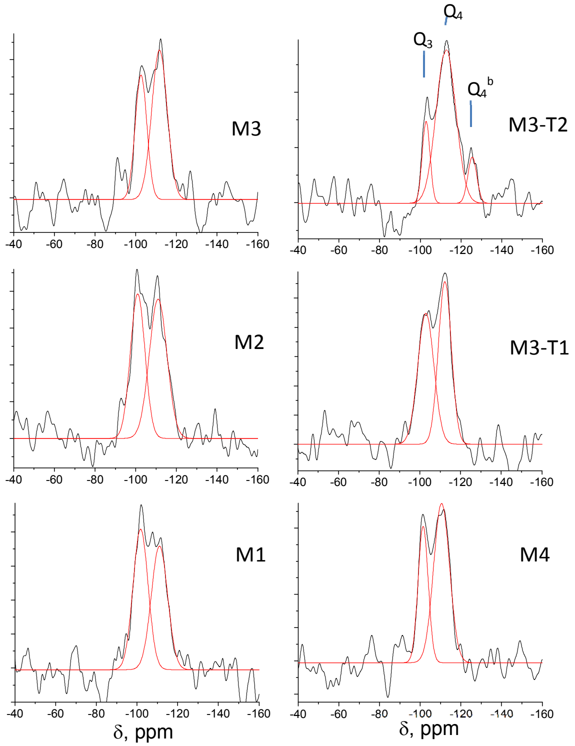

Fig 2 ^{29}Si NMR spectra of the silica-poly(vinyl alcohol) hybrid membranes films

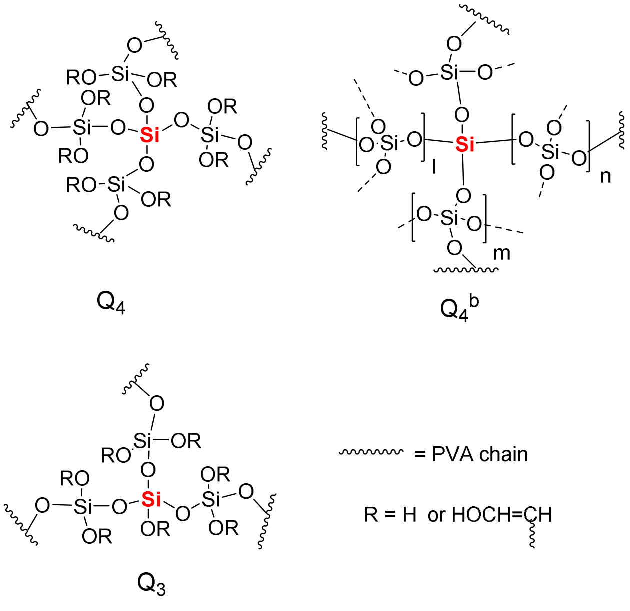

Fig. 3 Probable connectivity of SiO_4 tetrahedral units with PVA chains

This may be because of the use of the same acid concentration (HCl) of M4 with M1 except amount of silica (TEOS) which was twice in concentration for M4 as compared to that of M1. The M3-T1 exhibited a Q_4/Q_3 ratio of 1.8 while the M3-T2 exhibited a high Q_4/Q_3 ratio of 4.8. Furthermore, the M3-T2 showed an additional band at -125 ppm which is assigned as Q_4^b signal from bigger silica domains having larger -O-Si-O- network connectivity. The probable connectivity of SiO_4 tetrahedra with PVA chains are shown in Figure 3. These results indicated that the M3-T1 cured even at a higher temperature of 150 °C after the degassing step was of similar -O-Si-O- network connectivity with the M3 cured at 60 °C. On the other hand, Q_4 signal of SiO_4 tetrahedra was predominantly present in the structure of the M3-T2. This may be because the sample M3-T1 was treated at 60 °C until the complete dryness prior to heating at 150 ^{o}C in contrast to the sample M3-T2 which was directly heated at at 150 ^{o}C.

Silica particles were not visible in the TEM images of the M1, M2, M3, M4 samples. A representative TEM image of such membrane sample is shown in Figure 4 (a). This indicated silica domains are beyond the detection limit for the above hybrid membranes cured at at 60 °C whereas, the size of silica domains for the membranes cured at 150 °C were clearly visible in the TEM image. The increase in particle size of silica domain after heating the sample at 150°C is common for all the samples. The results of the M3 sample as a representative sample is only presented here. The M3-T1 sample showed silica particles of about 2-7 nm, as shown in Figure 4 (b). However, few larger silica particles of sizes 20-50 nm in addition to the 2-7 nm sized silica particles were observed in the TEM image of the M3-T2 sample as shown in Figure 4 (c). This might imply that the silica-poly (vinyl alcohol) hybrid structure of M3-T2 exhibited relatively less homogenous morphology. Furthermore, as shown by the optical images of the membrane samples (Figure 5), all the samples were transparent except the M3-T2 sample of which the image was black in colour.

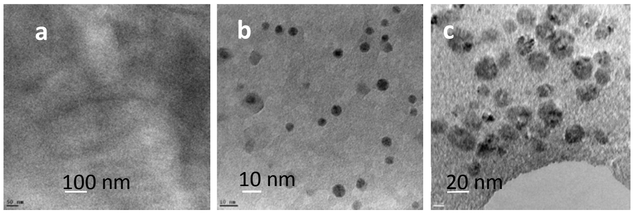

Fig. 4 TEM images of the hybrid sample cured at 60 °C (a), the sample M3-T1 cured at 150 °C after prior heating at 60 °C (b) and the sample M3-T2 cured directly at 150 °C (c).

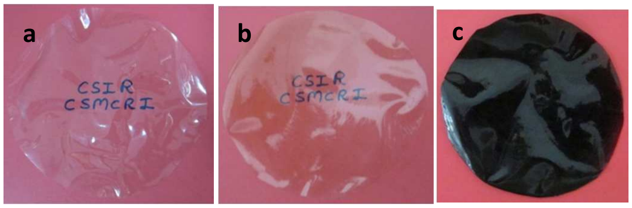

Fig. 5 Images of the hybrid sample cured at 60 °C (a), the sample M3-T1 cured at 150 °C after prior heating at 60 °C (b) and the sample M3-T2 cured directly at 150 °C (c).

Nanostructure and cross-linking density of the silica-poly (vinyl alcohol) hybrid membranes

The membrane nanostructure was characterized by small-angle scattering technique. Figure 6 displays the scattering curves as the intensity, I (Q) versus the scattering vector, Q of the M1, M2, M3, M3-T1 and M3-T2 samples. I (Q) decayed with a power law of the

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form I (Q) ~ $Q^{-(1.52\ \mathrm{to}\ 2.46)}$ for the samples. The exponent values were smaller from the power law of the form I (Q) ~ Q^{-4}, generally observed for the mono-dispersed spherical particles. [21] The decrease in the exponent values of the power law relation can be explained by the changes in scattering form factors, as far as such a power law I(Q) ~ Q^{-3} is typical of three-dimensional form and I(Q) ~ Q^{-2} typical of two-dimensional form or Gaussian polymer chain conformation. The exponential value of the power law was decreased in the order of -1.96 < -1.83 < -1.73 for M1, M2 and M3 sample, respectively. This indicated the silica-polymer composite structure formed from the solution of higher acid content produced a relatively lower dimensional structure. On the other hand, the composite structure of M3-T2 sample showed a power law of the form I (Q) ~ $Q^{-2.46}$.

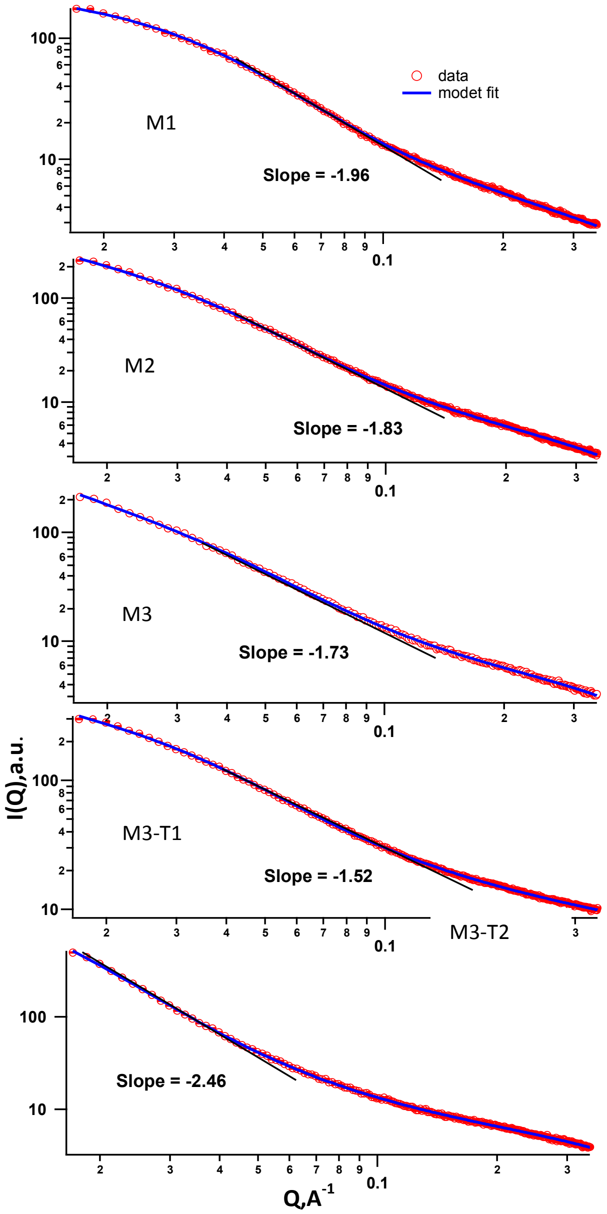

Fig. 6 SAXS profiles of the hybrid samples. Solid lines indicate DAB model fits

This indicated that the structure of the M3-T2 sample exhibited the highest dimensional structure among the samples. At the same time, the slope of the scattering curve for the M3-T2 was shifted over a lower Q range indicating scattering from larger scattering sizes. This could be due to the phenomenon as described below. When the silica-polymer hybrid sample was heated at higher temperature of 150 °C in presence of acid, the silica with terminal hydroxyl groups, -Si(OH)$_x$ might undergo further condensation reaction leading to larger silica domains (as observed by NMR and TEM). Consequently, the silica phase was separated from the polymer phase by a larger distance. Therefore, the scattering profile of the M3-T2 sample could be a combination of the scattering from a dominant polymer phase and segregated silica phase. In such case, the exponential value of the power law could be higher because of substantial contribution from high-dimensional segregated silica phase. In contrast, the M3-T1 sample exhibited the lowest dimensional structure (a power law of the form I (Q) ~ $Q^{-1.52}$) among all the samples. The lowest dimensional structure of the silica-polymer hybrid might indicate a better cross-linking between the silica and polymer as discussed above. This might imply that the further cross-linking of silica-polymer hybrid structure was taken place under the influence of subsequent heating of the completely dried sample at the higher temperature of 150 °C, but further self-condensation reaction of -Si(OH)$_x$ groups in absence of acid was largely prevented. The scattering profiles are fitted with the scattering model of Debye-Anderson-Brumberger (DAB) equation to calculate the scattering from a randomly distributed two-phase system [22] of the silica-polymer composite structure. The measure of the average spacing between two phase regions is given by ξ (correlation length). As shown in the Figure 6, there was good fits to the data using this model. This might be indicative of a two phase system with a perfectly random distribution of silica and polymer phases in the samples. The value of the Debye-Bueche correlation length, ξ, as a measure of the average size of scattering blocks estimated by the model fit was 23.4, 25.9, 24.1, 24.0 Å for M1, M2, M3 and M3-T1 samples, respectively. In case of sample M3-T2, the ξ value was found to be 74.3 Å which is about 3-times of the values of the other samples. This indicated a higher degree of segregation of the silica phase leading to larger scattering domains was occurred in the M3-T2 sample which was in agreement with NMR and TEM results as discussed above.

Cross-linking density of all the hybrid membranes V_c (mol. cm^{-3} of polymer), was calculated by using the Flory-Rehner equation based on equilibrium swelling of polymer in water using the Flory-Huggins interaction parameter value of 0.494 according to literature data. [23] The polymer film was kept in water at room temperature for few hours until a constant weight of swollen polymer film was obtained and the volume fraction of the polymer (ϕ) in swollen mass was determined. The calculated values of ϕ and V_c for the hybrid membrane samples are given in Table 3. The ϕ and Vc values for the sample were found in increasing order of M1 < M2 < M3 < M3-T1 < M3-T2. The Vc value 3.23 × 10^{-3} (mol/cm^3) of M3-T2 sample is about twice the value of the M1 sample and is close to the 3.58 × 10^{-3} (mol/cm^3) value of neat poly(vinyl alcohol) film cross-linked with organic molecules of maleic acid (13.3 wt. %). This indicated that M1 sample exhibited the least dense structure of silica-poly(vinyl alcohol) hybrid; and that, the hybrid structure, upon curing at a higher temperature of 150 °C without any prior treatment steps of lower temperature heating at 60 °C and degassing, can however be condensed to a very dense structure

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similar to the structure of maleic acid-cross linked-poly(vinyl alcohol) film.

Other physico-chemical properties of the hybrid membranes

The DSC studies of the samples were performed to observe the glass transition temperature (T_g) as well as the endothermic melting peaks of the hybrid membranes. As shown in Figure 7 (a), the DSC plots showed a broad endothermic peak at about 99 – 132 °C for the hybrid membranes and a relatively sharper endothermic peak at about 250 – 255 °C.

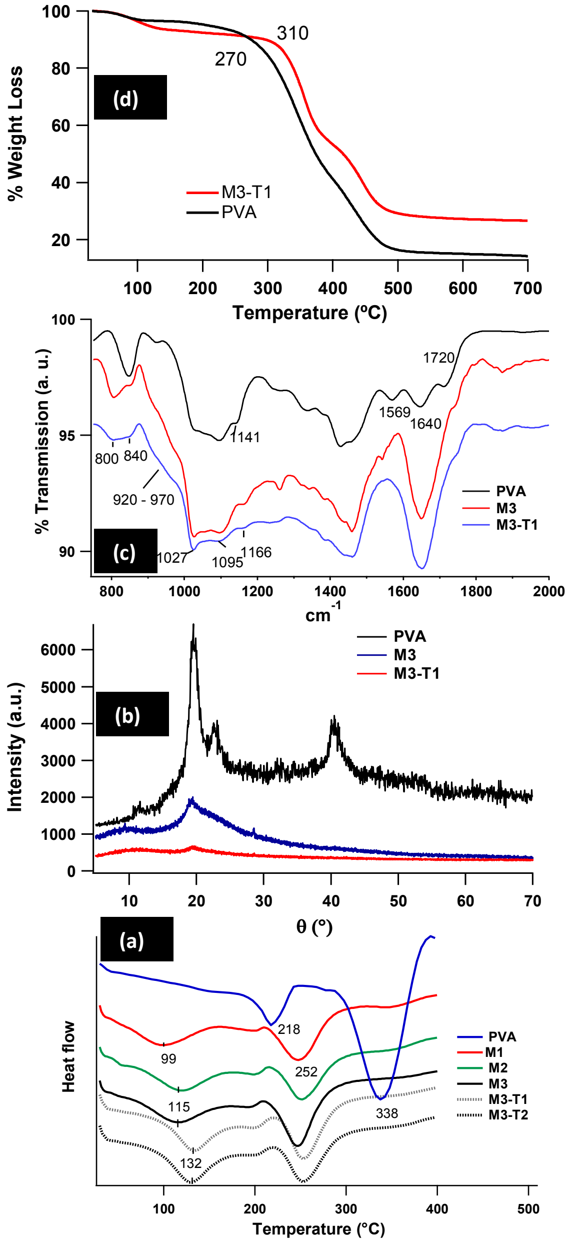

Fig. 7 DSC plots (a), XRD patterns (b), FT-IR spectra (c) and TGA plots (d) showing differences between the hybrid sample and neat poly(vinyl alcohol) (PVA) sample

The broad peak corresponds to the T_g due to the amorphous (glassy) nature of the hybrid while the sharper peak is due to melting peaks of crystalline portion of the hybrid. In comparison, the initial crystalline polymer had two sharp endothermic peaks at about 218 °C and 338 °C due to melting peaks of crystalline phase of poly (vinyl alcohol). Among all the hybrid samples, the lowest T_g value of 99 °C was observed in case of the M1 sample. The T_g value was shifted to about 115 °C for M2 and M3 samples. Furthermore, the T_g values for the hybrid samples cured at the higher temperature (M3-T1 and M3-T2) were shifted to a higher value of about 132 °C. The shifting of the T_g value to a higher value was consistent with the increase in cross-linking density of the hybrids as discussed above.

The transformation of amorphous structure of the hybrid from the crystalline structure of the initial poly (vinyl alcohol) can be observed by the XRD pattern of the samples. As shown in Figure 7 (b), the starting polymer has well defined XRD lines due to the crystalline atactic structure of the poly (vinyl alcohol). XRD peak intensities of the hybrid membranes were drastically reduced due to the significant loss of hydroxyl groups from the poly (vinyl alcohol) upon the cross-linking with the silica. The hybrid membrane cured at higher temperature of 150 °C exhibited the lowest intensity indicating such sample was of largely amorphous nature.

The cross-linking of the hybrid was confirmed by FTIR spectroscopy. The FTIR spectra of the initial polymer, cross-linked polymer at 60 °C and cross-linked polymer at 150 °C are shown in Figure 7 (c). The starting poly (vinyl alcohol) showed bands at 1141 cm^{-1} due to crystalline C-C bonding and the band at 1569 cm^{-1} due to C-O of C-OH groups and these bands were disappeared upon the cross-linking. Further, the intensities of peak at 1095 cm^{-1} due to C-O-H stretching mode and peak at 840 cm^{-1} due to O-H vibration (out of plane) mode of poly (vinyl alcohol) were decreased upon the cross-linking. Oppositely, the intensity of peak at 1027 cm^{-1} for the hybrid sample was higher as compared to that of the initial poly(vinylalcohol). The increase in intensity of peak at 1027 cm^{-1} for the hybrid sample might be contributed by the asymmetric stretching vibration mode of Si-O-Si network even though the peaks in this 1000-1100 cm^{-1} region is difficult to examine because overlapping alcohol stretching mode of C-O-H with asymmetric stretching mode of Si-O-Si. The symmetric stretching mode of Si-O-Si was observed at 800 cm^{-1} for the hybrid sample. Another additional band at 1166 cm^{-1} observed for the hybrid sample was assigned due to Si-O-C cross-linking network. Strong intensity of band at 1640 cm^{-1} for the hybrid sample was assigned due to the absorbed water. All the hybrid samples exhibited similar FTIR spectra in terms of peak positions and intensities except a slightly broader shoulder band in 920 -970 cm^{-1} region for the hybrid sample cured at higher temperature. These bands were assigned as silanol (-Si-OH) groups. Presence of a weak band at about 1720 cm^{-1} was assigned due to acetate groups of poly (vinyl acetate) impurities in the poly (vinyl alcohol).

TGA was used to study thermal properties of the hybrid membrane in the temperature range of 25 - 700 °C under nitrogen. All TGA curves (Figure 7d) showed weight loss at about 100 °C indicating loss of water. Subsequent weight loss occurred for the hybrid in the temperature > 120 °C was possibly due to further condensation of hydrolysed silica. The onset of decomposition temperature for the

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hybrid was about 310 °C as compared to 270 °C for the polymer. The residual weight after the decomposition step for the hybrid was about twice the value of the initial polymer. This could be due to the higher thermal stability of the cross-linked polymer-silica structure of the hybrid.

Table 3 The volume fraction of the polymer in swollen mass (ϕ) and cross-linking density (V_c) of the hybrid membranes

Membrane	ϕ	$V_c \times 10^{-3}$ (mol/cm^3)
M1	0.321	1.615
M2	0.335	1.855
M3	0.342	1.978
M3-T1	0.363	2.395
M3-T2	0.398	3.233

Membrane performance in pervaporation separation of saline water:

Performances of the silica-poly (vinyl alcohol) hybrid membranes were examined in pervaporation separation of saline water of 2000 ppm NaCl at room temperature. The performance of the silica-poly (vinyl alcohol) hybrid membranes in terms of water permeability and salt rejection efficiency are compared with the poly (vinyl alcohol)–maleic acid cross-linked membrane as well as reported data of poly (vinyl alcohol)–maleic acid-silica cross-linked membranes. The results are given in Table 4. All the membranes exhibited 99.9 % salt rejection (S/R) efficiency. The M1 membrane of silica-poly (vinyl alcohol) exhibited about 5-fold of the water permeability exhibited by poly (vinyl alcohol)–maleic acid cross-linked membrane. Changes in water permeability for the membranes may be related to the differences in the membrane structure denseness. The M1 membrane having the lowest Vc of 1.6 ×10^{-3} (mol/cm^3) exhibited the water permeability of 96 L m^{-2} h^{-1} µm, while a reduction in the water permeability by about 10-30 % was observed for the M2, M3 and M3-T1 of higher Vc 1.8-2.4 ×10^{-3} (mol/cm^3). The M3-T2 sample having about twice the Vc value of the M1 sample exhibited the lowest water permeability of 14 L m^{-2} h^{-1} µm similar to the water permeability value of dense membrane of maleic acid cross linked poly(vinyl alcohol) network. The results indicated the structure denseness of silica-poly(vinyl alcohol) membrane, which is responsible for water permeability can be changed to a wide range by changing synthesis condition and heat treatment steps. Similar effect of heat treatment on performance of poly (vinyl alcohol) membrane prepared by dual cross-linking with silica and maleic acid was observed.[17] We further observed that these unsupported membranes had poor mechanical strength and seems to be inappropriate for practical uses in the desalination process application and however, if membrane is thinly coated over a porous hollow fiber polymer support, it become mechanically stable. These results will be published elsewhere. The suitability of this membrane type for other separation applications will also be explored in near future.

Table 4 Comparison of silica-poly (vinyl alcohol) hybrid membranes from different preparations in desalination of saline water

Material type	Wt. % SiO_2	Wt. % MA[a]	Water Permeability L m^{-2} h^{-1} µm	Thickness µm	Salinity in PPM	% S/R	Reference
Poly(vinyl alcohol)-maleic acid	0	13	19.7	110	2000	99.9	Neat (This study)
Poly(vinyl alcohol)-SiO_2	29	0	96.0	75	2000	99.9	M1 (This study)
Poly(vinyl alcohol)-SiO_2	29	0	90.6	75	2000	99.9	M2 (This study)
Poly(vinyl alcohol)-SiO_2	29	0	74.1	75	2000	99.9	M3 (This study)
Poly(vinyl alcohol)-SiO_2	29	0	60.5	75	2000	99.9	M3-T1 (This study)
Polyvinyl alcohol-SiO_2	29	0	14.0	75	2000	99.9	M3-T2 (This study)
Poly(vinyl alcohol)-maleic acid-SiO_2	25	20	18.3	5	2000	99.9	15
Poly(vinyl alcohol)-maleic acid-SiO_2	10	20	27.6	5	2000	99.9	15
Poly(vinyl alcohol)-maleic acid-SiO_2	10	5	56.0	20	2000	99.9	16
Poly(vinyl alcohol)-GA[b] –PAN[c] –PET[d]	0	0	5.9	0.7	5000	99.9	24

[a] Maleic acid [b] Glutaraldehyde,[c]Polyacrylonitrile,[d]Polyethylene terephthalate

Conclusions

A new preparation route of silica-poly (vinyl alcohol) membrane is reported here. In this route, a sol-gel reaction to form hybrid membrane structure was carried out in acidified and hydrated ethanol. Amount of water present in the hydrated ethanol was varied from 2.4 to 6.5 moles per 1 mole of ethanol. The ^{29}Si NMR, TEM and the small-angle scattering studies were performed on the samples and the results indicated homogeneous structure of the hybrid membranes having Q^4/Q^3 ratio of SiO_4 tetrahedra in range of 1 to 1.6. The self-condensation reaction of silicate group was prevented in this case due to high amount of acidified ethanol in sol-gel synthesis system. Even when membrane was heated at 150 °C after prior degassing at 60 °C, the increase in the size of silica domains in the hybrid membranes was only limited up to 2 - 7 nm which might imply that silicate polymerization and aggregation at higher temperature leading to bigger silicate particle could be

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largely prevented by removal of hydrolysing agent and solvent prior to the heating step at higher temperature. The other physico-chemical properties of the membrane were also studied by DSC, IR, TGA, XRD and swelling studies. The hybrid membrane exhibited water permeability up to 96 L m^{-2} h^{-1} μm with 99.9 % salt rejection efficiency in pervaporation of saline water of 2000 ppm NaCl .

Acknowledgments

The authors would like to thank Council of Scientific and Industrial research, India for financial support as research grants (9/1/CS/CSMCRI (1)/2012-13-PPD) under 12th Five-year-plan CSIR Network project. The instrumentation facility provided by 'Analytical Discipline & Centralized Instrument Facility', CSIR-CSMCRI, Bhavnagar, is also gratefully acknowledged. CSIR-CSMCRI Communication Number: 139/2014

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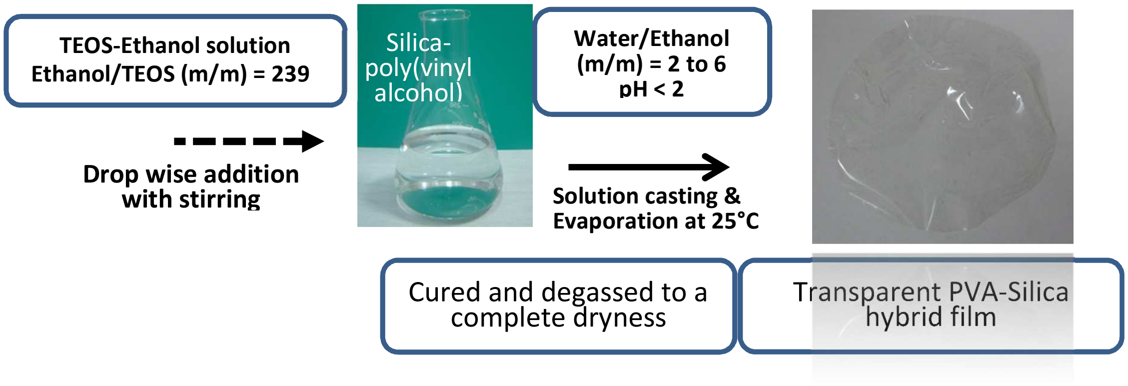
Graphical abstract

A synthesis route of sol-gel reaction in acidified and hydrated ethanol to prepare silica-poly (vinyl alcohol) hybrid membrane of nanoscale homogeneity is reported.



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