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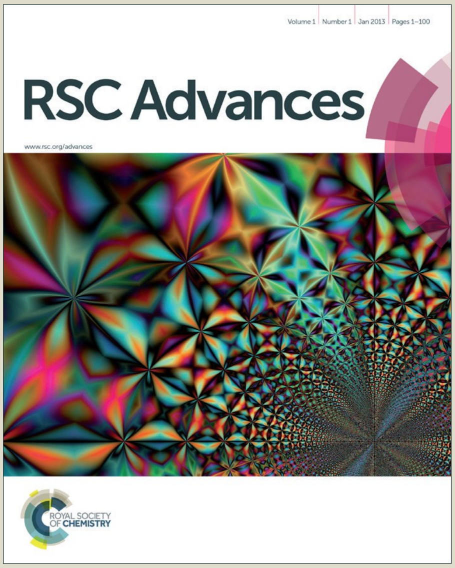

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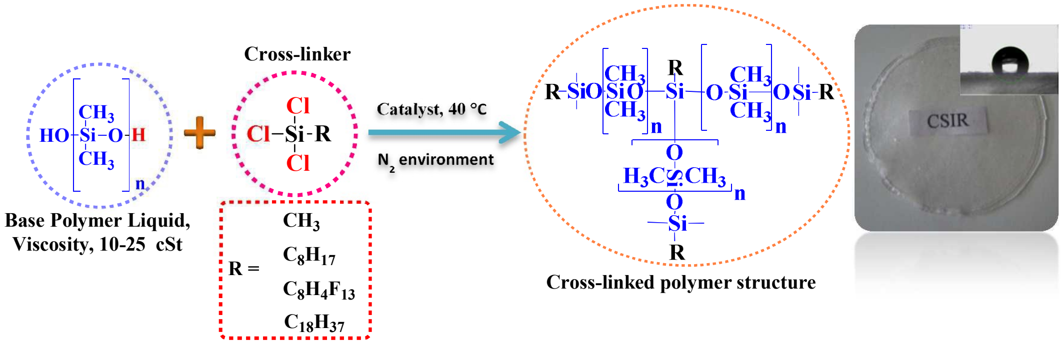
Graphical abstract



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Preparation and characterization of new poly(dimethylsiloxane) membrane series via a 'cross-linking' reaction using monomolecular trichloro(alkyl)silane of different alkyl chain and type

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Poly(dimethylsiloxane) (PDMS) membrane, which is generally prepared by cross-linking a hydroxyl-terminated-poly(dimethylsiloxane) liquid with a polymethylhydrosiloxane cross-linker through condensation reaction between the hydroxyl end groups and hydride groups liberating hydrogen, is one of the most studied polymeric membrane for separation of gases and liquids. Herein, new PDMS membrane series prepared by direct cross-linking hydroxyl terminated polydimethylsiloxane pre-polymer liquid with RSiCl$_3$ molecules of different types in *n*-heptane solvent under nitrogen environment were studied, where the alkyl chain R was varied as methyl CH$_3$, octyl C$_8$H$_{17}$, perflourooctyl C$_8$H$_4$F$_{13}$, octadecyl C$_{18}$H$_{37}$. For each membrane series, the amount of cross-linker to pre-polymer was varied as 13:87, 33:67 and 50:50 (w/w) to compare the membranes at different cross-linking densities. The cross-linked network structure of the membrane was comprised of dimethylsiloxane network structures of two cross-links and alkylsiloxane network structure of two or three cross-links. Changes in structure and properties of the membranes depending on concentration and type of trichloro(alkyl)silane used were observed using XRD, SEM, TEM, SANS, TGA, DSC, ^{29}Si NMR, IR, Cross-linking density, Contact angle (water) and ethanol-water separation performance measurements. The membranes with an optimal amount of trichloro(alkyl)silane cross-linker as about 10 – 30 % (w/w) performed better separation performance than the other reported conventional PDMS membranes in terms of the ethanol selectivity and flux from an aqueous feed containing 5% (w/w) ethanol. Among the prepared membranes, the membranes cross-linked with perfluorooctylsiloxane/ octadecylsiloxane showed better separation performance than those membranes cross-linked with methylsiloxane/ octylsiloxane.

Introduction

Poly(dimethylsiloxane) -Si(CH$_3$)$_2$O- (PDMS) membrane is one of the most studied polymeric membrane for separation of gases and liquids because of its hydrophobic property, large free volume and high permeability to gases and organic molecules[1-2]. The demand for new PDMS membrane with improved properties is increasingly urged in view of its effectiveness and reliability in industrial processes. The PDMS membrane is a cross-linked polymer in which important developments[3] such as (i) strain-induced crystallization through control of chain stiffness or stereo-chemical structure, (ii) dangling chain networks, (iii) possible thermoplastic elastomers, (iv) bimodal network chain-length distributions, and (v) cross-linking in solution, could be possible.

It is generally prepared by cross-linking the hydroxyl-terminated-poly(dimethylsiloxane) liquid pre-polymer with a polymethylhydrosiloxane cross-linker[4-12] through condensation reaction between the hydroxyl end groups and hydride groups in presence of a reduction catalyst liberating hydrogen. The properties of the PDMS membrane could be greatly influenced by the type of solvent used in the preparation, cross-linking reaction temperature, and curing conditions such as, degassing prior to curing and curing at different temperatures[9] as well as the membrane thickness[13]. The thin membrane film coated on porous support normally exhibited less-dense structure with higher amount of the chain aggregates. Alkoxysilane such as tetraethoxysilane Si(OR)$_4$[14-22] was also widely used as cross-linker in which the hydroxyl end groups of the PDMS pre-polymer liquid were cross-linked multi-dimensionally with the ethoxy groups (-OR) of the monomolecular Si(OR)$_4$ unit. By choosing trialkoxysilane R'Si(OR)$_3$, where R' is phenyl[23] or vinyl group[24], the PDMS membranes of different properties as a result of different distributions of network chain lengths, could be obtained. Recently, we have prepared improved PDMS membranes by cross-linking reaction between hydroxyl

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terminated polydimethylsiloxane macromolecules and polymethylhydrosiloxane macromolecules along with a small amount of monomolecular cross-linker either of trichloro(*n*-octadecyl)silane or trichloro(1H,1H,2H,2H-perflourooctyl)silane in toluene solvent, which showed a better separation performance as compared to the typical PDMS membrane in the removal of volatile organics from aqueous streams[25]. Some disadvantages of these monomolecular organosilane cross-linkers are formation of aggregated silica particles by hydrolysis of the organosilane with moisture present in the environment. By carrying out the reaction under moisture-free nitrogen environment hydrolysis of the organosilane may be almost prevented.

In the present work, new PDMS membrane series prepared by direct cross-linking hydroxyl terminated polydimethylsiloxane liquid with $RSiCl_3$ molecules of different types in n-heptane solvent under nitrogen environment were studied, where the alkyl chain R was varied as methyl CH_3, octyl C_8H_{17}, perflourooctyl $C_8H_4F_{13}$, octadecyl $C_{18}H_{37}$. For each membrane series, the amount of cross-linker to pre-polymer was varied as 13:87, 33:67 and 50:50 (w/w) to compare the membranes at different cross-linking densities.

Experimental

Materials and methods

Trichloro(methyl)silane; Trichloro(octyl)silane; Trichloro(1H,1H,2H,2H-perflourooctyl)silane; n-Trichloro(octadecyl)silane; Dibutyltindilaurate; Chloroform–D ($CDCl_3$); Hydroxy-terminated PDMS liquid of 18,000 – 22,000 cSt viscosity were purchased from the Sigma-Aldrich Chemical Co. Membrane structure networks were produced from a cross-linking reaction of the hydroxyl end-linked PDMS pre-polymer liquid with an tricholoro(alkyl)silane through condensation reaction between the hydroxyl end groups and chloride groups in presence of the dibutyltindilaurate catalyst releasing HCl. The functionality of the cross-linker which is the number of available sites per molecule for the cross-linking reaction is 3 in each case. A homogenous polymer solution of about 20 cSt viscosity was prepared by dissolving the hydroxyl-terminated PDMS pre-polymer (20 %, w/w) in *n*-heptane. *n*-Heptane was of analytical reagent grade and purchased form S.D Fine-Chem. Ltd., India. All the purchased chemicals were used as purchased. A required amount of trichloro(alkyl)silane cross-linker was added to the above solution and the solution was mixed well with stirring. Cross-link structures were formed by adding the dibutyltindilaurate catalyst (3 wt. % of catalyst with respect to total mass of polymer and cross-linker) and keeping the solution at 40°C for 45 minutes. All these steps were done in nitrogen environment. The condensation reaction process between the PDMS pre-polymer liquid and trichloro(alkyl)silane is shown in Scheme 1. The cross-linked polymer was poured into a petridish and kept inside a closed chamber; and it was then allowed to cure at room temperature for 12 h by evaporating the solvent under flowing nitrogen through the chamber. This resulted in formation of dense rubbery membrane film. The membrane film was further cured in an oven at 80 °C for another hour. Membranes were prepared for the following studies: (i) alkyl carbon chain length of the trichloro(alkyl)silane cross-linker was varied as C_1, C_8 and C_{18} to study the effect of the alkyl chain length of the cross-linker; (ii) two types of the C_8-alkyl: octyl (C_8H_{17}) and perfluorooctyl ($C_8H_4F_{13}$) were chosen to study the effect of hydrophobicity of the alkyl chain of same length; (iii) for each cross-linker, three proportions of the cross-linker to the pre-polymer PDMS, as 13:87, 33:67 and 50:50 (w/w) were taken for the comparison in their cross-linking densities. The synthesis compositions of all membrane samples studied are given in Table 1.

Table 1 Synthesis composition of the membranes studied

Sample series	Octadecyltrichlorosilane			Perfluorooctyltrichlorosilane			Octyltrichlorosilane			Methyltrichlorosilane		
	PDMS-ODS1	PDMS-ODS2	PDMS-ODS3	PDMS-FOS1	PDMS-FOS2	PDMS-FOS3	PDMS-OS1	PDMS-OS2	PDMS-OS3	PDMS-MS1	PDMS-MS2	PDMS-MS3
Cross-linker (alkyltricholorosilane), wt. %	13	33	50	13	33	50	13	33	50	13	33	50
Base polymer liquid (PDMS), wt. %	87	67	50	87	67	50	87	67	50	87	67	50

Membrane morphology

Surface morphology of the membranes was analysed by acquiring the surface images using scanning electron microscope instrument (LEO 1430VP) with 5-20 KV accelerating voltage. Philips X'pert MPD system diffractometer was used to carry out X-ray diffraction experiments of the samples over the 2θ range from 5 to 50° with the scanning rate of 2°/minute. Transmission Electron Microscopy (JEOL JEM 2100) image of the selected samples were taken to observe poly(alkylsiloxane) particles in the membranes. Thin polymer films were coated on the copper girds and imaging was carried out at 80–200 kV accelerating voltage.

Small-angle neutron scattering (SANS) study

SANS study was carried out to investigate the nanostructure of membrane materials prepared. The measurements were carried on a SANS instrument at Dhruva reactor, BARC, Mumbai, India[26]. The scattering measurements were carried out at

25 °C, over the wave vector (Q) range of 0.015 – 0.35 $Å^{-1}$. Q is defined as ($4\pi/\lambda$) sin Θ, where 2Θ is the scattering angle and λ is the wavelength of incident radiation. The measurements were carried out using samples kept in 2 mm path length Hellma quartz cells. The sample preparation was done in $CDCl_3$ by the same procedure described in our earlier studies[25]. The data analysis was done after carrying corrections from instrumental smearing and incoherent scattering. In general, the expression of intensity of scattering, $I(Q)$ is given by

$$I(Q) = \phi.\Delta\rho^2.V_p.P(Q).S(Q) \qquad (1)$$

ϕ is the number density of scattering unit, V_p is the scattering unit volume, $\Delta\rho^2$ is the contrast factor. The form factor $P(Q)$ reflects the distribution of scattering material in the scattering particle, while the structure factor, $S(Q)$ is related to the spatial distribution of the scattering particles in the surrounding medium such as solvent. When there are correlations of position or orientation between the scattering units, the $I(Q)$ is contributed from the both $P(Q)$ and $S(Q)$ factors. In such system, the Ornstein-Zernike approach can be applied to describe the correlation from direct interactions between the pair of interacting scattering units and interactions through other scattering units using the Lorentzian form of the scattering intensity to estimate the average distance between the interacting macromolecular segmental units of a cross-linked polymer. Thus, the scattering of polymeric chain can be defined by Ornstein-Zernike (OZ) formulation by Lorentzian equation to estimate the average distance given by the correlation length ξ_{OZ}[27]. A Lorentzian form for the Q-dependence of the scattering intensity, $I(Q)$ can be assumed as

$$I(Q) = \frac{I(0)}{1+Q^2\xi_{OZ}{}^2} \qquad (2)$$

Where $I(Q)$ is the forward scattering intensity at $Q = 0$

Debye-Anderson-Brumberger (DAB) equation is a Lorentzian-square term and it can be used to calculate the scattering from a randomly distributed (non-particulate) two-phase system[27]. The measure of the average spacing between two phase regions is given by ξ_{DAB}.

$$I(Q) = I(0)\frac{1}{[1+(Q\xi_{DAB})^2]^2} \qquad (3)$$

The scattering function given by the sum of a Lorentzian and a Lorentzian-squared term is the prediction of Random Field Ising Model as

$$I(Q) = \frac{A}{1+Q^2\xi_1{}^2} + \frac{B}{[1+(Q\xi_2)^2]^2} \qquad (4)$$

Where A and B are constants

The Random Field Ising Model can describe the correlation from interactions between the polymer chain segmental units where the correlation length varies between tens and hundreds of angstroms[28]. Further, the Gaussian characteristic for the polymer chains can be studied using Kratky plot [Q_2.I(Q) vs. Q] as described elsewhere[29].

Thermal properties

The differential scanning calorimetric studies were carried using a Mettler Toledo differential scanning calorimeter (DSC 822^e) instrument at the heat rate of 5°/ minute from -120 to 20°C. About 5 mg of the samples were taken and heated from -140°C to room temperature at a heating rate of 10°C/min for the measurements. Thermogravimetric (TGA) analysis of all the prepared membranes was carried out with NETZSCH TG 209F1 Libra TGA209F1D-0105-L instrument. About 10 mg of the samples were taken and heated from room temperature to 800°C at a heating rate of 10°C/min under nitrogen environment for the measurements.

NMR, IR, contact-angle, cross-linking density and separation performance studies of the membranes

The solid state ^{29}Si Nuclear magnetic resonance measurements were carried out using a Bruker AVANCE-II 500MHz instrument. Attenuated-total-reflectance Infra-red (ATR-IR) spectroscopy studies were recorded with a Perkin-Elmer Spectrum GX (with a resolution of ± 4 cm^{-1}, incident angle 45˚). The hydrophobicity of the membrane surface was measured by contact angle (water) measurements on DSA 100 Kruss GmbH instrument. The contact angles were measured for 5-6 times on different areas of the each membrane surface to get average value. The swelling degree measurements of all the membranes were carried out in carbon tetrachloride solvent. Membrane film of 1 cm^2 area was cut and dipped in the solvent for 30 minutes. After that, the sample was taken out from the solvent and immediately wiped with tissue paper and measured the weight of swollen membrane. Each measurement was repeated three times and average values were taken for calculations. The percent mass uptake of the swelled membrane sample upon was then obtained. The cross-linking density, V_c (mol. cm^{-3} of polymer) was calculated from the volume fraction of polymer (ϕ_p) in the swelled membrane using the Flory-Rehner equation as described elsewhere[25].

The separation performance of the membranes was evaluated through pervaporation experiments for the removal of organics from aqueous solutions. The experiments were carried out with laboratory fabricated unit described elsewhere[9] at 70 °C using aqueous feed solution containing ethanol. The effective membrane area was 18.86 cm^2. The downstream pressure was maintained at ~ 2 mbar generated by a two stage vacuum pump (Alcatel, France) and measured by MKS Series 925 pressure transducer with micro-pirani readout. Permeate was collected in a cold trap cooled in liquid nitrogen. Before every measurement the pervaporation system was stabilized for one hour and initial permeate of one hour was discarded. The feed and permeate concentrations were measured by an offline GC (Perichrom GC, France). The separation factor of mixture was expressed as,

$$\alpha = \frac{P_0/F_0}{P_w/F_w} \qquad (5)$$

Results and discussion

Preparation of PDMS membranes by cross-linking with trichloro(alkyl)silane

Series of membrane sheets were obtained by cross-linking of hydroxyl terminated PDMS pre-polymer liquid with $RSiCl_3$ and the amount of RSiCl3 to the PDMS pre-polymer was varied as 13:87, 33:67 and 50:50 (w/w) as mentioned in Table 1. The preparation strategy for the cross-linked polymer membrane is as shown in Scheme 1. Photographs of the membrane sample sheets were taken to compare the transparency of the membranes. These are shown in Figure 1.

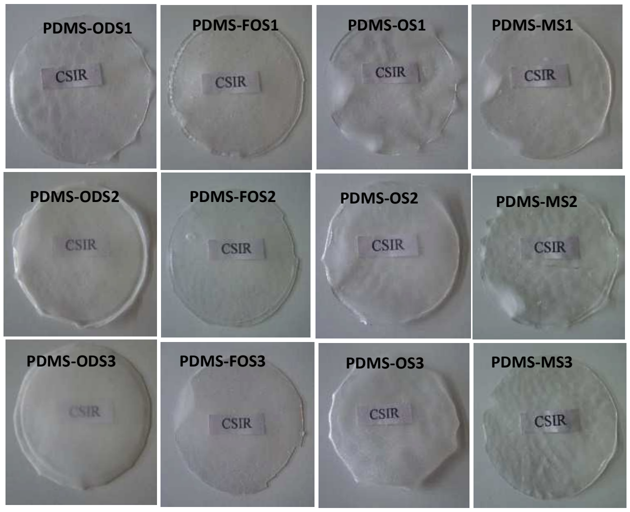
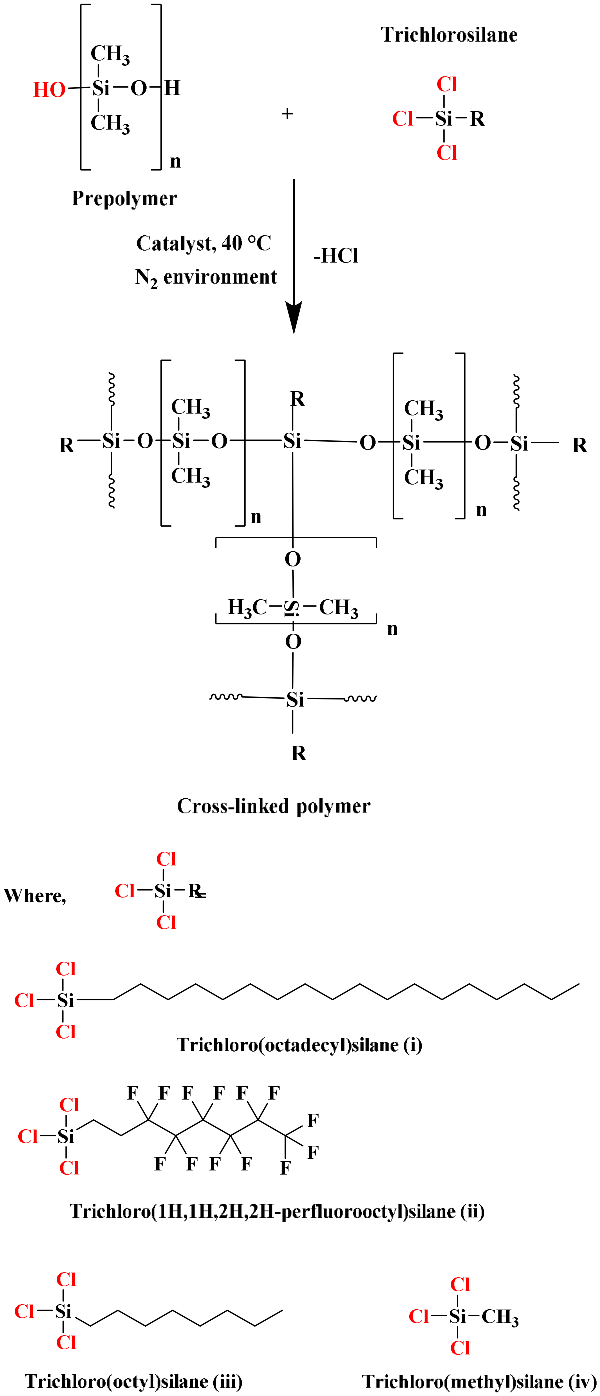


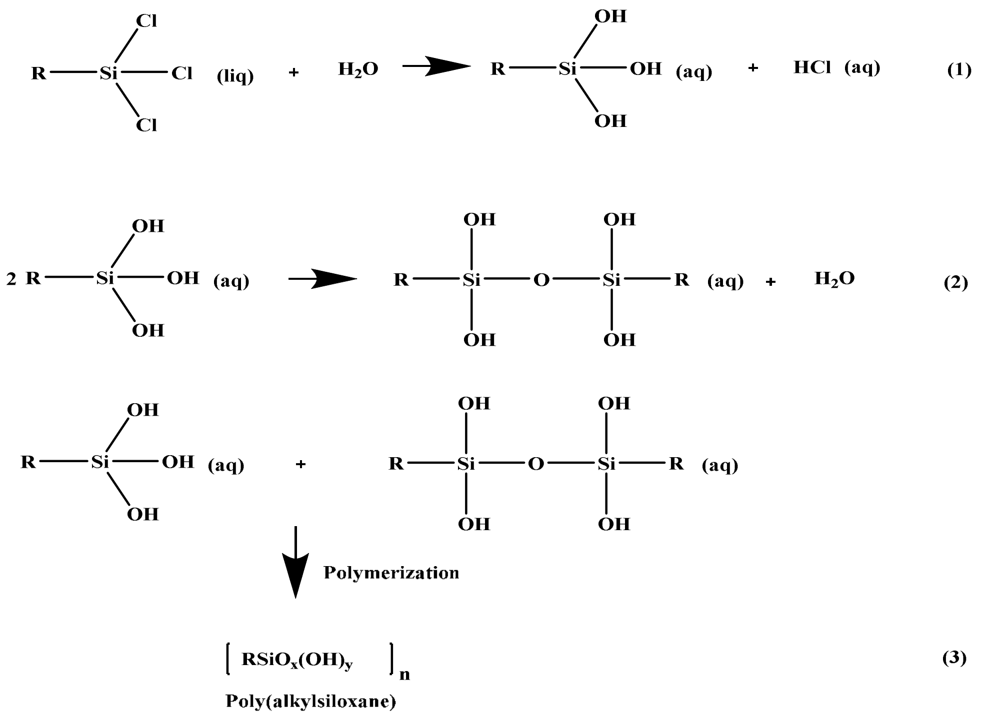
Fig. 1 Photographs of the membrane sample

Both the PDMS-MS and PDMS-OS membrane series cross-linked with trichloro(methyl)silane and trichloro(octyl)silane were very transparent at all the compositional (cross-linker : pre-polymer) ratios studied. Relatively, the film transparency was less for the PDMS-FOS and PDMS-ODS samples cross-linked with higher amounts (33-50 wt.%) of trichloro(perfluorooctyl)silane or, trichloro(octadecyl)silane. The highest opaqueness among the membrane films was the sample made with 50 wt.% of trichloro(octadecyl)silane. The film opaqueness is expected if aggregates or clusters are formed in the membrane film. This is possible if some of the trichloro(alkyl)silane molecules themselves polymerized to poly(alkylsiloxane) as a result of hydrolysis reaction of trichloro(alkyl)silane with moisture present in system environment. Formation of poly(alkylsiloxane) upon hydrolysis of trichloro(alkyl)silane, followed by condensation and polymerization reactions of the hydrolysed species is well-known[30] as shown in reaction 1, 2 and 3 of Scheme 2.



Scheme 1 Cross-linking reaction of PDMS with organosilanes

XRD patterns of the PDMS membrane samples as shown in Figure 2 also indicated the change in membrane structure after cross-linking with the trichloro(alkyl)silane. A broad diffraction peak at 2*Θ* value of about 12.1° was observed for the samples prepared from the cross-linking reaction with low amount of the trichloro(alkyl)silane (13 wt.%) suggesting a partly crystalline nature of PDMS. The intensity of the peak was decreased for the samples from the reaction with higher amount (33-50 wt.%) of the trichloro(methyl)silane whilst this peak was disappeared for the samples from the reaction with 33-50 wt.% of the trichloro(octyl)silane, trichloro(perfluorooctyl)silane or, trichloro(octadecyl)silane.



Scheme 2 Formation of poly(alkylsiloxane) upon hydrolysis of trichloro(alkyl)silane, followed by condensation and polymerization

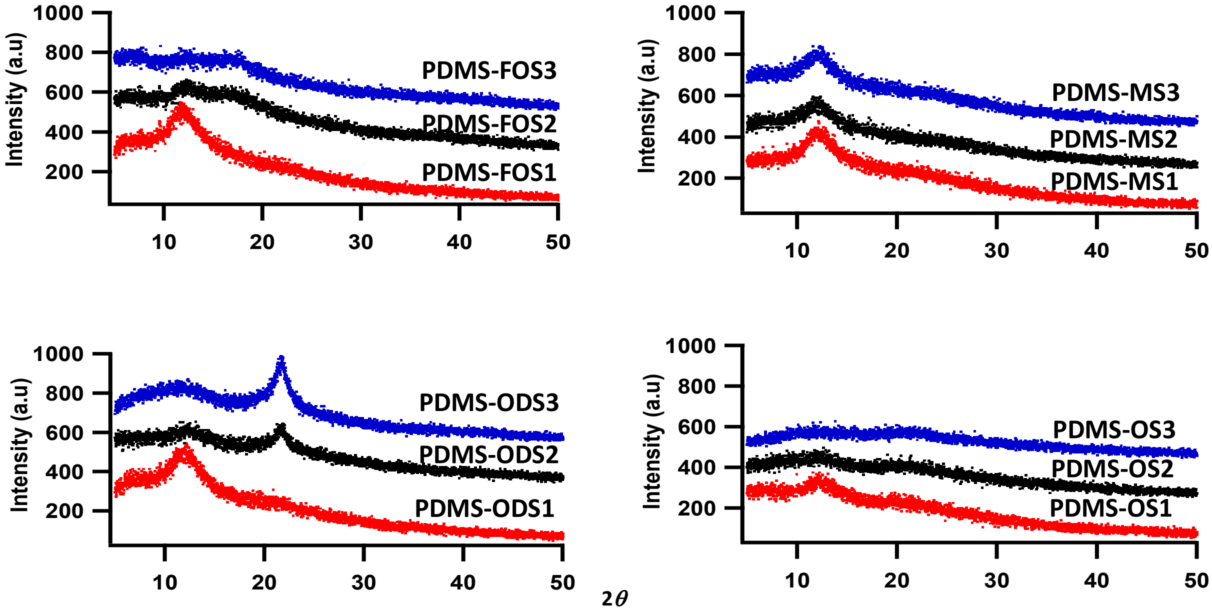


Fig. 2 XRD patterns of the all samples

The XRD results inferred that the PDMS membranes formed by crosslinking with trichloro(methyl)silane had crystalline regions even from the reaction with the 50 wt. % trichloro(methyl)silane in contrast to the others which exhibited a completely amorphous nature of PDMS after the reaction with the 33-50 wt. % trichloro(alkyl)silane. On the other hand, the sample cross-linked with 33-50 wt.% of trichloro(octadecyl)silane showed an additional broad peak at about 21.3° which is referred as poly(octadecylsiloxane)[30]. Changes in membrane structure in terms of microstructure morphology of the samples cross-linked with different amounts of trichloro(octadecyl)silane were clearly distinguishable by SEM images as shown in Figure 3 (A1, A2 and A3). The PDMS-ODS3 sample cross-linked with 50 wt. % of trichloro(octadecyl)silane showed rugged surface in micrometre-length-scale as compared to relatively smooth surface of the PDMS-ODS1 and PDMS-ODS2 samples prepared with 13 and 33 wt. % trichloro(octadecyl)silane. All other sample series (PDMS-MS, PDMS-FOS and PDMS-OS) cross-linked with trichloro(methyl)silane trichloro(octyl)silane, trichloro(perfluorooctyl)silane exhibited relatively more smooth surface than the PDMS-ODS samples. The rugged surface morphology of PDMS-ODS3 may be related to hybrid structure formed by PDMS and poly(octadecylsiloxane) components. The poly(octadecylsiloxane) is crystalline and so it is harder than the PDMS component. Therefore, it is likely that poly (octadecylsiloxane) crystalline components in excess, is separated from the PDMS components. Indeed, nanoscale particles presumably of the poly(octadecylsiloxane) material were clearly visible by TEM in the samples prepared by cross-linking with 33-50 wt.% of the trichloro(octadecyl)silane.

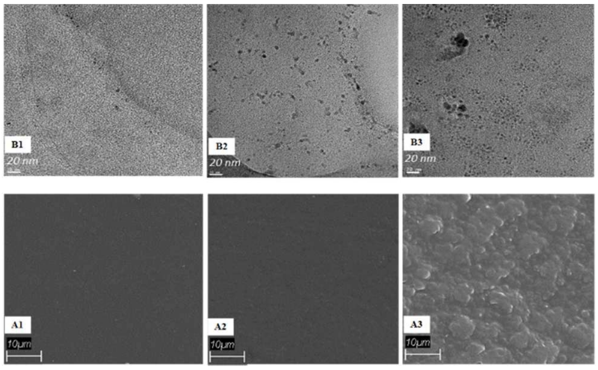


Fig. 3 A1, 2, 3 are SEM surface images while B1, 2, 3 are TEM images of PDMS-ODS1, 2, 3 respectively.

The TEM images of the PDMS-ODS samples are shown in Figure 3 (B1, B2 and B3). Large aggregation of these nanoparticles was clearly observed in the TEM image of the PDMS-ODS3 sample cross-linked with 50 wt.% of the trichloro(octadecyl)silane. Although such large nanoparticle aggregates were not observed in the other membrane series, formation of nanoparticles in the membrane series cross-linked with excess trichloro(alkyl)silane was evident from the TEM studies of the samples. SANS measurements on the samples were performed in order to probe membrane nanostructure in detail.

Nanostructure of the membranes as studied by SANS

As shown in the preparation route (Scheme 1), the PDMS membrane structure may comprise of two characteristic segments of dimethylsiloxane and alkylsiloxane. The dimethylsiloxane group may be considered as soft segment as it is being derived from the PDMS pre-polymer liquid precursor. On the other hand, the alkylsiloxane group may be of various types and hard structure as it is resulted from the cross-linking reaction directly with molecular trichloro(alkyl)silane or with the derived species from hydrolysis, condensation and polymerization reactions of trichloro(alkyl)silane as shown in Scheme 2. Thus, the cross-linked membrane structure may consist of soft and hard segments corresponding of dimethylsiloxane and alkylsiloxane groups. SANS study were performed on the membrane samples to examine the nanoscale structure morphology on the basis of their scattering signatures. The SANS patterns for the membranes at room temperature over the period of 8-12 h were measured to collect statistically meaningful data. Figure 4 shows the SANS patterns. The SANS pattern can display scattering from both the soft and hard segments of the polymer membrane. The correlations of position or orientation between the soft segmental units of the polymer membrane structure is described by the Ornstein-Zernike approach in which the $I(Q)$ is contributed from the both $P(Q)$ and $S(Q)$ factors. The Ornstein-Zernike approach estimate the average distance between the soft macromolecular segmental units of a cross-linked polymer using the Lorentzian form of the scattering intensity. On the other hand, a Lorentzian-square term as Debye-Anderson-Brumberger equation given in eq 2 can be used to calculate the scattering from a randomly distributed (non-particulate) two-phase system characterized by a single correlation length scale. This correlation length scale is of a much larger value than the value obtained by the Ornstein-Zernike approach. Using Lorentzian-square term of Debye-Anderson-Brumberger equation, the correlation length between the hard segmental units of the cross-linked polymer may be described for the reason that the correlation length scale between the hard segments of the polymer can be higher considering their less-flexible nature. Indeed, as shown in Figure 4, the SANS data of the cross-linked polymer samples were fitted excellently with scattering function given by the sum of a Lorentzian term from Ornstein-Zernike model and a Lorentzian-squared term from Debye-Anderson-Brumberger model. As expected, the correlation length ξ_{OZ} corresponding to the soft polymer segments were smaller as about 7 - 12 Å than the correlation length ξ_{DAB} values (20 – 63 Å) of hard polymer segments (Table 2). Commonly for each the membrane series, the ξ_{DAB} value was increased for the membrane with increase in the cross-linking degree with trichloro(alkyl)silane.

Kratky plots [$Q^2.I(Q)$ vs. Q] for the membranes (as shown in Figure 5) were compared to identify the structural differences in Gaussian characteristics of the scattering chains. All the plots were inclined to a horizontal asymptote implying Gaussian statistics of polymer chain.

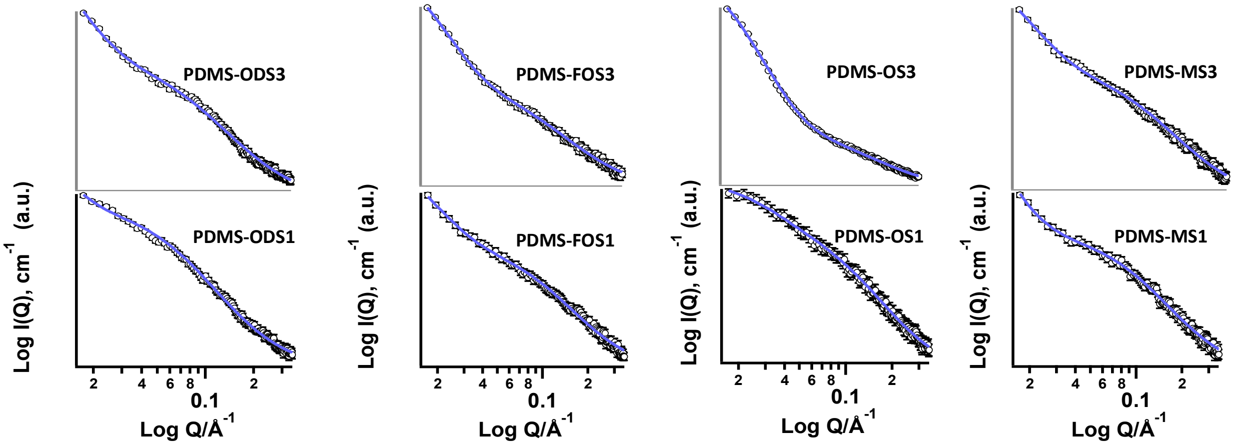


Fig. 4 SANS data of the cross-linked polymer membrane samples of the lowest and highest alkylsiloxane content, fitted excellently with scattering function given by the sum of a Lorentzian term from Ornstein-Zernike model and a Lorentzian-squared term from Debye-Anderson-Brumberger model

Table 2 The correlation length, ξ and the intensity of scattering, *I(0)* obtained by Ornstein-Zernike and Debye-Anderson-Brumberger model

Sample details	Ornstein-Zernike		Debye-Anderson-Brumberger	
	ξ_{OZ}, Å	$I(0)_{OZ}$, cm^{-1}	ξ_{DAB}, Å	$I(0)_{DAB}$, cm^{-1}
PDMS-ODS1	10.1	0.7	24.2	1.4
PDMS-ODS2	11.9	1.1	24.3	1.8
PDMS-ODS3	11.4	1.1	62.9	7.6
PDMS-FOS1	9.4	0.4	31.8	1.0
PDMS-FOS2	10.1	0.5	43.8	2.1
PDMS-FOS3	8.9	0.4	46.5	3.2
PDMS-OS1	7.5	0.3	19.9	0.5
PDMS-OS2	9.3	0.6	50.6	23.9
PDMS-OS3	7.0	0.5	52.7	31.8
PDMS-MS1	7.6	0.4	44.0	1.0
PDMS-MS2	7.3	0.3	44.6	1.2
PDMS-MS3	8.7	0.6	46.4	2.1

Two important observations from the Kratky plots are (1) the *Q* value at which the plateau value reached was lower for the PDMS-ODS membrane series than the other membrane series and (2) A peak at low Q value in each of PDMS-OS2 and PDMS-OS3 membrane was clearly observed. This indicated that the Gaussian segmental length of polymer chain networks was longer for the PDMS-ODS membrane series as compared to the other membrane series since the plateau *Q* value is inversely proportional to the Gaussian segmental length. On the other hand, the low Q peak observed in case of PDMS-OS2 and PDMS-OS3 may correspond to polymer mesh size or aggregated cluster of polymer chains formed by localized cross-linking. Such low Q peak was also seen in some PDMS membranes [12]. On closer examination of the Kratky plots, a shoulder peak at low Q was apparently present in the PDMS-ODS3, all the PDMS-FOS series and all the PDMS-MS series implying some degree of polymer chain aggregation in most of the samples.

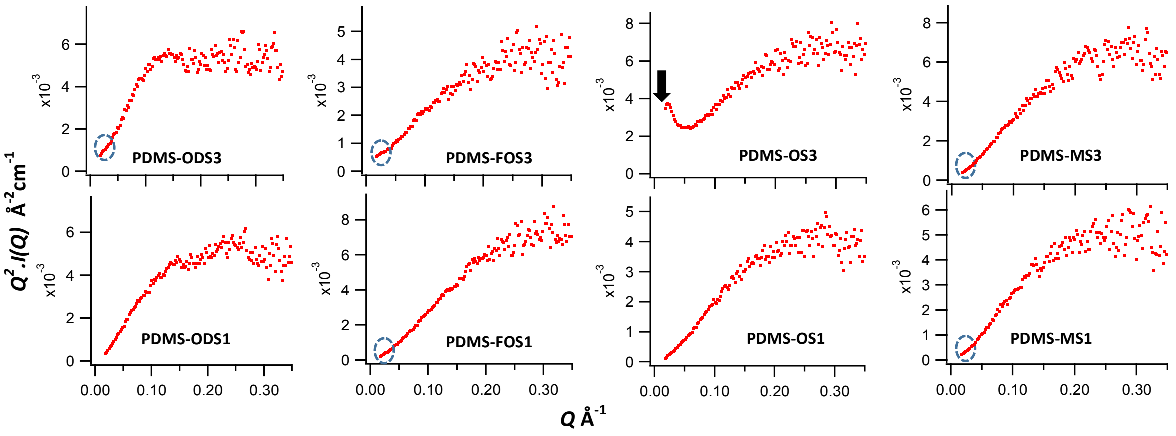


Fig. 5 Kratky plots [Q^2.*I(Q) vs. Q*] for the membranes of the lowest and highest alkylsiloxane content

TGA, DSC and cross-linking density measurements

The thermal stability of the membrane samples, as measured by TGA under nitrogen atmosphere is described in Figure 6. Among the sample series, the PDMS-FOS series decomposed relatively faster with onset and end point temperatures at about 300 °C and 590 °C, respectively. Whereas for PDMS-ODS sample series, the end point temperatures were extended to about 670 °C from the onset temperature of about 250 °C. The PDMS-OS and PDMS-MS series had the decomposition temperature range 270 °C – 650 °C and 260 °C – 620 °C, respectively. As shown in DTG (derivative of thermogravimetric analysis) plots (Figure 6 inset), the decomposition losses of samples were mostly at about 500 °C for all the PDMS-ODS and PDMS-FOS samples. But, two major decomposition steps with median peaks at about 400 °C and 520 °C were observed for the PDMS-OS and PDMS-MS samples of higher alkylsiloxane content (PDMS-OS2, PDMS-OS3, PDMS-MS2 and PDMS-MS3). This observation would mean that the base PDMS polymer chains were modified differently by cross-linking with the different types of alkylsiloxane.

Figure 7 shows the DSC plots of all the alkylsiloxane cross-linked PDMS membrane samples. The glass transition temperatures (T_g) for all the membranes were found to be similar at a temperature about - 100 °C while the melting peaks (T_m) were in the temperature range of - 48 ºC to - 40°C.

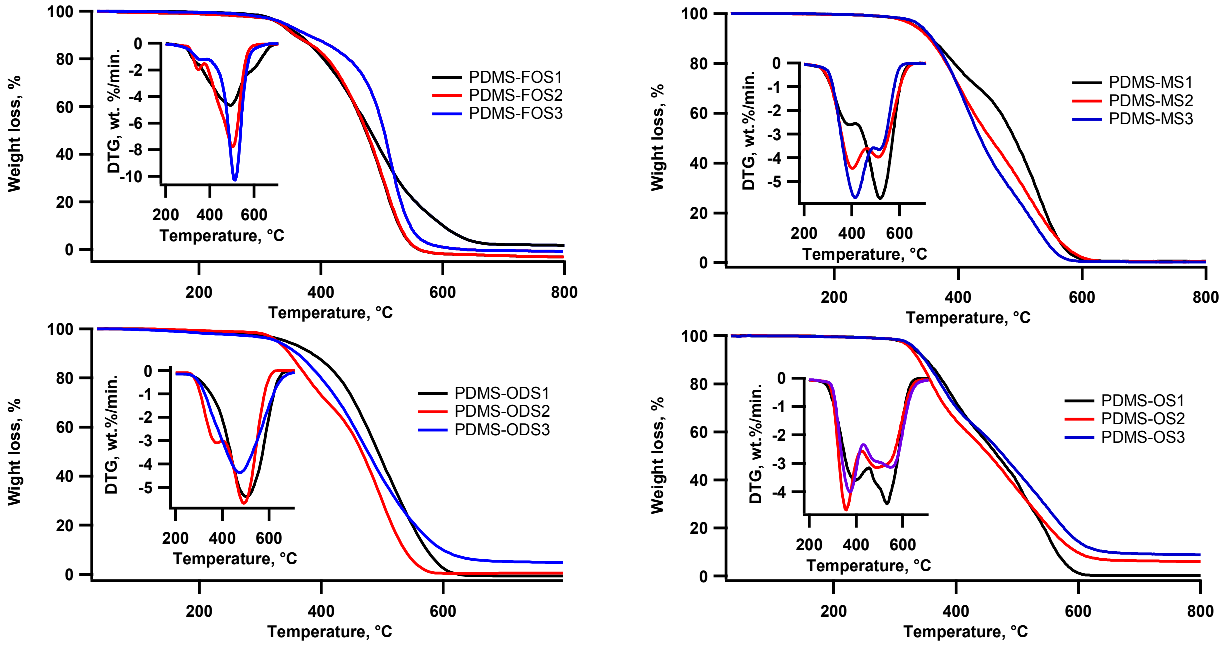


Fig. 6 TGA and DTG plots of the membrane samples

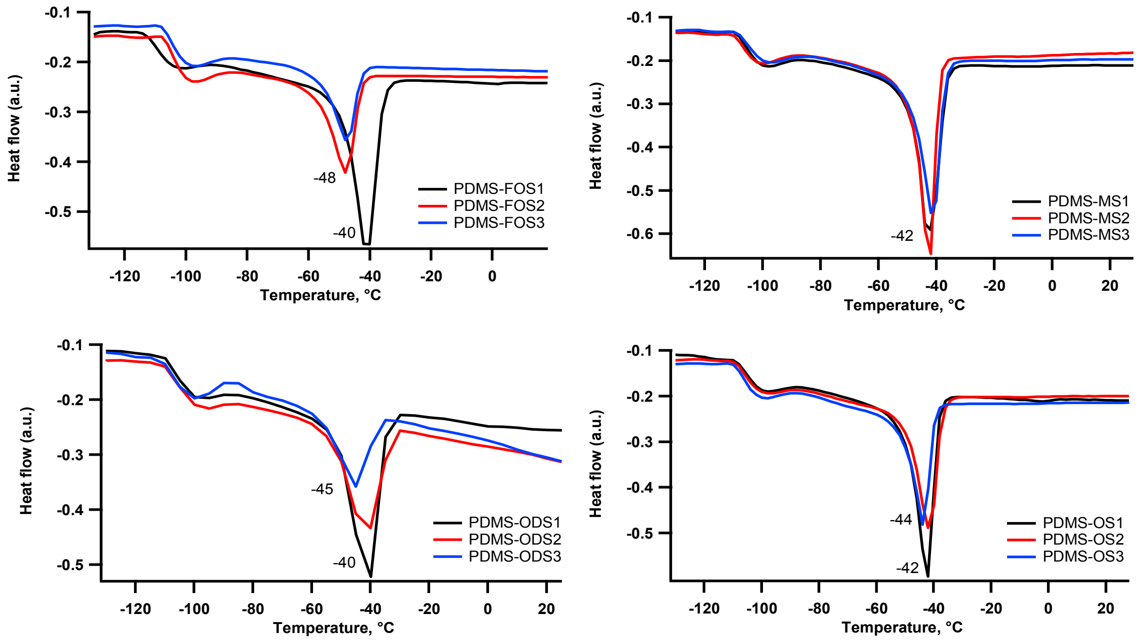


Fig. 7 DSC plots of the membrane samples

The presence of both the T_g and T_m peaks in the membranes indicated the semi-crystalline nature of the membrane material since the T_g peak corresponds to amorphous region while the T_m peaks corresponds to the crystalline region. For each membrane series, the intensity of the T_m peak for the membrane was found to be decreased by increase in the alkylsiloxane content. Furthermore, shifts of the T_m peaks towards lower values were observed for the PDMS-ODS (-40 °C to -45 °C), PDMS-FOS (-40 °C to -48 °C) and PDMS-OS (-42 °C to -44 °C) membranes of higher alkylsiloxane contents except the PDMS-MS samples which had the same T_m at about -42 °C. The decrease in the intensity and shifts to lower value of the T_m peak indicated the crystallinity of the initial PDMS structure was decreased by the cross-linking with alkylsiloxane. For the cross-linked structure, the segmental mobility of polymer chain is expected to be decreased resulting to decrease in the value of heat capacity.

The denseness of membrane structure in terms of cross-linking density (V_c) was examined by the membrane swelling in carbon tetrachloride. From the swelling experiments, the volume fraction of polymer (ϕ_p) was estimated. The V_c values were calculated from the ϕ_p values using the Flory-Rehner equation for all the membrane series. The M_c value for the sample was calculated based on the relation M_c = density × V_c^{-1} in which the density of the PDMS membrane was taken as density of pure polydimethylsiloxane material, 0.97 g cm^{-3} [31]. The results are given in Table 3.

Table 3 The volume fraction of polymer (ϕ_p), cross-linking density (V_c) and molecular weight between the crosslinks (M_c) of the membranes

Membrane	ϕ_p	V_c × 10^{-5} mol cm^{-3}	M_c g mol^{-1}
PDMS-ODS1	0.139	8.3	11563
PDMS-ODS2	0.204	19.0	5098
PDMS-ODS3	0.233	25.8	3761
PDMS-FOS1	0.176	13.8	7042
PDMS-FOS2	0.227	24.2	4011
PDMS-FOS3	0.258	32.6	2972
PDMS-OS1	0.147	9.4	10268
PDMS-OS2	0.225	23.8	4068
PDMS-OS3	0.315	53.3	1820
PDMS-MS1	0.109	5.1	18844
PDMS-MS2	0.127	7.0	13857
PDMS-MS3	0.133	7.7	12570

Among all the membranes, the V_c value 5.1 × 10^{-5} mol cm^{-3} of the PDMS-MS1 was the lowest. The denseness of membrane structure was found to be affected by type of trichloro(alkyl)silane used as well as the trichloro(alkyl)silane concentration. The membrane structure denseness in terms of the ϕ_p, the V_c and the M_c values was the highest for the PDMS-FOS1 at low loading (13 wt. %) of trichloro(alkyl)silane. Whereas, at the high loading (50 wt. %) of trichloro(alkyl)silane, the highest V_c 53.3 × 10^{-5} mol cm^{-3} with the corresponding M_c 1820 g mol^{-1} was observed for the PDMS-OS3,which is about 10-times of the corresponding value of PDMS-MS1. PDMS-MS sample series exhibited relatively loose membrane structure with the V_c value range of 5.1 - 7.7 × 10^{-5} mol cm^{-3}.

^{29}Si NMR and FT-IR studies

The solid state ^{29}Si NMR spectra of the modified PDMS membrane series are shown in Figure 8. All the spectra show a prominent peak at -22 ppm which is assigned as the repeating D2 units (dimethylsiloxane units) of the polysiloxane chain[32, 33] and two small peaks at -57 ppm and -68 ppm. The ^{29}Si resonance at -57 ppm and -68 ppm of the spectra can be assigned, respectively, with general alkylsiloxane structures of $(HO)(R)Si(OSi)_2$ [isolated silanol, T^2 units] and $(R)Si(OSi)_3$ [siloxane, T3 units], where R = alkyl[30]. Although the resonance peaks of the T units were weak for some samples of low alkylsiloxane content, the T resonance peaks were well-resolved for most of the samples. The observation of presence of some T^2 units in the spectra indicates that the portions of network structures exhibit two cross-links with isolated silanols whereas the presence of T^3 units in the spectra indicating the network structures of three cross-links was more. Geminal silanol group $(HO)_2(R)Si(OSi)$ (T^1 unit) was absent in all the samples.

The Infra-red spectra of the membrane series are given in Figure 9. A broad absorption band at about 3230 cm^{-1} due to O-H stretching vibrations of the absorbed moisture, was observed in all the spectra. The absorption band due to O-H stretching vibration can be at higher wave number range if they are from structural O-H group of the materials, such as silanol alkylsiloxane structures (HO)(R)Si(OSi)2 of the membranes. Depending on the nature of OH groups, such as free OH groups, hydrogen bonded pairs (OH....HO), perturbed OH, etc. various structural OH absorption bands can be present in the spectra.[34]

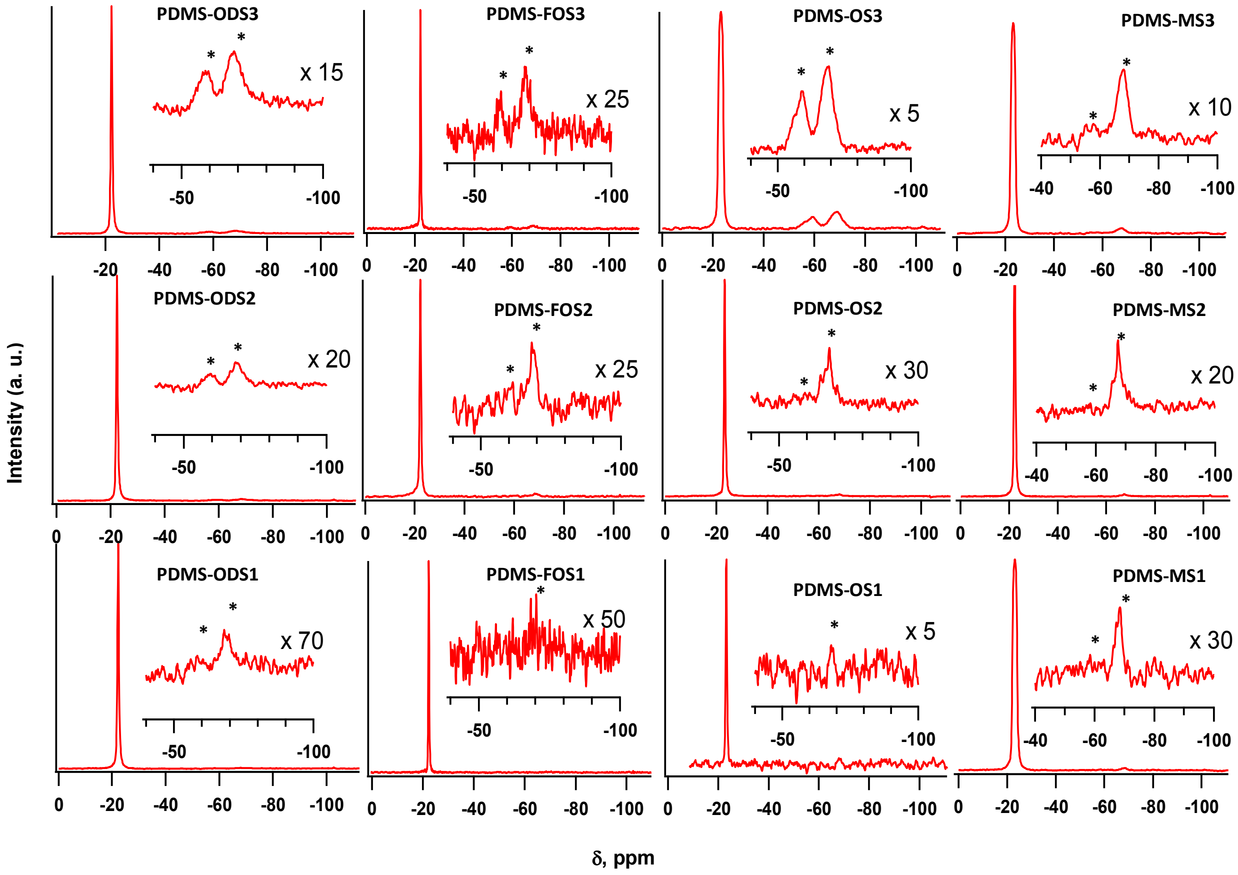


Fig. 8 The solid state ^{29}Si NMR spectra of the PDMS membrane series

This is what has been observed in all the spectra which show three weak bands at about 3600 cm^{-1}, 3723 cm^{-1}, 3820 cm^{-1} due to the silanols (T^2 units) in the network structure of the membranes. The bands in wave number range of 1500 – 1690 cm^{-1} are assigned as (Si)O-H••O(Si) vibrations in which (Si)O-H group form hydrogen bonding with oxygen of the siloxanes and bending mode of absorbed water. Such water and hydroxyl-related bands were observed in the IR spectra of silicate glasses[35]. Strong absorption band observed at 800 cm^{-1} is due to symmetric stretching vibration of Si-O-Si, rocking alkyl group and stretching vibration of Si-C bond of the alkylsiloxane structure of the membranes. The asymmetric stretching vibration of the Si-O-Si (siloxane) bonds for the membranes was observed at 1020 and 1090 cm^{-1}. Long chains of the D siloxane units generally show two distinct bands at 1020 and 1090 cm^{-1} [36]. The other absorption band due to O-Si-C linkage can also interfere at this range[37]. The Si-alkyl group from the D and T units was identified by two overlapping absorption bands at about 1240-1260 cm^{-1}. This may be due to the chemical cross-linking of hydroxyl group of polymer precursor with trichloro(alkyl)silane

Hydrophobicity and Separation performance of the membranes

Contact angle (water) measurements were carried out to check hydrophobicity of the membrane. The results are shown in Figure 10. It was found that PDMS-FOS membrane prepared by cross-linking with the trichloro(perflurooctyl)silane showed the highest contact angle (water) of 120° than the other cross-linkers. This may be due to the highly hydrophobic nature of perfluorooctyl chain present in the membrane structure. Based on the contact angle values, the order of hydrophobicity of membrane was followed as PDMS-FOS > PDMS-ODS > PDMS-OS > PDMS-MS.

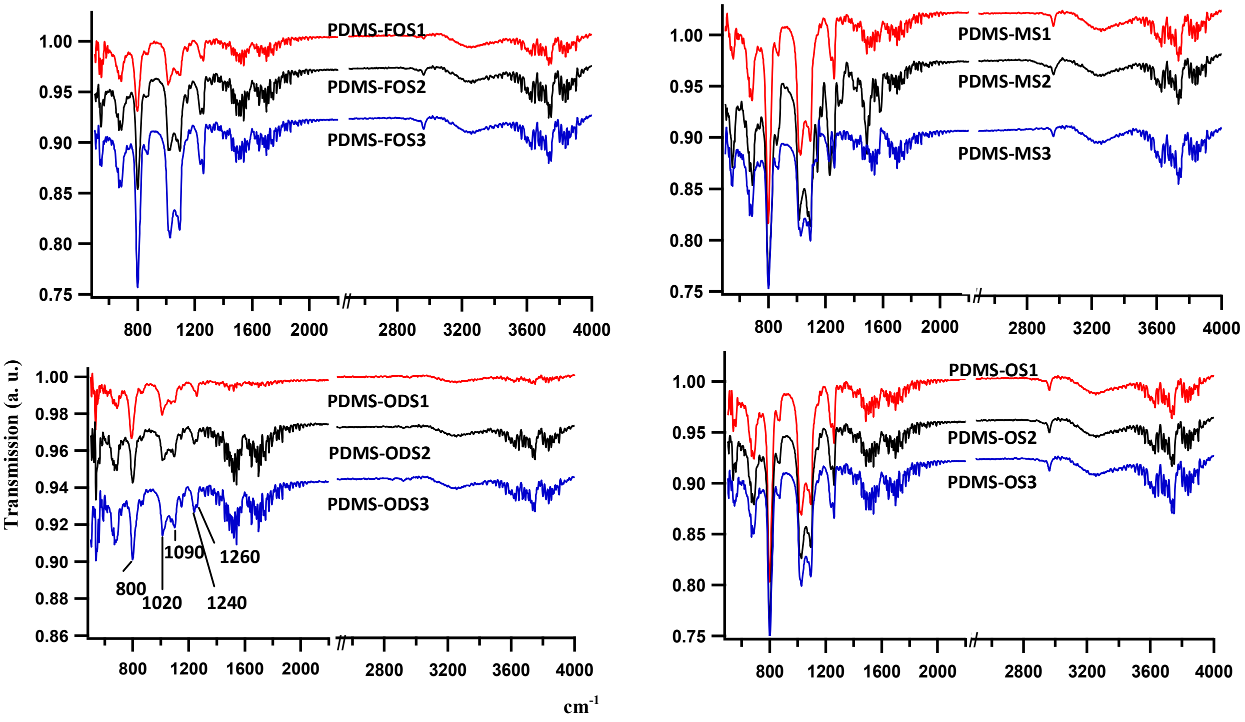


Fig.9 The Infra-red spectra of the PDMS membrane series

Furthermore, the membrane prepared with trichloro(alkyl)silane of longer alkyl chain showed higher contact angle which indicated the long alkyl chain in the structure aided to increase the hydrophobicity of the membrane.

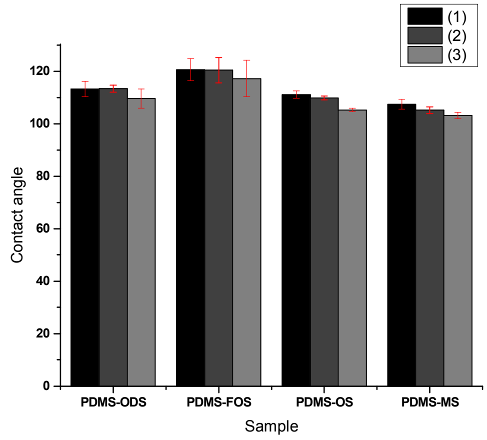


Fig. 10 Contact angle (water) of the PDMS samples

On the other hand, the more amount of cross-linker was not helpful to increase the hydrophobicity. The PDMS-FOS1 and PDMS-FOS2 had similar contact angle value of 120° which are slightly higher than PDMS-FOS3 value of 117°. The same trend was observed for PDMS-ODS series in which both the PDMS-ODS1 and PDMS-ODS2 showed contact angle value of 113° while the PDMS-ODS3 had the value of 110°. In case of PDMS-OS and PDMS-MS series, the contact angle decreased from 111° to 105° and 108° to 103°, respectively with increase in the cross-linker amount. This may be due to secondary reaction of trichloro(alkyl)silane hydrolysis when used in excess forming poly(alkyl)siloxane inside the membrane as discussed above. The separation performance of the membranes in terms of the ethanol selectivity and flux from an aqueous feed containing 5% (w/w) ethanol was examined.

Figure 11 shows the performance comparison of the present PDMS membranes prepared by trichloro(alkyl)silane cross-linking and the other conventional PDMS membranes prepared by cross-linking with polymethyl(hydro)siloxane. The highest ethanol/water separation factor of 18 and normalized permeate flux of 183 g m^{-2} h^{-1} (flux normalized per unit membrane thickness of 100 μm) was observed for sample PDMS-FOS1 while a slight decrease in the ethanol/water separation factor 17, but a slight increase in the flux 190 g m^{-2}

h^{-1} was observed for sample PDMS-ODS1. Both the PDMS-OS1 and PDMS-MS1 samples exhibited a higher flux of about 210 g m^{-2} h^{-1} but with a moderate separation factor of 14. There were reduction in membrane performance for all the membranes series prepared with increase in amount of cross-linker loading which may be due to poly(alkyl)siloxane particle formation in the membrane film rather than cross-linking as discussed above. The details of the membrane performance studies of all the membrane series in ethanol-water as well as butanol-water separation will be published elsewhere. It can be seen from the Figure 11 that the present PDMS membranes prepared with an optimal loading of trichloro(alkyl)silane cross-linker performed better than the other reported conventional PDMS membranes.

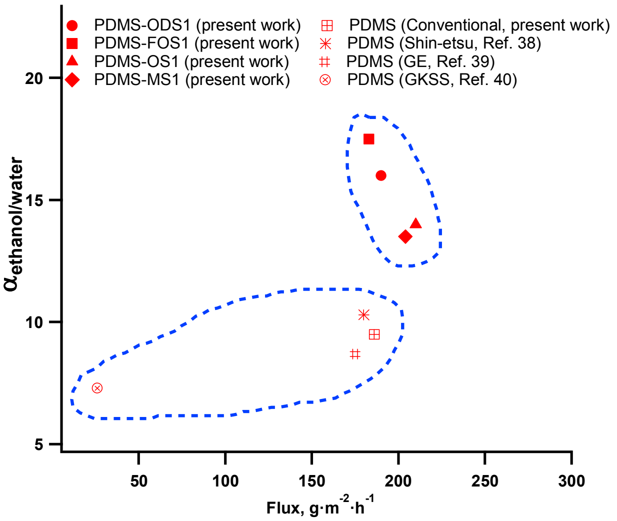


Fig. 11 comparison of the present PDMS membranes with other reported conventional PDMS membranes. Experimental conditions: Present work: Feed = 5 % (w/w) of ethanol in water, operating temperature = 70 °C. Ref. 38: Feed = 1.5 % (w/w) of ethanol in water, operating temperature = 66 °C. Ref. 39: Feed = 6 % (w/w) of ethanol in water, operating temperature = 65 °C. Ref. 40: Feed = 7 % (w/w) of ethanol in water, operating temperature = 22 °C. All the membrane fluxes were normalized per membrane thickness of 100 µm.

Conclusions

A new preparation method of the PDMS membrane by cross-linking the hydroxyl-terminated-poly(dimethylsiloxane) oligomer with a molecular trichloro(alkyl)silane through condensation reaction between the hydroxyl and chloride groups in n-heptane solvent under nitrogen environment liberating HCl, is reported here. Membranes were prepared from the reaction system in which the trichloro(alkyl)silane cross-linker was varied as trichloro(methyl)silane, trichloro(octyl)silane, trichloro(1H,1H,2H,2H-perflourooctyl)silane and trichloro(*n*-octadecyl)silane and for each cross-linker, three proportions of the cross-linker to the base polymer liquid, as 13:87, 33:67 and 50:50 (w/w) were taken for the comparison in their cross-linking densities. XRD, SEM, TEM, SANS, TGA, DSC, ^{29}Si NMR, IR, Cross-linking density, Contact angle (water) and ethanol-water separation performance measurements were performed to assess the prepared membranes.

The membranes formed by crosslinking with trichloro(methyl)silane had crystalline PDMS regions even from the reaction with 50 wt. % trichloro(methyl)silane in contrast to the others which exhibited a completely amorphous nature of PDMS after the reaction with 33-50 wt. % trichloro(alkyl)silane. Additional presence of poly(alkylsiloxane) groups from self-condensation of trichloro(alkyl)silane was observed in the membranes formed with 33-50 wt.% of trichloro(alkyl)silane. The cross-linked network structure comprising of dimethylsiloxane network structures of two cross-links and alkylsiloxane network structure of two or three cross-links were observed by ^{29}Si NMR and IR spectra. Thus, the PDMS membrane structure was comprised of two characteristic segments of dimethylsiloxane and alkylsiloxane units. The dimethylsiloxane networks are long chain polymeric networks and may be considered as soft segment as it is being derived from the PDMS pre-polymer liquid while the alkylsiloxane networks are short chain networks and hard structure resulted from the cross-linking reaction directly with molecular trichloro(alkyl)silane or with the derived species from hydrolysis, condensation and polymerization reactions of trichloro(alkyl)silane. SANS models of the Ornstein-Zernike approach and Debye-Anderson-Brumberger equation described the soft and hard segments corresponding of dimethylsiloxane and alkylsiloxane groups of the cross-linked membrane structure. The hard segment of the membrane was found to be increased in the membrane samples formed with more amount of trichloro(alkyl)silane. Changes in thermal properties and structure denseness of the membranes depending on concentration and type of trichloro(alkyl)silane used were also observed.

An optimal amount of trichloro(alkyl)silane cross-linker as about 10 – 30 % (w/w) was required to prepare uniformly homogenous membrane and these membranes performed better separation performance than the other reported conventional PDMS membranes in terms of the ethanol selectivity and flux from an aqueous feed containing 5% (w/w) ethanol.

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