

# Insight on to Mechanical, Thermal, Long-Term, Hydrothermal, and Chemical Stability of PSf Based Membrane Systems for Separation of O<sub>2</sub> /N<sub>2</sub>

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## Research Article

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# Abstract

MMMs have been opened up a new window in gas separation and purification applications, but the actual viability can be reckoned on the basis of performance achieved in realistic feed conditions. This research highlights the selection of silica decorated graphene for the first time to prepare nanocomposite membranes. In the study, XRD, Raman, and UV validated the existence of the different fillers within the host Polysulfone (PSf), while TEM authenticated their distribution. The burst strength and thermal properties were also investigated. Besides, it covered a prudent step towards resolving the dominant ingredients, which routinely appraise the stability and durability of the membranes. These indexes are long-term gas permeation up to 120 hours coupled with sustainability against hydrothermal and chemical resistance under various conditions similar to real-life separation applications. Finally, the report demonstrated that the nanohybrid integrated membrane systems displayed optimum separation performance and stability than their parent counterparts: PSf/mSiO<sub>2</sub>, PSf/GO.

## 1. Introduction

Recently, the researchers have been centralized their attention towards the development of a high performance membrane system, which must be contemplated as a viable candidate for diverse lab as well as large-scale industrial gas separation and purification applications. The eye-catching momentums as-received from numerous reports endowed that the membrane technology is an affordable and competent approach for the separation of gases [1]. The introduction of mixed matrix membrane (MMM) has been shortly experiencing substantial growth, breakthrough, and enormous prosperity for the selective permeation of penetrant with greater perm-selectivity [2]. Various legitimate attempts have been devoted for identifying unique membrane-forming materials, which would retain promising characteristics to realize improved performance. Besides, the separation behavior should close to the “Robenson upper bound limit”. It is an empirical limit that has been envisaged as the benchmark against which the viability of diverse membranes is compared [3]. Nevertheless, the frequent emergence of a couple of prominent issues, inclusive of interfacial adhesion between two phases, selection of appropriate filler phase on the basis of size, pore diameter, attachment of different surface functionalities, affinity to chosen gases, and degree of dispersion or distribution status within the matrix should be focused to attain the desired level of properties for the MMMs [4].

These consistently arising issues need to be suitably addressed to accomplish the as-expected performance. In the middle of recognition of phenomenal dispersed phase, NPs (silica -SiO<sub>2</sub>) decorated graphene has been greatly recommended, inspiring from its advantageous features [5]. This nanohybrid has been successfully implemented in miscellaneous areas, like bio-medical application [6], liquid purification [7], anti-corrosion hydrophobic coating [8], Li-ion battery [9], biosensor [10], etc. However, from the best of our knowledge, there is no report concerning the development of nanocomposite membrane structures with the incorporation of this particular hybridized nanosheet for the separation of gases. The nanohybrid has been encompassed with multi-functionalities, which would play an imperative role to intensify the dispersive characteristics, ultimately reinforce the interfacial interaction between the phases

[11]. Further, it not only boosts the affinity with the species but also contributes to facilitate the origination of several diffusion channels or pathways at the interfacial region within the membrane. As a consequence, it stimulates the formation of smooth transport avenues for the resistance-free permeation of gases across the surface of the hybrid membrane.

The proficiency of the membrane for the separation of targeted gases consistently predict on the basis of the performance tested on the bench scale under favorable absolute conditions and setups but conspicuous deviation may be realized with its implementation under realistic processing parameters for large-scale industrial purposes [2]. Thus, it is extremely difficult to translate the performance of the system from small-scale lab setting to the conditions of real-life applications. The durability and long-term stability are the crucial factors to evaluate the authenticity of the performance. Also, the hydrothermal stability is a predominant parameter to appraise the extent of the capability of a membrane towards water vapor environment. The manifold impurities such as  $\text{SO}_2$ ,  $\text{NO}_2$ , mostly persist within the supplied gas stream; those may combine with the absorbed moisture on the surface of the membrane that possibly forms acid. Consequently, it would degrade the structure and decline the expected performance[12].

This investigation highlights the development of high performance MMM systems with the selection of surface decorated silica based graphene nanohybrid as the potential dispersed phase along with its parent counterparts. Especially, it concentrates to investigate the viability of the as-prepared membranes in terms of mechanical and thermal stability. Further, the long-term performance, hydrothermal, and chemical resistance over the permeation testing for the chosen gas pair have been assessed in the frame of this work. Also, the deviation has been analyzed from the originally recorded permeabilities and selectivities at normal parameters with the prescribed applied conditions.

## 2. Materials And Experimental Methods

### 2.1. Materials

20  $\mu\text{m}$  size of Graphite powder was provided by Sigma Aldrich. GO was prepared by modified Hummer's procedure and the required chemicals, such as  $\text{NaNO}_3$ ,  $\text{KMnO}_4$  were procured from Merck,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  were purchased from HiMedia, and  $\text{H}_2\text{O}_2$  aqueous solution was supplied by RFCL Gelest INC. The surface decoration of the synthesized GO was conducted by silica self-assembly precursor solution through an *in-situ* sol-gel technique. The precursor solution consisting of  $\text{NH}_4\text{Cl}$  with M.W 53.49 g/mol, and TEOS ( $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ ) (M.W 208.33 g/mol) were provided by Aldrich, APTES with M.W 221.37 g/mol, Ethanol ( $\text{C}_2\text{H}_6\text{O}$ ) of M.W 46.068 g/mol were supplied from HiMedia, and  $\text{NaOH}$  with M.W 39.99 g/mol was acquired by Fisher scientific. The synthesized nanohybrid was reduced by a non-toxic reductant L-Ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ) with M.W 176.13 g/mol, which was acquired by Fisher. Tetrahydrofuran ( $\text{C}_4\text{H}_8\text{O}$ ) with M.W 72.11 g/mol and purity level  $\sim 99.00\%$  was utilized as a solvent for the preparation of the membrane systems, which was provided by HiMedia. (PSf) Polysulfone pellet (M.W 35,000) and nano

silica (SiO<sub>2</sub>) with specific surface area between 175 to 225 m<sup>2</sup>/g as measured by BET were supplied by Aldrich.

## 2.2. Procedure to develop membranes

The detailed methodology for the synthesis and relevant characterization studies of APTES modified nano silica (mSiO<sub>2</sub>), graphene oxide (GO), silica decorated oxidized graphene (SGO), and silica decorated reduced graphene (RSGO) have been deliberately discussed in our previous report [13]. The unfilled Polysulfone (PSf) membrane and different fillers comprised MMMs were prepared through solution blending technique. Figure 1 illustrates the systematic scheme to prepare the membrane systems.

The method for the preparation of different membranes was meticulously described in our earlier report [14]. In this investigation, 04 numbers of nanofillers (mSiO<sub>2</sub>, GO, SGO, and RSGO) incorporated membranes were prepared and designated as C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>, respectively in the next section while; the nascent PSf membrane was entitled as N<sub>0</sub>.

## 2.3. Characterizations

### *X-RD analysis*

The structural characteristic of the membranes was determined by X-ray diffractometer (Schimadzu XRD-7000L, Japan) employing CuK<sub>α</sub> radiation ( $\lambda = 1.514 \text{ \AA}$ ). The membrane samples were examined at a scanning rate of 2°/min over a range of diffraction angle with  $2\theta$  interval from 3–70°.

### *Raman spectroscopy*

The Raman spectra of different systems were analyzed by Micro Raman spectrometer (M820, Renishaw, UK). The analysis was conducted at room temperature with 532 nm excitation wavelength and laser power of 0.5 %. The spectra were measured at 10s exposure time in the range from 101.77 to 3502.19 Raman shift/cm<sup>-1</sup>.

### *Ultraviolet–visible (UV) spectroscopy*

The UV spectrum of the membrane systems was recorded by UV-Shimadzu 2450. The spectra were analyzed within the wavelength ( $\lambda$ ) range from 200 to 800 nm.

### *Transmission electron microscopy (TEM)*

The dispersion quality of diverse nanofillers throughout the host PSf matrix was examined by TEM JEOL-JEM1400, Japan with an accelerating voltage of 120 kV. The samples were cut by Leica ultracut microtome equipped with a diamond knife. The ultrathin section of the sample was placed on the copper grid for imaging.

### *Burst strength*

The burst strength of the prepared membrane samples was measured by burst strength tester BST-A101 within a pressure range from 0.1 to 14.0 kgf/cm<sup>2</sup>.

### *Thermal properties (TGA, DSC)*

The thermal stability of the membrane samples was studied by Thermogravimetric analyzer (TGA, Q50, TA Instruments USA). The samples of around 7–10 mg were scanned at a linear heating rate of 10° C/min over the temperature range from 30 to 800° C.

Differential scanning calorimetry (DSC) analysis was conducted (Q20, M/s TA Instruments, USA) to measure glass transition temperature ( $T_g$ ) of the membranes. The samples of about  $\leq 7$  mg were scanned from room temperature to 350°C with a heating rate of 10°C/min under nitrogen atmosphere.

### **Gas Permeability Coefficients**

Gas transmission rate (GTR) analyzer (N530, GBPI, Packaging equipment, Hemtech) was used to analyze the transmission rate of penetrants through the surface of the membrane systems. The author has chosen light gases, such as O<sub>2</sub> and N<sub>2</sub>, which exhibit kinetic diameter of 3.46, and, 3.64 Å, respectively. The measuring range was at [ $m^3(\text{STP}) m^{-2} h^{-1} \text{bar}^{-1}$ ] within the temperature from 5 to 50°C and the permeation of single gases was conducted separately as per ASTM D 1434 at 1 bar constant pressure. The permeability coefficients ( $P_i$  and  $P_j$ ) of the gases were measured by taking 3 replicate membrane samples from each system and the average coefficient values have mentioned. Subsequently, the ideal selectivity ( $\alpha_{i/j}$ ) factor can be estimated by using the equation as follows, which can be stated as the ratio of pure gas permeances ( $P_i$ ) over ( $P_j$ )

$$\alpha_{i/j} = \frac{P_i}{P_j}$$

### **Long-term permeation, hydrothermal stability and chemical resistance of the systems**

The long-term permeation stability of the membranes was evaluated by exposing the samples for continuous permeation testing up to 120 hours without any interruption for the chosen gases. Meantime, the permeability values were collected at each 24 hours. To determine the hydrothermal stability, the unfilled PSf and nanocomposites were located over a concealed container occupied by distilled water and allowed to heat at 100°C for 12 hours to maintain a factitious vapor environment under lab-scale conditions. After fulfilment of the treatment, the samples were detached and conserved for parched at 60°C for 12 hours prior to analyze for testing. The similar procedure was conducted for evaluating the chemical resistance of the membranes, instead, an acidic and alkaline medium with pH of 1 and 14 were maintained, respectively. The diluted sulfuric acid and ammonia solution were occupied by the container and the samples were placed separately in different mediums. The treated samples were dried and the

permeation measurements were carried out. This was repeated many times to observe the accuracy of the recorded permeabilities for the treated membrane samples.

## 3. Results And Discussions

### 3.1. XRD (X-Ray Diffractometer)

Figure 2 illustrates the XRD of the membranes (a) Unfilled PSf ( $N_0$ ) (b) PSf/mSiO<sub>2</sub> ( $C_1$ ) (c) PSf/GO ( $C_2$ ) (d) PSf/SGO ( $C_3$ ) and (e) PSf/RSGO ( $C_4$ ).  $N_0$  exhibited a broad peak at 20° with  $d$ -spacing of 4.74 Å, indicating the amorphous structural characteristic of the backbone [16]. On the contrary, the characteristic bands for the tested nanocomposites were slightly shifted to lower angle with conspicuous decrement in broadening of the peaks, which signified the interaction between PSf chains and incorporated fillers [15]. Besides, the spacing was found higher for MMMs than  $N_0$  confirming the perceptible change in the structure after consequent insertion of the filler. However, the basic framework, i.e. the characteristic band of the native  $N_0$  was discerned in all the nanocomposites.

For  $C_1$  membrane, the characteristic band was observed at  $2\theta = 17^\circ$  with  $d$ -spacing of 5.12 Å. It accredited to the incorporation of silica segments into the nascent PSf matrix. This XRD diffractogram implied a fragile influence on crystallization behavior owing to the entrenched interaction between silanol groups with the existing sulfone of the PSf backbone. The chain packing was revised by means of hydrogen bonding, which possibly entangled the PSf with silica network. Rafiq et. al. [17] reported an analogous trend of behavior for the nano silica filled composite system.

The XRD diagram of  $C_2$  displayed that the characteristic peak of GO was almost weakened, suggesting an exfoliated morphology with depreciated van der Waal's forces. The diffraction angle at 18° with a greater  $d$ -spacing of 4.56 Å was recorded, which indicated the interfacial interaction between the phases with proper intercalation of the chain segments into the sheets. The expanded spacing can be explained by the attachment of the oxygeneous groups in terms of hydroxyl and epoxy at the basal plane and carbonyl, carboxyl at the edges along with a number of water molecules absorbed within the graphitic gallery [18] as discussed by Ionita et. al. for the GO reinforced nanocomposite.

$C_3$  hybrid system exhibited a broadened peak, implying exquisite intercalation of hybridized sheets into the PSf chain segment. The increment of the diffraction band to nearly 3° than the parent counterparts and the slight enlargement in the  $d$ -spacing to 5.93 Å evidently persuaded the presence of multi-functional groups within the hybrid system. The decoration of silane moieties precluded the restacking propensity of sheets and agglomeration of particles. Besides, a supplementary synergistic effect might be established, which shall be expected to reinforce the role of the hybrid dispersed phase within the host matrix [19]. Additionally, the interaction of SGO led to the formation of efficient and regular packing and ascertained the intermolecular periodicity for the hybrid membrane. Harei et. al. revealed analogous trend for SiO<sub>2</sub>-GO filled epoxy nanocomposite [20].

A closer d-spacing of 3.85 Å and broadness in reflection was achieved for the C<sub>4</sub> reduced hybrid system. It suggested conjugated  $\pi - \pi$  networks (sp<sup>2</sup> carbon) had restored during the executed two-step reduction methods and an intensive exfoliation was recorded with the removal of hydroxyl and epoxy groups from basal plane. The appearance of the amorphous peak substantiated grafting of the silane moieties on graphene and attached to PSf backbone.

## 3.2. Raman spectroscopy

The Raman spectroscopy was performed and the received spectra are displayed in Fig. 3.

The Raman spectrum of the native N<sub>0</sub> sample consisted of the peaks at 1142 and 1584 cm<sup>-1</sup> corresponds to asymmetric C–O–C, aromatic ring chain vibration, respectively as displayed in (a). The peak at 788 cm<sup>-1</sup> can be correlated to asymmetric C–S–C bonding. The appearance of these bands confirming the presence of PSf backbone. Similar trend was reported by Ionita et.al. [16].

The spectrum of PSf/mSiO<sub>2</sub> as shown in (b) illustrates the obvious appearance of a number of humps demonstrating the intrinsic halo amorphous structural characteristics. The presence of a few bands at higher wavenumbers suggested the existence of Si-OH, isolated silanol group, and interaction between the silanol with existing sulfone of the backbone [21]. The Si–O–Si siloxane bond centered at around 1154 cm<sup>-1</sup> indicating the attachment of organosilane on the surface of membrane. The Raman intensity of nano silica is very weak; hence it is strenuous to differentiate all the observed signals. But, the outcome conveniently implied the insertion of mSiO<sub>2</sub> into the PSf [22].

The spectrum as displayed in Fig. 3 (c) was dominated by the presence of two prominent bands D and G at 1342 and 1596 cm<sup>-1</sup>, respectively along with the 2D band at 2932 cm<sup>-1</sup>. The D band denotes to sp<sup>3</sup> disordered carbon structure associated with vacancies at the edges and grain boundaries referred as out-of-plane breathing mode of A<sub>1g</sub> translational symmetry. The G band presents planar configuration of sp<sup>2</sup> ordered crystalline stacking of graphite-like structure and the stretching movements to in-plane E<sub>2g</sub> phonon mode [5]. It can be observed that the intensity of the D band was predominantly heightened owing to defective structure and deformation, which ascribed to the dense presence of oxygen-rich groups. Strikingly, the disappearance of the characteristic band of the native PSf, further signified the occurrence of exfoliation of the sheets [16]. The G band might be overlapped by the peak of the aromatic rings of the molecular chain segments implied the favorable insertion of the GO into the neat PSf membrane as described by Lee et. al. [23].

The spectrum for hybrid C<sub>3</sub> membrane displayed the shifting of the characteristic peaks of the GO to high wavenumbers at 1350 and 1602 cm<sup>-1</sup> corresponding to the D and G, respectively as shown in Fig. 3(d). The shifting of these bands revealed the exfoliation and better interfacial interaction of the hybridized sheets within the base matrix. Further, the presence of the peaks at lower wavenumbers (792 and 1146 cm<sup>-1</sup>) revealed the obvious attachment of hydrated silicate network on the surface [20]. The band intensity ratio (I<sub>D</sub>/I<sub>G</sub>) was found to be 0.99 for the hybrid membrane while; the GO impregnated PSf

system exhibited a lower value of 0.80. This fact insisted on the formation of disordered structure owing to the attachment of multifunctionalities within the hybrid system. Apart from this, the peak related to asymmetric C-S-C bonding and aromatic ring vibration can be supposedly identified. The observation of these bands validated the addition of SGO into the PSf.

The D and G bands, as represented in (e) for the C<sub>4</sub> hybrid composite was indexed at 1359 and 1609 cm<sup>-1</sup>, respectively. The 2D band was found broaden illustrating the arrangement of new graphitic in-plane sp<sup>2</sup> domains with shortened cluster size by virtue of the stretching of C-C bonding and scattering of phonon mode [24]. A higher I<sub>D</sub>/I<sub>G</sub> ratio of 1.4 was figured for the reduced hybrid system than the SGO integrated sample. Moreover, the existence of the bands related to the silicate network and PSf as explained earlier were also observed.

### 3.3. Ultra-Visible (UV) spectroscopy

The UV spectra of the membrane samples are depicted in Fig. 4. The absorbance at 280 nm was recorded for N<sub>0</sub> corresponding to π-π\* electron orbital transition of aromatic benzene rings as observed by Jyothi et. al.[25].

C<sub>1</sub> system displayed an absorbance with λ<sub>max</sub> of 265 nm validating the existence of the silanol groups. The absorbance at 350 nm shall be ascribed to the attachment of organosilane on the silica networks. Moreover, the defected structure might have originated owing to the oxygen vacancies and the presence of silica segments on the surface of C<sub>1</sub> [8]. In C<sub>2</sub> nanocomposite, the π-π\* transition of aromatic C = C bonds associated to hexagonally arrayed sp<sup>2</sup> structure was shifted to 201 nm. This might be attributed to better interaction of GO within the host matrix. Meanwhile, the n-π\* transition related to C = O bonds was not significantly changed and observed at 292 nm, which confirmed the dense attachment of oxygen-rich groups on the membrane structure [16].

The presence of a narrow peak at 203 nm was found for the C<sub>3</sub> system. The peak at 254 nm accompanied by a small peak at 320 nm might have originated as a result of the excitation of plasmon graphitic. Further, the red-shifting might be attributed to the loss of stacking layers indicating the formation of disordered structure within the membrane. This suggested strong interaction between nanosheets attached silane moieties and PSf matrix [11]. The broad peak confirmed the origination of oxygen vacancies and defect centre due to the change in surface chemistry with the presence of multifunctionalities across the hybrid system. The appearance of these bands related to silane moieties as well as oxygen active groups in C<sub>3</sub> insisted proper distribution of the nanohybrids within the matrix. From the spectrum of C<sub>4</sub>, red shifting of the plasmon peak to 260 nm provided a strong evidence for the insertion of reduced hybridized graphene into the host PSf with the formation of aromatic C = C bond. The broad shoulder peak was vanished, demonstrating the increment of π-electron concentration and restoration of conjugated sp<sup>2</sup> carbon after the reduction.

### 3.4. Transmission Electron Microscopy (TEM)

TEM was carried out to investigate the distribution and dispersion status of divergent fillers throughout the host matrix. Figure 5 represents the TEM micrographs of the unfilled PSf and its nanocomposites. A clear, smooth surface with defect-free structural features was observed for the  $N_0$  as shown in (a). The appearance of some superfluous gaps and open spaces indicated rapid gelation of low viscose polymeric solution [8].

The image (b) displayed an uneven dispersion status of  $mSiO_2$  within PSf, which could be observed due to the presence of undesired agglomerates and clusters on the surface. It seemed like the particles are extracted from the surface and the originated gaps between the phases illustrated an inferior interfacial interaction. The inorganic domains are not distributed like the isolated particles but fused together forming a chain-like structure and heterogeneous morphology was resulted. The interfacial voids were created by virtue of particle clusters and massive structural defects, which appeared as bright contrast within the micrograph [27]. This category of morphological view was consistently proclaimed as "sieve in a cage", as reported by Adachi et.al. [21]. The particles agglomeration may constrain the transportation path.

The micrographs of the nanocomposites comprising of GO or GO-derived hybrids depicted ultrathin structures with folded and wrinkled features as well as silk-like morphology. Figure 5 (c) showed a translucent and disordered rippled structure with the appearance of superfluous gaps or crevices indicating the presence of GO. Also, it suggested the demolition of Van der Waal's interactions between the layers with the introduction of oxidative functionalities [16]. The appearance of black dot-like structure or some dark portion might have affirmed the flocculation and restacking pattern of the sheets within the matrix. Further, the characteristic features of GO also created a long and tortuous avenue for the permeation of gases [18].

The image as depicted in Fig. 5 (d) disclosed the appearance of creases and roughened texture with better exfoliation of hybridized nanosheets throughout the host PSf without any obvious segregation. No visible cracks could be identified from the surface, suggesting that the hybrid system might not suffer embrittlement [19]. It exhibited improved dispersive characteristics by the dense grafting and precipitation of silane moieties on the corrugated sheets. Especially, uniform, homogeneous adsorption of  $SiO_2$  on the basal plane contributed to the enhancement of interfacial morphology. Moreover, a synergistic effect might have assembled between the membrane-forming materials, which could prevent aggregation and re-stacking propensity of individuals also have complied better thermal fluctuations [11]. The formulated nanochannels could be observed, which might have led to irregular protuberances [20]. The outcomes are considered as favorable configuration to provide better surface area, which would facilitate smooth permeation of gases through the hybrid system.

From the micrograph (e), the features like long, sharp lines with rougher morphology were observed. The appearance of corrugation, folded structure, and scrolling delineated the characteristic geometries of intrinsic graphene. Moreover, the existence of a number of holes and voided structure can be evidently identified, which might be ascribed to the evacuation of oxygen functionalities and residual water

molecules from the graphitic gallery. The existence of high-density, close-packed SiO<sub>2</sub> grains on the surface of restored lattice fringes of the graphene confirmed successful insertion of RSGO into the PSf [9].

### 3.5. Burst strength

Burst pressure can be represented as a realistic reflection of strength to measure the extent of force needed to rupture the membranes under planar stress-state. The sample is subjected to increased pressure until the failure takes place. The point, where the failure occurs for the exposed membrane sample, can be recorded as the bursting pressure or bursting strength [31]. By analyzing the data it can be possible to estimate the competency of the systems. The bursting strength of the samples was measured and plotted in Fig. 6. The strength of the neat N<sub>0</sub> was found to be 0.38 MPa. The analogous result was discussed by Yang et. al. for the neat PSf. The burst strength for N<sub>0</sub> was found lower than the tested composites [32]. The similar progression in the strength values was recorded here with successful introduction of divergent nanofillers into the host matrix.

For C<sub>1</sub> nanocomposite, the upgraded strength of 0.45 MPa was achieved and the probable explanation may be attributed to better interfacial interaction between PSf chains and mSiO<sub>2</sub>. Several factors, like smaller size of inserted filler, greater surface area, and higher stability might be served a way to accomplish exquisite blending. Besides, the attachment of coupling agent conceivably assisted for the origination of a number of surface active centres, which reinforced the affinity and surface contact area between the two phases [33].

GO infused C<sub>2</sub> nanocomposite has experienced a curtailed burst strength of 0.42 MPa than the C<sub>1</sub> but a heighten value as compared to the neat membrane. The justification behind the lower strength might be due to the formation of aggregated structure and restacking of the layers. The  $\pi - \pi$  interaction might be the detrimental cause for the shrinkage of dispersion of the oxidized nanosheets within the matrix. As a consequence, it resulted in inferior polymer-filler interaction and a lessened strength was assigned to the membrane [30].

The hybrid membranes C<sub>3</sub> and C<sub>4</sub> have appraised greater burst strength of 0.69 and 0.61 MPa, respectively. The outstanding strength shall be elucidated on account of the synergistic effect between *in-situ* SiO<sub>2</sub> and nanosheets. The extreme manifestation of the existence of assorted functionalities on the surface of dispersed phase might have favored to accomplishing an excellent dispersive pattern [11]. The interspaces between the decorated SiO<sub>2</sub> and GO within PSf matrix acted as extensions to stimulate the adequate load transfer between the two phases and enhanced the strength. However, the C<sub>4</sub> hybrid membrane displayed a lessened value, which might be ascribed to the insertion of reduced graphene sheets with minimal oxidative groups. This dispersed phase possessing insufficient organo-functionalities, which promoted the origination of a number of aggregated layered structure on account of devaluation of effective aspect ratio. As a consequence, it could not contribute to find substantial interfacial region for efficient stress transfer. Ultimately, the reduced hybridized nanosheets divulged a

slightly weaker membrane structure, in contrast to the SGO comprised system but still remain tenacious against the parent counterparts.

## 3.6. Thermal properties (DSC and TGA)

### 3.6.1. DSC (Differential Scanning Calorimetry)

Figure 7 shows the DSC thermograms of the PSf and its composite membranes, while Table 1 outlines the attained  $T_g$  of the investigated samples. It was recorded that the  $T_g$  increased in case of all the composites, irrespective of single or hybrid nature, which may be attributed to the reduced flexibility of the molecular chain segments.

The native PSf membrane exhibited a wide range of  $T_g$  of 150°C as reported by Mannan et. al. [34]. A perceptible increment in the  $T_g$  value was noticed for the single nanoscopic MMM systems (PSf/mSiO<sub>2</sub> and PSf/GO). This behavior can be elucidated in terms of free volume concept; wherein the filler phases occupied the desired volume, increased the rigidity by virtue of arose stress during the fabrication. Consequently, higher thermal energy might be required for the rotation or consecutive movements of the chain segments [35].

Table 1  
 $T_g$  of investigated membrane systems

Sl. No.	Membrane Samples	$T_g$ (°C)
1	Neat PSf (N <sub>0</sub> )	150
2	PSf/mSiO <sub>2</sub> (C <sub>1</sub> )	175
3	PSf/GO (C <sub>2</sub> )	170
4	PSf/SGO (C <sub>3</sub> )	227
5	PSf/RSGO (C <sub>4</sub> )	224

PSf/mSiO<sub>2</sub> membrane displayed an increased  $T_g$  of 175°C. The interaction of small inorganic domains predominantly affected long-range segmental mobility of the molecular chains. The organosilane moieties penetrated and entangled closely and led to enhance the rigidity and restricted the mobility of the polymeric chains. This caused to increase the  $T_g$  for the mSiO<sub>2</sub> based membrane structure [33].

For C<sub>2</sub> membrane, a significant gain in the  $T_g$  value of 170°C was registered. This can be explained owing to the bridge bonding between the PSf chains and GO sheets containing rich-oxygen active functionalities [37]. The adsorption of the PSf chain on the filler surface suppressed the flexibility and intensified the  $T_g$ . Additionally, the improved interfacial interaction between the carbon skeleton and oxygen moieties on the basal planes and edges boosted the affinity between the phases, which assisted to revise the thermal properties of the membrane.

The C<sub>3</sub> hybrid system displayed an enhanced T<sub>g</sub> of 227°C, which may be interpreted by the established synergistic effect between the *in-situ* decorated SiO<sub>2</sub> and oxidized graphene with the host matrix. Better exfoliation of the sheets enriched with silica led to maximum contact surface area and stimulated the dispersive characteristics by virtue of the colossal attachment of -OH functionalities. Further, the covalently attached NPs are purported to act as solid-state exfoliating agents, which could have hindered the crumpling phenomena and facilitated fine dispersion pattern within the entire volume of the PSf [11]. The steric hindrance induced by the improved dispersion of the nanohybrid promoted the chain rigidification and hence the heat flow rate [29]. Thus, a higher T<sub>g</sub> was attained for the hybrid system. Also, a greater T<sub>g</sub> contributed better resistance towards plasticization.

For the RSGO based hybrid membrane, a T<sub>g</sub> of 224°C was obtained, ascribed to the penetration of transition zone surrounding the dispersed phase into the polymer chain gaps and vice-versa [30]. However, the absence of the oxygen-rich functionalities led to a slight reduction in the T<sub>g</sub> in comparison to the PSf/SGO hybrid system.

### 3.6.2. TGA (Thermogravimetric Analysis)

TGA thermograms of the membranes are displayed in Fig. 8 and the related data are indexed in Table 2 in terms of initial degradation temperature (T<sub>i</sub>), temperature at 10% (T<sub>10</sub>) and 50% weight loss (T<sub>50</sub>), final thermal degradation (T<sub>d</sub>), and the remaining % of char residue. The thermograms depicted three prominent stages of decomposition profile: corresponding to the desolvation of residual volatile moisture, thermal degradation of existing organic ligands, and disintegration of polymeric backbone as well as the carbonization of degraded products. The introductory weight loss was virtually initiated at a temperature above 100°C indicating the presence of traces of solvent or moistures over the surface of the membranes.

Table 2  
TGA parameters of the investigated membranes

Sl. no	Samples	T <sub>on</sub>	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	T <sub>d</sub> (°C)	Char (%)
1	Neat PSf (N <sub>0</sub> )	465	175	522	550	-
2	PSf/mSiO <sub>2</sub> (C <sub>1</sub> )	476	183	524	568	27
3	PSf/GO (C <sub>2</sub> )	472	198	525	555	26
4	PSf/SGO (C <sub>3</sub> )	485	305	535	585	34
5	PSf/RSGO (C <sub>4</sub> )	480	211	527	574	28

The TGA plot of the neat PSf sample demonstrated the primary loss was observed between 100 to 200°C signified the removal of absorbed water molecule or excess solvent. The weight loss in between 450–500°C ensued owing to the thermal degradation of polymeric backbone and sulfone rupture. The neat

sample displayed a complete degradation profile at 540°C with no residue content. Ionita et.al. also revealed a similar trend for the unfilled PSf [18].

PSf/mSiO<sub>2</sub> membrane showed an improved T<sub>d</sub> at 568°C. It might be assigned to rigidification of the chains at the interface owing to the close contact of mSiO<sub>2</sub> with the PSf. As observed in DSC, the SiO<sub>2</sub> particles caused restricted mobility of the chains leading to improved thermal stability. Additionally, high heat resistant silica could have trapped the volatile degradation and delayed the diffusion out of the polymer by virtue of the protection of pore-wall [17]. The preeminent mass loss within the range 450–520°C was assigned to the degradation of the attached functionalities and the decomposition of terminal absorbed amine groups. The char residue of 27% along with improved T<sub>10</sub> and T<sub>50</sub> validated better stability of the C<sub>1</sub> system. An analogous trend has been reported by Wahab et. al. [38].

For the C<sub>3</sub> membrane, the inserted GO was behaved like a mass transport barrier and limited the movement of the chain segments [16]. The primary mass loss event under 250°C shall be credited to the evaporation of residual moisture and presumable decomposition of polar group existed within the graphitic gallery. The hydrophilic nature of the GO could have promoted to bind water molecules tightly into their stacked structure, which enabled to serve as catalyst to improve the stability. This phenomenon accelerated the degradation of segments, ultimately yield CO, CO<sub>2</sub>, water as byproducts [18]. The eventual mass loss was credited to pyrolysis of the main polymeric backbone.

The thermogram of the C<sub>4</sub> hybrid system demonstrated the confined mobility of the segments at the interface and enhanced the stability with T<sub>d</sub> of 585°C. The intercalation of silica on the GO surface acted as a bridge to facilitate the formation of an intimate link between two phases and reinforced the contact area [11]. The attachment of multi-functionalities behaved like a physical protective barrier, which could regulate the mobility of the chains and retarded the degradation [39]. The higher char yield of 34% was manifestly reflecting the massive grafting of functional moieties on the surface of SGO inserted hybrid membrane. While the C<sub>4</sub> system exhibited slightly curtailed stability than the former owing to the demobilization of oxygen content. The mass loss of ~ 40% was assigned to the evacuation of remaining residual groups and the subsequent burning of the graphitic sketch. Also, the tortuous path effect of the graphene delayed the release of volatile degradation and improved the stability of the reduced hybrid system.

### **3.7. Stability analysis**

In our previous research [14], we had measured the permeability coefficients of single gases (O<sub>2</sub> and N<sub>2</sub>) through the neat PSf its MMMs including, PSf/mSiO<sub>2</sub>, PSf/GO, PSf/SGO, and PSf/RSGO. The permeabilities and ideal selectivities had analyzed and the recorded data are compiled in Table 3 and the detailed description has provided in the supplementary section. In the current study, we have investigated long-term permeation testing, hydrothermal and chemical stabilities of the samples and inspected the discrepancy from the initially recorded values. These stability studies evaluate the viability of the membrane systems for large-scale separation applications under realistic feed conditions.

Table 3  
indexes permeability coefficients and selectivity of membrane systems

Sl. No.	Membrane samples	Permeability coefficients		Selectivity ( $\alpha_{i/j}$ )
		O <sub>2</sub> ( $P_i$ )	N <sub>2</sub> ( $P_j$ )	(O <sub>2</sub> /N <sub>2</sub> )
1	Neat PSf (N <sub>0</sub> )	4.66	2.33	2
2	PSf/mSiO <sub>2</sub> (C <sub>1</sub> )	9.41	4.08	2.30
3	PSf/GO (C <sub>2</sub> )	7.79	3.75	2.07
4	PSf/SGO (C <sub>3</sub> )	70.20	5	14.04
5	PSf/RSGO (C <sub>4</sub> )	50.83	4.16	12.21

### 3.7.1 Long-term gas permeation stability

The long-term stability and durability factor of the prepared membranes were measured on account of continuous gas permeation testing for a period of 120 hours without any obvious uninterrupted conditions. Figure 9 (a) and (b) illustrates the long-term stability of the membrane systems for penetrant gases O<sub>2</sub> and N<sub>2</sub> respectively at each 24 hours of the testing time, while Fig. 10 depicts the fluctuation in ideal selectivities at both regular and long-term conditions.

From Fig. 9, it was noticed that all the exposed membranes could not withstand 120 hours. Hence, the permeation testing was continued till the strength of the sample was intact or the measurement was terminated. From the plotted graphs, it can be disclosed that the tested MMM systems maintained better long-term permeation stability than the unfilled PSf sample. After 24 hours of testing, the permeability of the neat PSf membrane for O<sub>2</sub> was marginally increased to 1.82% as compared to the previously registered data, thereafter found constant at 4.89. The permeation measurement was automatically abolished, on removing the tested PSf sample; it was observed the ruptured surface with the emergence of cracks. Meanwhile, the permeation rate of N<sub>2</sub> was found to be 2.20 at 36 hours. After 36 hours the gas flow rate was stopped for the unfilled sample. From the graph, it can be affirmed that only a slight deviation in permeability and selectivity was noticed for both the penetrant as against the recorded values at regular testing conditions.

However, the tested MMM systems displayed amplified constancy contrary to the imposed conditions for testing. The C<sub>1</sub> and C<sub>2</sub> systems exhibited a perpetual permeation behavior till 72 hours and after that, the gas flow rate was refused and the measurement was disrupted. Both the penetrants displayed a similar pattern in terms of smooth permeation of O<sub>2</sub> and a declined transportation rate of N<sub>2</sub>. The permeability coefficient of C<sub>1</sub> membrane for O<sub>2</sub> was found to be 9.3, 9.48, and 9.75 at 24, 48, and 72 hours, respectively while, the permeabilities of 7.8, 7.82, and 7.89 were recorded for the C<sub>2</sub> at endorsed time period. The permeabilities of N<sub>2</sub> were found to be 4.25 and 3.71 after 72 hours of testing time for C<sub>1</sub> and

C<sub>2</sub> membranes, respectively. From the achieved results, it was revealed that the permeability coefficients of C<sub>1</sub> and C<sub>2</sub> were improved even though marginally against the recorded data. The selectivities at regular and long-term testing conditions were only slightly varied for the tested MMMs. The obligatory portrait for the outcome of preeminent long-term permeation stability can be systematically documented taking into account of augmented burst strength against the native PSf as explained earlier. The enhanced stress transfer efficiency of C<sub>1</sub> and C<sub>2</sub> subsequently prompted sustainability to applied feed pressure for a longer period of time, which provided a strongest evidence for the above findings. The existence of fillers within the PSf possessing an exemplary affinity for the penetrants, which probably maximized the quota of interaction for a prolonged time. The solubility and diffusivity of the gases might have improved with the appearance of the fillers containing abundant functionalities. These facts might extend the testing time period and may favorably facilitate the real-life gas separation applications [43].

The hybrid C<sub>3</sub> and C<sub>4</sub> membranes delineated improved permeability coefficients as well as selectivity as compared to their counterparts. The hybrid systems smoothly executed to finish the distinct period, which was resolved here to assess the long-term stability. It was observed that C<sub>3</sub> and C<sub>4</sub> membranes displayed splendid sustainability till 120 hours of the testing time. No obvious damage, cracks and holes were identified on the surface of tested hybrid samples. During the long-term testing, it was noticed that within 24 hours the saturated permeation values were observed for the systems as recorded previously at the regular testing conditions. The permeabilities of the C<sub>3</sub> membrane were found to be 72, 72.66, 74.5, 74.89, and 75 while the C<sub>4</sub> hybrid system exhibited the values of 50, 51.15, 52.02, 52.89 and 53 at 24, 48, 72, 96 and 120 hours of testing time respectively. Moreover, the transportation rate of 5.55 and 4.4 was measured for N<sub>2</sub> across the surface of C<sub>3</sub> and C<sub>4</sub> hybrid membranes at 120 hours. After the completion of 120 hours, it was noticed that the hybrid samples attained slightly higher permeabilities than the initial values at the normal testing procedure. This increment shall be attributed to the nanogaps created over the surface of the exposed samples during the testing. The ensued homogeneous interpenetrating architectures owing to the enhanced surface area and expanded volume of formulated deformation zone with the insertion of hybridized sheets into the host PSf matrix might be the relevant cause for the long-term stability.

Moreover, the existence of a number of nanochannels, intersegmental spacing, along with the conspicuous emanation of auxiliary cavities or polar sites assisted the findings of ameliorated long-term stability for the hybrid composites [3]. These circumstances possibly enlarged the stability such that the exposed sample emphatically conveyed the applied feed pressure for a longer time without any deterioration in structure as well as performance. Additionally, the augmented burst strength of the hybrid samples than their counterparts have well supported the findings of the long-term permeation stability. The presence of multifunctionalities on the surface of hybridized sheets might stimulate to maintain the stability and steady permeability over a longer period of time. Thus, it can be declared that the hybrid membranes displayed excellent stability and durability even after long-term exposure than the parent counterparts.

### **3.7.2 Hydrothermal stability**

Here the tolerance of water vapor treated membranes towards the permeation analysis for the penetrants was observed. Figure 11 (a) represents hydrothermal stability of the treated systems, while (b) shows the selectivities of the treated and untreated samples.

From the outcomes, it can be demonstrated that the permeability characteristics of the treated  $C_1$  and  $C_2$  nanocomposites were predominantly affected. Meanwhile, the unfilled PSf and the hybrid systems were only marginally varied even after exposure to the controlled water vapor environment. In our previous report [14], we demonstrated the hydrophilisation characteristic of the membranes in terms of Water Contact Angle (WCA) measurement. From the analysis, it was observed that the single filler based systems rendered hydrophilic behavior, while; a preponderant shift towards hydrophobicity was recognized for the PSf and hybrid samples. Thus, it is apparent that the permeation behavior of the hydrophilic membranes would be distressed more by the vapor treatment than the hydrophobic one. Depending on the surface nature from WCA, the influence of the treatment on the gas permeation characteristics can be expected in order of PSf/GO > PSf/mSiO<sub>2</sub> > neat PSf > PSf/SGO > PSf/RSGO membrane. The vapor treatment demonstrated a pessimistic influence on the permeation behavior of the treated  $C_1$  and  $C_2$  with reduced O<sub>2</sub> permeabilities of 6.25 and 4 while, 4 and 2.25 were noted for N<sub>2</sub>. Nevertheless, the treated N<sub>0</sub> and hybrid systems were only marginally afflicted. The permeabilities of 4.08 and 2.15 were registered for O<sub>2</sub> and N<sub>2</sub> respectively for the treated N<sub>0</sub>. The  $C_3$  displayed permeabilities of 61.51 and 4.05 meanwhile, the treated  $C_4$  sample was only slightly varied with moderate selectivity. The decrement in performance can be elucidated on the basis of the ensued plasticization effect of absorbed moisture on the surface of the treated hydrophilic samples. The adhered vapor may endorse the formulation of intra-sheet hydrogen bonding between the existing functionalities on the surface of different fragments. This might have facilitated the origination of a bridge network across the surface of treated hydrophilic membranes. This phenomenon probably precluded the smooth openings of transport avenues, free gaps or channels which prevented the resistance-free permeation of the gaseous species. From the achieved permeabilities and selectivities, it can be revealed that the performance of the exposed samples predominantly relies upon the intensity of attachment of oxygen-rich or hydrophilic functionalities on the surface of membrane sample. Thus, it can be disclosed that the specimen containing polar groups would display lower hydrothermal stability and hence reduced permeation characteristics under the moist conditions.

### **3.7.3 Chemical stability**

After the chemical treatment in acidic and alkaline medium, the treated membrane samples were exposed to measure the gas permeation characteristics of the targeted penetrants (O<sub>2</sub> and N<sub>2</sub>). Table 4 summarizes the selectivities of untreated and chemically treated samples (in both acidic and alkaline medium). The permeability coefficients of the treated N<sub>0</sub>,  $C_1$ , and  $C_2$  were only marginally varied against the untreated ones meanwhile; the hybrid systems displayed almost similar values as like the original. Irrespective of the type of filler (single or hybrid), the prepared membrane displayed excellent chemical stability, which may be ascribed to the inherent chemical inertness of the PSf backbone. Thus, it can be

revealed that the membrane systems are also chemically stable under both acidic and alkaline medium, justifying their suitability for intended applications.

Table 4  
summarizes chemical stability in terms of selectivity of membrane systems

Sl. No.	Membrane samples	Selectivity ( $\alpha_{i/j}$ )(O <sub>2</sub> /N <sub>2</sub> )		
		Untreated	Treated samples in acidic medium	Treated samples in alkaline medium
1	Neat PSf	2	2.12	2.05
2	PSf/mSiO <sub>2</sub>	2.30	2.36	2.23
3	PSf/GO	2.07	2.01	2.19
4	PSf/SGO	14.04	14	14.02
5	PSf/RSGO	12.26	12.24	12.26

## 4. Conclusions

In summary, we had prepared high performance PSf based MMMs. The membranes were developed by taking nanofillers inclusive of mSiO<sub>2</sub>, GO, SGO and RSGO. XRD, Raman and UV spectroscopy had done to affirm the existence of inserted fillers within the host matrix. TEM imaging had performed to acquire knowledge on dispersive characteristics. The thermal properties (DSC and TGA) had investigated; the hybrid system displayed improved thermal stability among all the tested samples. Silica decorated graphene based hybrid system shown improved performance in terms of excellent permeability as well as selectivity as compared to the tested parent and native membrane. The hybrid systems retained numerous channels, free spaces, and active sites for smooth permeation of gases over the counterparts. The hybrid MMMs were proved themselves as the qualified candidate for large-scale gas separation and purification applications owing to better long-term stability. The hydrothermal and chemical stability of the treated samples over the permeation characteristics were supported the derived conclusion on the pertinency of the hybrid MMM systems for a range of commercialization in the separation field.

## Abbreviations

MMMs-Mixed matrix membranes

NPs-Inorganic nanoparticles

GO-Oxidized graphene

mSiO<sub>2</sub>- APTES modified nano silica

SGO-Silica decorated oxidized graphene

RSGO-Silica decorated reduced graphene

$P$ -Permeability coefficient

$P_i/P_j$ - Permeability coefficient of gas (i) over (j)

$\alpha_{i/j}$ - Selectivity factor

$l$ - Thickness of membrane sample

## Declarations

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