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Enhancement of \(\gamma\)-radiation stability of polysulfone membrane matrix by reinforcement of hybrid nanomaterials of nanodiamond and ceria†

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For the first time, a hybrid nanoparticle system of nanodiamond (ND) and cerium oxide (ceria) is used as reinforcement materials in order to enhance the \(\gamma\)-radiation stability of polysulfone (Psf) host membrane matrix. Control Psf and Psf-(ND+Ce) hybrid membranes are synthesized and characterized, with the loading of each nanomaterial varying from 0.25 to 0.5 wt%. Membranes are put in \(\gamma\)-radiation for different doses (up to 1000 kGy) and the effect of radiation on the Psf matrix is evaluated. The gel permeation chromatography studies confirm that the average molecular weight of the hybrid membranes is restored to a reasonable extent, as against the control Psf membrane, which has reduced by 45% at 1000 kGy of radiation dose. The optimum loading of ND and ceria in the membrane matrix is found to be 0.5% each, which offers a remarkable ~10 times enhanced radiation stability, compared to the control Psf membrane, making it a novel membrane material for potential applications in radioactive environment. The enhanced stability of optimum hybrid membrane owes to the ability of ND and ceria in scavenging the secondary \(\epsilon_{\text{in}}\) and \(\text{OH}^*\) radicals, respectively, generated due to radiolysis of water, as confirmed by the free radical scavenging studies.

1 Introduction

Polymeric membranes have a wide range of applications including water and waste water treatment,\(^12\) fuel cell application,\(^8\) gas separation,\(^3\) haemodialysis,\(^9\) sensors,\(^8\) industrial effluent treatment,\(^b\) etc. They have received extensive attention due to their reproducible properties, such as mechanical strength, flexibility, thermal stability, negligible secondary waste generation, as well as low cost availability.\(^b\) In nuclear industry, during various stages of nuclear fuel cycle, high amount of radioactive effluent is generated and there is a need for safe and effective management of these effluents.\(^8\) Materials used for such treatments should be stable in radioactive environments. Polysulfone (Psf) stands out to be a remarkable polymer, among other thermoplastic polymers, by virtue of its usability at high temperature and pressure, as well as chemical inertness.\(^8\) Psf has reasonably high strength and high glass transition temperature due to its aromatic backbone,\(^k\) while being resistant towards radiation.\(^k\) Hence, it is the most preferred choice to work in the challenging environments, such as nuclear waste treatment\(^k\) and space craft application.\(^k\)

Psf is a commonly used polymeric material for membrane fabrication. Not many studies have investigated the effects of radiation on Psf membranes, while some researchers have reported that both cross-linking and chain-scission of Psf take place when the membrane is placed under \(\gamma\)-rays.\(^13\)\(^14\) Moreover, radiolysis of water produces highly reactive free radicals under \(\gamma\)-radiation.\(^9\) The free radicals induced by \(\gamma\)-ray irradiation leads to accelerated chain scissioning and cross-linking of Psf, leading to the disintegration of the polymer host matrix, as well as the performance degradation of the membrane. Considering the above findings, there is an extensive interest in establishing systems which can prevent degradation of Psf membrane matrix from \(\gamma\)-radiation, as well as trap in situ the free radicals generated from the \(\gamma\)-radiolysis of water.
Nanomaterials possess unique properties, such as high surface area, high mechanical strength, tunability, low density, high porosity, resistance to harsh environment etc. These properties offer unprecedented opportunities to tailor-make membranes with desirable attributes keeping in to account the targeted application. Nanodiamond (ND) has been found to be a distinctive filler material for composite membranes by virtue of their mechanical and thermal properties, as well as superior abundant surface chemistry. In addition, their chemical stability and biocompatibility make them specially suitable for biomedical applications. Furthermore, incorporation of ND in polymers revealed significant enhancement in mechanical strength, wear resistance, adhesion, electromagnetic shielding and thermal conductivity of the polymers. On the other hand, the cerium atom displays feasibility in conversion between $Ce^{4+}$ and $Ce^{3+}$. An oxygen vacancy also gets created, transferred and eliminated in sync with cerium atom. This property of cerium improves absorption of reactive oxygen radicals and promotes electron transfer. Moreover, cerium oxide nanoparticles (ceria) can act as radiation absorber. This is suggested by the fact that ceria is known for shielding against $\gamma$-rays by its K absorb boundary in 40 to 80 kV voltage range.

In order to develop radiation resistant membranes, in our previous work, nanocomposite polymeric membranes were developed by reinforcement of ceria in to the Psf host matrix, wherein the free radical scavenging property of ceria resulted in $\sim$ 5 times enhanced radiation stability of Psf-ceria composite membrane, compared to the control Psf membrane. Similar findings were obtained with impregnation of ND. However, these composite membranes lose their stability after 500 kGy of radiation dose. In the present study, in order to further increase the lifetime of the membrane in radiation environment, through stabilizing the membrane structure and providing the mehanical strength to the membrane, ND and ceria together were considered as hybrid filler material in the Psf membrane matrix. In order to exploit the properties, and take on board the synergistic effects of both the nanomaterials (ND and ceria), for the first time, hybrid nanocomposite membranes (Psf-(ND+Ce)) are developed and their stability in $\gamma$-radiation environment is evaluated. Compared to the control Psf membrane, the hybrid membranes are found to offer $\sim$ 10 times enhanced radiation stability. It has also been confirmed that the hybrid membranes with reinforcement of 0.5 wt% ND and 0.5 wt% of ceria is about 2 times more stable as compared to the membranes impregnated with 0.5 wt% of ND or ceria alone. To the best of our knowledge, this is the first of its kind study undertaken, that highlights the importance of reinforcement of hybrid nanomaterials in significant enhancement of radiation resistant attributes of a polymer membrane.

## 2 Experimental

### 2.1 Materials

Details of materials procured for experimentation are given below.

1. AR-grade cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$) with purity $>99.9%$ was obtained from Indian Rare Earth Limited, India.

2. Citric acid ($C_6H_8O_7 \cdot H_2O$) of purity $>99%$ was procured from Merck, India.

3. Nanodiamond powder (ND, particle size $< 10$ nm (Figure S1 of Supplementary Information, Section S1 $\dagger$), assay $\geq 97%$, MW: $12.01$ g mol$^{-1}$, density: $3.5$ g ml$^{-1}$) was procured from Sigma-Aldrich.

4. Polysulfone (Psf) (Molecular weight: $60$ kDa) was procured from Solvay Specialties India Pvt. Ltd, India.

5. N-methyl-2-pyrrolidone (NMP) assay $\geq 99.5%$ was purchased from SRL Pvt. Ltd, Mumbai, India.

6. Polyvinyl pyrrolidone (PVP) (K-30; molecular weight: $40$ kDa) of AR grade was purchased from SRL Pvt. Ltd, Mumbai, India.

7. Polyethylene oxide (PEO) (molecular weight: $100$ kDa) was procured from Sigma-Aldrich.

### 2.2 Preparation of ceria nanoparticles

Cerium oxide (ceria) nanoparticles were prepared by gel-combustion method using cerium nitrate as oxidant and citric acid as fuel. In this method, pre-calculated amount of cerium nitrate and citric acid was initially dissolved in de-ionized water and then dehydrated at $120$ $^\circ$C to form a gel precursor. Later, the temperature was further increased to $200$ $^\circ$C which resulted in auto ignition of the gel precursor, leading to formation of cerium oxide nanoparticles. The fabricated powder was then calcined at $700$ $^\circ$C for 1 h to remove residual carbonaceous products. Calcination process resulted in formation of pure, crystalline ceria nanoparticles of 12 nm average particle size (Figure S2 of Supplementary Information, Section S1 $\dagger$). Further description about preparation and characterization of the cerium oxide nanoparticles is given in our earlier work.

### 2.3 Preparation of control Psf and Psf-(ND+Ce) hybrid membranes

Control Psf and Psf-(ND+Ce) hybrid membranes were fabricated by phase inversion technique. For fabricating these membranes, dope solutions were prepared as per the composition provided in Table I. In Psf-(ND+Ce) hybrid membranes, ND and ceria were mixed as per proportion given in Table I. The nanomaterials was then dispersed in 100 mL of NMP and then kept in sonication bath for 30 minutes. Base polymer, Psf (25 g), and additive PVP (7.5 g) were then added to the dispersion. The dope solution was kept for continuous stirring until a homogeneous casting solution was obtained. The stirring process usually takes up to 24 h. The dope solution for the control Psf membrane was prepared without addition of any nano additives, following the same procedure.

Both control Psf and Psf-(ND+Ce) hybrid membranes with a thickness of 200 $\mu$m were prepared using flat-sheet table top casting machine at ambient temperature and then gelled in demineralized water. Composition and label of different membranes are given in Table I.
Table 1 Compositions of dope solution for the membrane synthesis.

| Type of membrane     | Membrane label | Psf (g) | NMP (ml) | PVP (g) | ND (%/Psf) | Ceria (%/Psf) |
|----------------------|----------------|---------|----------|----------|------------|---------------|
| Control Psf          | Psf            | 25      | 100      | 7.5      | 0          | 0             |
| Psf-(ND+Ce) hybrid   | 0.25ND-0.25Ce  | 25      | 100      | 7.5      | 0.25       | 0.25          |
|                      | 0.25ND-0.5Ce   | 25      | 100      | 7.5      | 0.25       | 0.5           |
|                      | 0.5ND-0.25Ce   | 25      | 100      | 7.5      | 0.5        | 0.25          |
|                      | 0.5ND-0.5Ce    | 25      | 100      | 7.5      | 0.5        | 0.5           |

2.4 Irradiation of membranes

The as-prepared individual membranes immersed in demineralized water were sealed in zip-lock polyethylene bags for irradiation. Both control Psf and Psf-(ND+Ce) hybrid membranes were exposed to 100, 500 and 1000 kGy of radiation using a 60Co source Gamma Chamber GC-5000 (Board of Radiation & Isotope Technology, BRIT, India) with dose rate of about 1.5 kGy h⁻¹ (Fricke dosimetry).

2.5 Membrane characterization

The surface and cross-sectional morphology of membranes was observed using field-emission scanning electron microscope (FE-SEM, Make: AURIGA 4553) at operating voltages of 20 and 5 kV, respectively. Using a sputter coater with gold-palladium alloy target, the membranes were made electrically conducting at 15 mA current for 100 seconds.

The average pore size of the membranes was determined using the porometer (Porolux 1000 model, Benelux Scientific, Belgium). The data acquisition and analysis was carried out using LabView software for the 25 mm diameter of membrane sample. The “Porefill” solution (Benelux Scientific, Belgium, γ = 16 dyne/cm, vapour pressure = 3 mm Hg at 298 K) was used as a wetting liquid for capillary flow porometry, as it is a non-toxic inert fluorocarbon wetting fluid having zero contact angle in membrane, that is Cos θ = 1.

Topography of the membrane surface was analyzed through atomic force microscope (AFM, Model: SOLVER next, NT-MDT, Russia). For AFM analysis, a small (1 cm²) dry piece of membrane was taken and pasted onto the metal substrate. AFM images were obtained in tapping mode using a silicon cantilever NSG 10 (NT-MDT, Russia) with spring constant 11.8 N m⁻¹ and resonating frequency 240 kHz. The imaging was carried out at room temperature and ambient pressure and surface roughness of these membranes was obtained by NOVA-P9 software. The effect of nanomaterials (ND and ceria) loading and irradiation dose on surface roughness of the membrane was examined within a scan range 3μm × 3μm.

Using KRUSS Advance drop shape analyzer (DSA100, Germany) water contact angle at the membrane surface was measured under ambient conditions. A small piece of membrane was placed on a glass slide and water was dropped onto the surface of the membrane. The drop was illuminated from one side and a camera at the opposite side recorded an image of the drop. KRUSS Advance software was used to analyze the image. Contact angles in three different regions on each membrane were measured and an average was taken.

Gel permeation chromatograph (GPC) system (Malvern 270 dual detector, UK) equipped with refractive index detector and light scattering detector (λ = 670 nm, consisting of two scattering angles: 90° and 90°) along with T6000M, general mixed organic column (300 × 8 mm) (Viscotek, Malvern, UK) was used to determine average molecular weight of the membranes. The detector and column temperature was kept at 22 °C. The mobile phase consisted of tetrahydrofuran (SD Fine Chemicals Ltd., India) at a flow rate of 0.5 mL min⁻¹. FTPE syringe filter with 0.22 μm pore size and 25 mm diameter (AxivaSichem Biotech, India) was used to filter the samples. The volume injected was 100 μL. Both detectors were calibrated with polystyrene standards having narrow molecular-weight distribution. Viscotec OmniSEC 5.12 software was used to analyze the data.

Differential scanning calorimetry (DSC) thermograms of unirradiated and 1000 kGy irradiated membranes were recorded in differential scanning calorimetry (DSC 1 STARE system, Mettler-Toledo AG (MTANA), Switzerland) unit over the temperature range of 40 to 600 °C in flowing oxygen atmosphere (flow rate: 40 ml min⁻¹). DSC unit was calibrated for temperature and heat flow measurements using multiple standards (Hg, In, Sn, Pb and Zn) prior to measurements. For the DSC measurement, a small peace of each membrane was sealed in to the 40 µl aluminium pan by covering lid with the small hole in it.

Universal testing machine (UTM, Hemteck Techno Instrument, model LRX Plus, India) was used to measure mechanical properties of the membranes at room temperature and 40-50% relative humidity. Dumbbell shaped specimens of the membranes, each of 5 cm length and 0.6cm width, were prepared for analysis. During the analysis, a constant deformation rate of 100 mm min⁻¹ was applied. NEXYGEN plus software was used to calculate tensile strength (TS) and percent elongation at maximum force (%E) for the membrane.

2.6 Membrane performance evaluation

Performance of the membranes was studied in an ultrafiltration test skid (cross-section area A = 14.5 cm²) at room temperature and 1 bar trans-membrane pressure. Steady state pure water permeability (PWP) was established by measuring flow of permeate in litre per square meter per hour (L m⁻² h⁻¹). PWP through the membrane area (A, in m²) was calculated using the volume (V, in L) collected during a time period (T, in h) and expressed by Equation [1].
Membranes were initially placed for compaction for 1 h in water to ensure ultrafiltration test conditions to achieve stabilized performance. The solute rejection behavior of membranes was studied using 200 ppm solutions of polyethylene oxide (PEO, average molecular weight 100 kDa) at room temperature and 1 bar trans-membrane pressure. TOC analyzer (ANALYTIC, SGE analytical science, Australia) was used to analyze concentration of PEO in both feed and permeate samples by measuring total organic carbon content. Rejection (R) of PEO offered by the membranes was calculated using Equation (2):

\[ R(\%) = \frac{C_f - C_p}{C_f} \times 100 \]  (2)

Here, \( C_f \) is the concentration in the feed and \( C_p \) is the concentration in the permeate side.

2.7 Pulse radiolysis studies for evaluation of \( e_{aq}^- \) scavenging capability of ND particles

Pulse radiolysis experiments were carried out with high-energy electron pulses (7 MeV, 500 ns) obtained from a linear electron accelerator. Transient species formed by pulse radiolysis were detected by optical absorption method. Aerated aqueous solution of KSCN (1 x 10^{-2} M) was used for determining the dose delivered per pulse, monitoring the transient (SCN)^- at 475 nm, using Ge (475 nm) = 2.59 x 10^{-4} m^2/J. Here, G denotes radiation chemical yield in mol J^{-1} and e denotes molar extinction coefficient in m^2/mol. The dose per pulse was close to 10-12 Gy/pulse (1 Gy = 1 J kg^{-1}). Radiolysis of \( N_2 \)-saturated neutral aqueous solution leads to radiolysis of water as given in Equation (3):

\[ H_2O \rightarrow H^*, OH^*, e_{aq}^- H_2, H_2O_2, H_3O^+ \]  (3)

In studies, the ability of ND particles to scavenge \( e_{aq}^- \) was investigated by using different concentration of ND in de-mineralized water, and compared with de-mineralized water without adding any nanomaterial in it.

2.8 Hydroxyl radical scavenging studies

Scavenging activity of nanomaterials (ND and ceria) was evaluated by performing competition kinetics using MG (malachite green) as reference solute. Hydroxyl (OH*) radical was generated by Fenton reaction, where \( Fe^{2+} \) ion is oxidized by hydrogen peroxide as shown in Equation (4):

\[ Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^* \]  (4)

MG is a triphenyl methane dye which is intense green in colour, having absorption peak at 615 nm. The OH* radicals formed reacts instantly with MG and oxidizes it, as shown in Equation (5):

\[ Mg + OH^- \rightarrow MgO \]  (5)

Final composition of reaction mixture contains 12 \( \mu M \) MG, 0.15 mM FeSO_4 and varying concentration of nanomaterial (ND or ceria). The reaction was initiated by adding 1 M hydrogen peroxide. Absorbance-time plot in absence and presence of different scavengers was fitted with first order kinetics. These studies were performed using UV-Vis spectrometer (JASCO V-630 spectrophotometer) in a quartz cuvette (1 cm x 1 cm).

3 Results and discussion

3.1 Studies on membrane morphology and topography

The surface and cross-section morphologies of membranes are shown in Figure 1. All the membranes demonstrate the typical morphology observed in the films produced by phase inversion technique, with a dense top layer supported by finger-like structure. The top surface of control Psf membrane is comparatively dense, while the membranes impregnated with ceria and ND nanoparticles have more free volume (shown in Figure 1(a) to (e)). The free volume of the membrane represents pore channels that assist in enhancing the permeability of the membrane.

During phase inversion, addition of nanoparticles (ND and ceria) delays the exchange of solvent and non-solvent due to increased viscosity of casting solution, resulting in a wide finger-like structure. The hydrophilic hydroxyl and carbonyl functional groups attached to ND (shown in supplementary information Figure S3 and Figure S4) attract water molecules which increases the pore density of the membranes, as shown in Figure 2. The surface and cross-section morphology (Figure 1) show that by impregnating ND and ceria nanoparticles into the Psf host matrix, free volume of the membrane increases due to the increased pore density (shown in Figure 2), while pore size is not affected by the impregnation of nanoparticle (confirmed by the average pore size using porometer later). The \( \gamma \)-radiation alters the morphology of membranes due to simultaneous chain scissoring and cross-linking of Psf chain.

As a result, control Psf membrane showed lower pore density, but increased pore size. However, the presence of ceria and ND protects the Psf matrix and prevents, to a reasonable extent, the onset of any deteriorating effects in the porous morphology. Therefore, the pore density and average pore size of the hybrid membranes increases after irradiation, leading to enhancement in permeability and decline in solute re-jection abilities (discussed later). However, 0.5ND-0.5Ce hybrid membrane does not show much variation in average pore size of the membrane matrix even after 1000 kGy of radiation does, while pore density increases. There is no observable change in the membrane cross-section morphology after irradiation, as compared to the unirradiated ones (Figure S5 of Supplementary Information, Section S3). The 0.5% optimum concentration each of ND and ceria results in strong interfacial interation with polymer matrix that prevent from the \( \gamma \)-induced degradation, which leads to water permeability enhancement without much variation in solute rejection (discussed later). The energy dispersive spectrometer (EDS) mapping of Psf-ceria composite is shown in Figure S6 of Supplementary Information, showing the signature of
ceria in the composite. However, when several locations of the hybrid MMM were investigated with EDS, the signature of ceria was not observed. This could be due to the hydroxyl functional groups present on the surface of ND, and ceria being hydrophobic, which leads to preferential migration of ND to the top surface of the composite membrane during their synthesis through phase inversion technique, which is an important observation made here.

The average pore size of the unirradiated membranes obtained from porometer is found to be in the range of 0.08-0.1 μm (Figure S7 of Supplementary Information, Section S4) for all the unirradiated membranes (control Psf and hybrid), confirms that the nanoparticles have not affected the pore size of the membrane matrix. After 1000 kGy of radiation dose, average pore size increases up to 0.13, 0.26, 0.31, 0.23, and 0.16 μm for control Psf, 0.25ND-0.25Ce, 0.25ND-0.5Ce, 0.5ND-0.5Ce, and 0.5ND-0.5Ce membranes, respectively (Figure S8 of Supplementary Information, Section S4). The increase in the pore size leads to the decline in the solute rejection abilities (discussed later). It is important to note that the 0.5ND-0.5Ce hybrid membrane shows the least variation in pore size, and hence the solute rejection attribute has not been significantly affected.

Figure 3 shows membrane surface roughness obtained from AFM studies. Impregnation of nanomaterials (ND and ceria) slightly increased the surface roughness of the membranes from 3.26 (control Psf membrane) to 3.62 nm (0.5ND-0.5Ce hybrid membrane). This is due to enhanced porosity of the membrane, as observed in FESEM images (Figure 2). Pore size of the control Psf membrane increases after irradiation (Figure 2 (f)), leading to increase in surface roughness with radiation dose. The surface roughness of hybrid membranes also increases with increase in radiation dose due to increase in pore density (shown in Figure 2 (g) to (j)). However, up to 1000 kGy radiation dose, increase in the roughness for 0.5ND-0.5Ce hybrid membrane is only 8.6%, compared to the increase of 18.8% for the control Psf membrane. Rise in the surface roughness resulted in the increased transportation of solvent through membrane, as observed in the pure water permeability values discussed in the later section.

3.2 Studies on physico-chemical properties of the membranes
Hydrophilicity/ hydrophobicity of membrane surface was determined by water contact angle studies. As shown in Figure 4, water contact angle of control Psf membrane is about 85°, which slightly increases up to 85° on addition of ceria and ND nanoparticles. The small rise in contact angle is due to hydrophobic and hydrophilic characteristic of ceria and ND nanoparticles, respectively, wherein the effect of ND dominates leading to a resultant hydrophilic hybrid membrane. This is due to the preferential migration of ND onto the top surface of the MMM during the synthesis by phase inversion technique. The contact angle of each membrane decreases with the radiation dose due to increased surface roughness, as discussed in previous section (Figure 3).

The decline of contact angle is more pronounced in hybrid membranes (at 1000 kGy radiation dose, 64.5, 71.6, 57, and 60.9° for 0.25ND-0.25Ce, 0.25ND-0.5Ce, 0.5ND-0.25Ce, and 0.5ND-0.5Ce, respectively), compared to control Psf membrane (73.6° at 1000 kGy radiation dose). This is due to increased pore density (shown in Figure 2 (g) to (j)) with radiation, resulting in higher water uptake and enhancement of hydrophilicity. Radiation enhances the water permeability by enhancing hydrophilicity, while the nanoparticles stabilize the membrane matrix in radiation.

Fig. 3 Variation in root mean square surface roughness of the membrane with the ND and ceria loadings, at different radiation dose.

Fig. 4 Variation in membrane surface-water contact angle with different loadings of ND and ceria nanoparticles, at different radiation dose.

Weighted average molecular weight ($M_w$) of the membranes was determined by gel permeation chromatography (GPC) to observe cross-linking and chain-scissioning phenomena during irradiation. As shown in Figure 5, $M_w$ of control Psf membrane slightly decreased after 100 kGy irradiation, while that of hybrid membranes increased. The variation in $M_w$ indicates the chain scissioning in control Psf, and cross-linking in hybrid membranes, as predominant phenomenon. For control Psf membrane, influence of chain scissioning phenomenon increases with radiation dose, and therefore $M_w$ decreases from 63241 Da for the unirradiated Psf (Psf-UR) to 34954 Da for the Psf irradiated up to 1000 kGy (Psf-1000 kGy). On the other hand, hybrid membranes exhibit cross-linking phenomenon up to 500 kGy radiation dose. Above 500 kGy radiation dose, chain-scissioning predominates
and consequently $M_w$ starts to decrease. The 0.5ND-0.5Ce hybrid membrane does not show significant difference in $M_w$ even up to 1000 kGy of radiation dose. The results confirm the enhanced stability of Psf membrane matrix up to 1000 kGy due to the presence of 0.5% ND and 0.5% ceria. This stability against $\gamma$-radiation can be attributed to the free radical scavenging property of ceria and ND (discussed later).

### 3.3 Studies on the oxidative degradation of the membranes

Thermal oxidative stability of the membranes were investigated by the differential scanning calorimetry (DSC) studies. Figure 5 (a) shows DSC thermograms of unirradiated membranes, where the effect of ND and ceria loading can be observed on the thermal oxidative degradation of the membrane matrix. DSC thermogram of the control Psf membrane shows three exotherms with increasing temperatures having peaks at $\sim 430$, $\sim 530$, and $\sim 590$ °C. Since Psf is a polymeric network, it undergoes crystallization/partial crystallization with heating (which also gives exothermic DSC trace). Reinforcement of Psf with ND and ceria nanoparticles (0.25-0.50 wt%) do not show any observable effects on peak temperature of the first exotherm ($\sim 430$ °C). While all the four membrane samples show single peak, the membrane 0.5ND-0.5Ce shows two peaks before the onset of second exotherm, indicating that higher loading of ND and ceria has affected the thermal response of Psf towards this exothermic phenomenon. Stage 2 exotherm also remains almost invariant in terms of peak temperature ($\sim 525$ to $529$ °C). Stage 3 exotherm shows distinct behavior with ND and ceria loading, wherein the peak at $\sim 589$ °C for the control Psf goes down sharply by $\sim 15$ °C for the 0.5ND-0.25Ce membrane sample, indicating that composite membrane has a reduced thermo-oxidative stability as compared to the control Psf membrane. Also, the onset of exotherm is shifted to lower temperatures, further corroborating the inference of composite's lowered thermal stability. Decomposition is apparently completed before 600 °C for both the 0.25ND-0.25Ce and 0.5ND-0.50Ce membrane samples, which was incomplete for the control Psf membrane sample up till 600 °C. Further reinforcement of nanoparticles shows reduction in peak temperature to $\sim 565$ °C (reduced by $\sim 10$ °C) for the 0.5ND-0.25Ce membrane, which is in line with the observed trend. However, at the same time, the exotherm clearly broadens with additional high temperature exotherm overlapped with the 565 °C peak exotherm, which can be seen from the shoulder type peak. This suggests that ND addition has distinct effect on thermo-oxidative stability than that of ceria reinforcement. Very interestingly, 0.5ND-0.5Ce
degradation. Branes offering the enhanced stability against thermo-oxidative degradation. Such samples show an anomalous increase in peak decomposition temperature (stage 3), which indicates increased thermal stability. Also, decomposition is not completed till 600 °C (similar to that of control Psf). The findings show distinctly higher thermal stability of this composite membrane, while the ones with lower loadings (0.25ND-0.25Ce, 0.25ND-0.5Ce and 0.5ND-0.25Ce) show opposite trend. Regarding the irradiated samples, lowering of peak temperature of stage 1 by 5-6 °C for control Psf membrane indicates radiation induced degradation in the Psf matrix, which led to reduced stability of polymer membrane around 430 °C. Increase in stage 1 peak temperature (430 °C) of irradiated composite membranes with higher ND loading (0.5ND-0.25Ce & 0.5ND-0.5Ce) again indicates that ND does have a stabilizing effect towards thermal response. Stage 2 and 3 of irradiated Psf is highly overlapped. Interestingly, stage 2 peak has shown upward shift while that of stage 3 has shown significant downward shift in temperature. Since it is control Psf, these effects are manifestation of irradiation on weakening the polymer network. In all the irradiated samples, stage 2 is much more intense than stage 3, while the reverse is observed in all the unirradiated samples. Due to the radiation induced damage of the membrane matrix by chain scissioning and cross-linking, the range of order in Psf chain has been altered, which is clearly observed in Figure 5(b). Psf-1000 kGy is showing a broad peak in the range 534 to 556 °C, which indicates diverse sizes of Psf chains occurred due to chain scissioning and cross-linking phenomena (as observed in GPC analysis, shown in Figure 5). Table 2 shows only small effect for higher order chains in stage 3 for hybrid membranes due to chain scissioning at 1000 kGy (as observed in GPC analysis, Figure 5). This is clear from the comparison of thermograms of unirradiated membrane samples with that of irradiated ones that the Psf network is affected significantly by the irradiation, compared to that of the composite membranes, with 0.5ND-0.5Ce membranes offering the enhanced stability against thermo-oxidative degradation.

3.4 Studies on mechanical properties of the membranes

Mechanical properties of the membranes were investigated in terms of tensile strength (TS) and percentage elongation (%E) at maximum force, as shown in Figure 7. Tensile strength and percentage elongation of the control Psf membrane are 3.07 MPa and 14.2%, respectively. By impregnation of ND and ceria, the mechanical strength of all the hybrid membrane has increased, with the TS and %E of 4.17 MPa and 19.2%, respectively, for the membrane with 0.5% each of ND and ceria. The mechanical properties of the membranes mainly depend on two factors. One is the size of nanoparticles, which is crucial for interfacial interaction between nanoparticles and Psf. The average size of the ND nanoparticles is about 5 nm (Figure S1 of supplementary information) and that of ceria is about 12 nm (Figure S2 of supplementary information), which leads to high surface to volume ratio of nanoparticles and hence, an excellent interfacial area for enhanced interaction between the polymer and nanomaterials. Another factor is the distribution of nanoparticles in the membrane matrix. The uniform distribution of nanoparticles provides strong interaction, while agglomeration reduces the number density of the particles resulting in reduced interaction. The 0.5% loading each of ND and ceria in Psf host matrix was found to be an optimum in terms of uniform distribution and strong interaction, thus offering enhanced mechanical properties. After 100 kGy of irradiation, control Psf membrane starts losing its mechanical strength due to chain scissioning, as observed in GPC analysis shown in Figure 5. On the other hand, the value of %E got slightly increased, because the chain scissioning leads to the increased flexibility of Psf chain. Similar observation has been made for the 0.25ND-0.25Ce membrane, as the small amount of loading of the nanomaterials has not much affected the rigidity of the Psf matrix. On the other hand, the higher loading of nanomaterials introduced the rigidity in Psf matrix. Further increment in the radiation dose leads to the chain scissioning of Psf chains, as a result of which mechanical properties deteriorate. The increase in pore density of hybrid membranes (as observed in pore distribution images, Figure 2) due to radiation also results in reduced TS and %E with dose. Reduction in %E of hybrid membranes is less

![Fig. 2 FESEM images of the membrane surface of unirradiated (a, b, c, d, and e) and 1000 kGy irradiated (f, g, h, i, and j) Psf, 0.25ND-0.25Ce, 0.25ND-0.5Ce, 0.5ND-0.25Ce, and 0.5ND-0.5Ce membranes, respectively.](image-url)
than that of control Psf membrane for up to 1000 kGy radiation dose, as shown in Figure 2 (b). Results indicate that mechanical properties of hybrid membranes are restored even after 1000 kGy radiation dose. The 0.25ND-0.25Ce and 0.5ND-0.5Ce hybrid membranes are found to be most stable in radiation environment in terms of their mechanical properties.

3.5 Studies on performance of membranes

Figure 8 shows the membrane performance based on pure water permeability and solute rejection attributes of membranes for PEO-100 kDa. Permeability offered by control Psf membrane was found to be about 156 \( L \, m^{-2} \, h^{-1} \) with 94.6% rejection, while all the hybrid membranes exhibited improved permeability and rejection. The inherent trade-off found in any polymeric membrane systems is observed to have reduced to a reasonable extent in the hybrid membranes. The permeability of 0.5ND-0.5Ce increased up to 192 \( L \, m^{-2} \, h^{-1} \) with solute rejection of 97.6%. The performance is enhanced due to increased pore density of the membrane, as shown in the FESEM image Figure 2 (e) [59]. This indicates that the presence of ND and ceria nanoparticles could create additional pathways for water flow, without increasing the pore size. The enhanced surface roughness (Figure 3) and hydrophilic groups present on the ND surface (Figure S3 and Figure S4 of Supplementary Information [51]) also contribute to increase in permeability. Hence, the solute rejection as well as the solvent flux increases. On exposure to radiation, the permeability of control Psf membrane decreased to 120 \( L \, m^{-2} \, h^{-1} \) and rejection rate to 87%, which could be due to increase in pore size and reduced pore density of the membrane, as can be seen in FESEM image Figure 2 (f). This is due to the degradation of Psf matrix by chain scissioning in \( \gamma \)-radiation environment, as confirmed by the GPC analysis shown in Figure 5. On the other hand, due to increased pore density of hybrid membranes in radiation environment (FESEM images Figure 2), the permeability is enhanced with slight reduction in rejection attributes. At 1000 kGy radiation dose, 0.5ND-0.5Ce hybrid membrane shows permeability of 288 \( L \, m^{-2} \, h^{-1} \) with 88.5% rejection. This ascertains the resist-tance of hybrid membranes against chain scissioning and cross-linking phenomena, as also confirmed by the consistent molecular weight of the membrane (GPC analysis, Figure 5). These results clearly confirms the improved performance of membranes and stability in radiation environment with impregnation of ND and ceria nanoparticles.

A mathematical modeling of solute rejection behaviour of membranes was carried out with inputs from porometry data, as provided in Section S5 of Supplementary Information [51]. Since the porometer could not capture the pore sizes of membranes that are less than 70 nm, there is not a good agreement between
the model and the experimentally determined values. Whereas, the model is validated fairly well for the Psf-ND composite membranes based on the inputs of pore size determined from BET analysis.

3.6 Free radical scavenging activity of ND and ceria nanoparticles

3.6.1 $e_{aq}$ scavenging capability of ND particles

The characteristic absorption spectrum of $e_{aq}$ has a broad, structureless band with a maximum around 700 nm in aqueous system. In general, reactivity of $e_{aq}$ is investigated by monitoring time absorption plot at 700 nm in presence of different concentration of ND particles. Scavenging of $e_{aq}$ radical by ND particles was confirmed by monitoring their reaction with varying concentration of ND particles (Figure 7). Results showed that increasing ND concentration leads to rapid decay of hydrated electron, which confirms that ND is responsible for scavenging the most reactive radiolysed product ($e_{aq}$) of water.

3.6.2 Hydroxyl radical scavenging capability of ND particles

Maximum absorption peak of MG is at 615 nm. To understand participation of ND particles in the reaction, oxidation of MG was performed by $OH^\bullet$ radical in presence of different concentration of ND particles. Figure 8 shows degradation of MG in presence of different concentration of ND. As shown in inset of Figure 8 with increase in the concentration of ND, degradation rate of MG decreases. This indicates scavenging of $OH^\bullet$ radical by ND particles. The $OH^\bullet$ radical scavenging phenomenon of ND particles can be expressed in Equation (6).

$$\text{ND} + OH^\bullet + H^+ \rightarrow \text{NDNO}_2 + H_2O$$  \hspace{1cm} (6)

Decrease in degradation rate of MG ($k_{obs}$) with concentration of ND confirms increase in $OH^\bullet$ radical scavenging activity of ND.

3.6.3 Hydroxyl radical scavenging capability of ceria nanoparticles

Maximum absorption peak of MG is at 615 nm. To understand participation of ceria nanoparticles in reaction, oxidation of MG...
Fig. 9 Absorption-time plot of hydrated electron of water at 700 nm in presence of varying concentration of ND particles suspended in aqueous solution containing 1 M t-butoxide at pH 7 under N2 saturated condition. Here, plot corresponds to ND concentration at (a) = 1.65 µg/ml, (b) = 4.12 µg/ml, (c) = 8.25 µg/ml, (d) = 16.5 µg/ml, (e) = 33 µg/ml, (f) = 49.5 µg/ml, (g) = 66 µg/ml. Inset shows the plot of observed rate of hydrated electron as a function of ND particles concentration at pH 7.

Fig. 10 Hydroxyl radical scavenging by ND particles. Inset shows inhibition of absorbance of MG due to OH• radical induced degradation in presence of different concentration of ND particles (5 - 81 µg/ml).

by OH• radical in presence of different concentration of ceria nanoparticles. Figure 11 shows degradation of MG in presence of different concentration of ceria. As shown in inset of Figure 11 with increase in the concentration of ceria, degradation rate of MG decreases. This indicates scavenging of OH• radical by ceria nanoparticles. The OH• radical scavenging phenomenon of ceria nanoparticles can be expressed in Equation (7):

\[ Ce^{3+} + OH^* + H^+ \rightarrow Ce^{4+} + H_2O \]  

(7)

Decrease in degradation rate of MG \((k_{obs})\) with concentration of ceria confirms increase in OH• radical scavenging activity of ceria.

Fig. 11 Hydroxyl radical scavenging by ceria nanoparticles. Inset shows inhibition of absorbance of MG due to OH• radical induced degradation in presence of different concentration of ceria nanoparticles (5 - 81 µg/ml).

4 Conclusions

With an objective of expansion of application of polymeric membranes in γ-radiation environment, Psf-(ND+Ce) hybrid membranes were synthesized by impregnation of nanodiamond (ND) and cerium oxide nanoparticles (ceria) into the Psf host matrix. Ceria protects the Psf membrane matrix by scavenging secondary free radicals generated due to γ-radiolysis of water, while ND offers strength and enhances the overall lifetime of the membrane in γ-radiation environment. These Psf-(ND+Ce) hybrid membranes are found to offer increased free volume, compared to the control Psf membranes, due to the enhanced pore density. This results in increased surface roughness and permeability of the hybrid membranes, without compromise in the selectivity. Me-chanical properties of the hybrid membranes also get improved in terms of tensile strength and percentage elongation. In addition, the loading of ND and ceria makes the Psf matrix stable against oxidative degradation at high temperature in the radiation environment. All the Psf-(ND+Ce) hybrid membranes are found to be stable up to 500 kGy of radiation dose, while 0.5ND-0.5Ce membrane is found to be stable up to 1000 kGy. The hybrid membrane with optimum composition of 0.5 wt% each of ND and ceria is found to be ~ 10 times radiation resistant, compared to the control Psf membrane. The free radical scavenging studies undertaken here provide important and interesting insights and evidences into the role and mechanism of ND and ceria nanoparticles in offering radiation resistant properties to the hybrid membranes with synergy. The present study has made a classic beginning to the development of an important class of hybrid membranes with enhanced radiation stability.

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