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# Synthesis, characterization and optimization of sulfonated poly-ether-ether-ketone (sPEEK)/functionalized carbon nanotubes (c-CNTs) nanocomposite membranes for fuel cell application

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ABSTRACT

Poly-ether ketone (PEEK) was modified to sulfonated poly-ether ketone (sPEEK) by sulfonation process with a degree of sulfonation 49.5%. Carbon nanotubes were acid-treated with sulfuric acid and nitric acid solution (3:1, *v/v*) for functionalization. sPEEK and sPEEK/c-CNT membranes were prepared by solvent casting method using dimethyl sulfoxide (DMSO) as solvent. The experimental part was conducted as per design of experiment employing response surface methodology consisting of three factors, namely (A) c-CNT (wt.%), (B) mixing temperature (°C), and (C) sPEEK concentration (mg/mL). The ion exchange capacity was found to increase with c-CNT (wt.%). Fourier-transform infrared spectroscopy confirms the sulfonation of PEEK. X-Ray diffraction investigates the influence of the sulfonation in the crystal structure of the sPEEK and sPEEK/c-CNT. Scanning electron microscopy images show that c-CNTs are dispersed well in the sPEEK matrix. The results showed slightly increasing water uptake and swelling ratio of the composites membranes. The analysis of variance (ANOVA) revealed that c-CNT (wt.%) is highly affecting the responses. Proton conductivity of sPEEK specimen is about 23.9 mS/cm, which is significantly increased to 57.0 mS/cm for sPEEK/0.12 c-CNT (wt.%) membrane suggesting its application for fuel cell.

## 1. Introduction

Production and consumption of energy is one of the parameters of the progress of a country. Therefore, due to environmental and other issues, producing clean energy is the need of the hour. In recent years, fuel cells have been widely considered to be the most important and most effective devices for generating clean energy. The fuel cell can change the chemical energy to electrical energy with high efficiency while avoiding the emission of gases that negatively affect the environment [1,2]. Proton exchange membrane fuel cell (PEMFCs) are favorable new energy gate for portable vehicles and devices [3–5]. To fabricate large PEMFC, the polymer membrane must have several properties such as proton conductivity close to 0.1 S/cm under operating condition, good thermal stability, good mechanical properties and reduced permeability. Reduction of cost of fabrication of membrane is also necessary for economic reasons. Further, the membrane within the fuel cells ought to operate at about 120 °C for a long time [6–8]. Moreover, a perfect proton exchange membrane (PEM) should include the features viz: (i) durability under sharp mechanical stress as well as different operating conditions, (ii) stability beneath hydrolytic, radical environments and oxidant, (iii) control to decrease the swelling ratio, (iv) optimum bound water content, and (v) capacity to transport protons [9]. Sulfonated poly-ether-ketone (sPEEK) is one of the membranes which can be used as fuel cell membrane because of its low cost, excellent chemical and mechanical properties [10–14]. sPEEK membrane can be directly synthesized from sulfonation of poly-ether-ether-ketone (PEEK) [15–17].

Recently, enhancements in properties of PEM by incorporation of carbon nanotubes (CNT) as fillers have been accomplished and reported [18–22]. Incorporation of CNT in polymer matrix exhibits excellent mechanical properties of polymer/CNT nanocomposites. However, it has been reported that the CNT ratio should be less than the percolation

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**Table 1**
Factors and levels of RSM-CCD design of experiment (sPEEK/c-CNT).

| Factors | Levels | |
|---|---|---|
| | L1 | L2 |
| c-CNT (wt.%) | 0.03 | 0.1 |
| Mixing Temperature (°C) | 40 | 60 |
| sPEEK concentration (mg/mL) | 30 | 60 |

threshold to avoid agglomeration of CNT in the polymers [23]. The modification of the CNT surface is required for the strong polymer/CNT interface. The strong interface is a must for load transfer from matrix to reinforcement. Modification of the CNT surface which includes covalent and non-covalent functionalization as well as defect functionalization is considered as the primary approach to prevent the aggregation to get uniform distribution of CNT in the polymer matrix. However, non-covalent functionalization does not include any structural loss in the CNTshell. Further, attachment of functional groups like COOH or OH with CNTs is accomplished by oxidation in air or acidic medium. The polymer composite processing includes a good distribution of CNT of the polymer solution. For good distribution of CNT in the polymer solution, the ultrasonication method is used followed by magnetic stirring to evaporate the solvent at a higher temperature. All these steps have been successfully incorporated by the researchers for the fabrication of polymer and polymer nanocomposite membranes [24–26]. Various parameter affects the final properties of the polymer/CNT nanocomposites. Literature survey shows that most of the previous studies on the properties of the polymer/CNT nanocomposites are based on conventional ways to vary one parameter at a time and coupling of factors have not been explored completely. Therefore, to the best of our knowledge this is the first study in which effect of a combinations of various parameters has been explored on the properties of sPEEK/c-CNT nanocomposite membranes by employing design of experiment. The response surface methodology (RSM) results yield quantitative relationship in the form of a model either in coded or in engineering units.

The present study aims to determine the influence of the various factors like c-CNT wt.%, mixing temperature and sPEEK concentration on the key responses such as proton conductivity, ion exchange capacity, water uptake and swelling ratio of sPEEK/c-CNT nanocomposite membrane. The design of experiment was accomplished according to the RSM. This design of experiment (DoE) has suggested 20 sets of the experimental run. Hence, 20 samples of sPEEK/c-CNT nanocomposite membrane were synthesized by varying various parameters. The casted membranes were subjected to various characterizations to check their suitability for fuel cell application.

**Table 3**
Design of experiment as per RSM-CCD for sPEEK/c-CNT.

| | Factors | | |
|---|---|---|---|
| Std. Order | A: c-CNT (wt.%) | B: Mixing temp (°C) | C: sPEEK conc. (mg/mL) |
| 1 | 0.030 | 40.00 | 30.00 |
| 2 | 0.100 | 40.00 | 30.00 |
| 3 | 0.030 | 60.00 | 30.00 |
| 4 | 0.100 | 60.00 | 30.00 |
| 5 | 0.030 | 40.00 | 60.00 |
| 6 | 0.100 | 40.00 | 60.00 |
| 7 | 0.030 | 60.00 | 60.00 |
| 8 | 0.100 | 60.00 | 60.00 |
| 9 | 0.006 | 50.00 | 45.00 |
| 10 | 0.120 | 50.00 | 45.00 |
| 11 | 0.065 | 33.18 | 45.00 |
| 12 | 0.065 | 66.82 | 45.00 |
| 13 | 0.065 | 50.00 | 19.77 |
| 14 | 0.065 | 50.00 | 70.23 |
| 15 | 0.065 | 50.00 | 45.00 |
| 16 | 0.065 | 50.00 | 45.00 |
| 17 | 0.065 | 50.00 | 45.00 |
| 18 | 0.065 | 50.00 | 45.00 |
| 19 | 0.065 | 50.00 | 45.00 |
| 20 | 0.065 | 50.00 | 45.00 |

## 2. Experimental

### 2.1. Design of experiment (DoE)

DoE is an asymmetric method to find the relationship between the factors affecting a process and the responses of that process. The experiments were conducted according to RSM of the DoE. The central composite design (CCD) is based on 3-factors and 2-levels. These factors are (factor A) c-CNT (wt.%), (factor B) mixing temperature (°C), and (factor C) sPEEK concentration (mg/mL). Two levels, i.e., L1 and L2, show the range of variation of each factor as given in Table 1. Four responses namely proton conductivity, ion exchange capacity, water uptake and swelling ratio were chosen for getting the optimal values, as given in Table 2. Table 3 tabulates the design of experiment as per RSM-CCD for sPEEK/c-CNT.

### 2.2. Materials and method

PEEK powder and multi-walled CNTs were obtained from Sigma Aldrich. Dimethyl sulfoxide (DMSO), sulfuric acid ($H_2SO_4$, 95/98%) and sodium hydroxide (NaOH) were purchased from Central Drug House (CDH), India. Hydrochloric acid (HCl) was purchased from Fisher Scientific, India. All chemicals were used without further purification.

**Table 2**
RSM-CCD design summary.

| | | | | | |
|---|---|---|---|---|---|
| Study Type: | Response surface | Runs : | 20 | | |
| Initial Design: | Central composite | Blocks: | No blocks | | |
| Design Model: | Quadratic | | | | |

| Factor | Name | Units | Type | Low Actual | High Actual | Low Coded | High Coded | Mean | Std. Dev. |
|---|---|---|---|---|---|---|---|---|---|
| A | c-CNT | wt.% | Numeric | 0.030 | 0.100 | −1.000 | 1.000 | 0.065 | 0.029 |
| B | Mixing Temp | °C | Numeric | 40.00 | 60.00 | −1.000 | 1.000 | 50.00 | 8.263 |
| C | sPEEK conc. | mg/mL | Numeric | 30.00 | 60.00 | −1.000 | 1.000 | 45.00 | 12.395 |

| Response | Name | Units | Min | Max | Mean | Std. Dev. | Ratio | Model |
|---|---|---|---|---|---|---|---|---|
| Y1 | Proton conductivity | mS/cm | 26.80 | 57.0 | 43.34 | 9.617 | 2.127 | Linear |
| Y2 | IEC | mmol/gm | 1.514 | 1.62 | 1.575 | 0.023 | 1.072 | R2FI |
| Y3 | Water uptake | % | 22.50 | 37.2 | 31.265 | 4.534 | 1.653 | RCubic |
| Y4 | Swelling Ratio | % | 1.70 | 8.30 | 5.155 | 1.508 | 4.882 | Linear |

**Obs**: 20; **Analysis**: polynomial; **Trans**: non

### 2.3. Sulfonation process of PEEK and functionalization of CNTs

PEEK powder was dried in a vacuum oven for 24 h at 100 °C. 30 g of dried PEEK powder was dissolved in 600 mL $H_2SO_4$ and vigorously stirred at room temperature for 72 h. Then the polymer solution was continuously added drop by drop to an ice-cold water by separating funnel with constant stirring. sPEEK beads were precipitated out. The precipitated polymer (sPEEK) was filtered and beads of sPEEK were obtained. These beads were washed several times with distilled water until their pH became neutral. Afterwards, beads were dried in vacuum oven for 24 h at 100 °C.

For the surface modification of CNT, 0.5 g of CNTs were added to 80 mL of $H_2SO_4/HNO_3$ solution (3:1, *v/v*) and the mixture was ultrasonicated for 30 min at 70 °C. The black solid produced was filtered and washed several times with distilled water. Finally, dried in a vacuum oven at 80 °C for 15 h and c-CNTs were obtained.

### 2.4. Formation of sPEEK membrane

sPEEK membranes were obtained using the solution casting method. 10 wt.% sPEEK sample was first dissolved in a suitable amount of DMSO as per DoE and continuously stirred at room temperature for 12 h to form a homogeneous solution. After that, the homogenous sPEEK solution was casted into a petri dish. The casted membrane was dried out at room temperature overnight and then kept in a vacuum oven at 100 °C for 24 h [27].

### 2.5. Formation of sPEEK/c-CNT membranes

sPEEK was dissolved in DMSO according to required concentration of solution as per DoE. In all 20 (sPEEK/c-CNT) nanocomposite membranes were prepared by varying various parameters as detailed in Table 3. The desired amount of c-CNT was added to sPEEK solution. The resulting mixture was stirred for 16 h and further ultrasonicated for 30 min at ambient temperature. The homogenous solution of sPEEK/c-CNT was then casted into a petri dish and kept in a vacuum oven at 100 °C for 24 h to remove the solvent.

## 3. Characterization

### 3.1. X-ray diffraction (XRD)

The structure of the membranes were examined by X-ray diffraction (XRD) method with a solid detector and Cu-K$\alpha$ radiation with wavelength ($\lambda$ = 1.54 Å) using Bruker D8 Advance X-ray diffractometer. The 2$\theta$ values ranged from 10° to 80° and the scanning rate of the data collection was 0.05° per second.

### 3.2. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX)

The structure and morphology of the membranes were studied using SEM (JEOL, JSM 6510LV). A thin layer of gold (Au) was vacuum sputtered on the membrane before the scanning. Elemental distribution in the component membranes was assessed by EDX attached with the SEM.

### 3.3. Transmission electron microscopy (TEM)

The morphology of the membranes was examined by a TEM (JEOL, JEM-2100). The sPEEK/c-CNT was transformed into solution in DMSO and a thin layer was directly casted onto TEM grid itself.

### 3.4. The degree of sulfonation (DS) and ion exchange capacity (IEC)

The degree of sulfonation (DS) was calculated by the back titration method. The sPEEK and sPEEK/c-CNTs membranes were cut into small pieces. 0.1 g of the sample was put in 20 mL of calibrated aqueous solution of 0.05 N NaOH. Sodium ions ($Na^+$) replaced the hydrogen in the backbone of sPEEK. After three days the solution was titrated against calibrated 0.05 N HCl aqueous solution using phenolphthalein as a pH indicator. The number of sulfonated repeat units (X) in sPEEK molecules were calculated from Eq. (1).

$$X = V_{\mathrm{NaOH}}\, M_{\mathrm{NaOH}} - V_{\mathrm{HCL}}\, M_{\mathrm{HCL}} \tag{1}$$

where $V$ and $M$ indicate the volume and morality of HCl acid and NaOH aqueous solution, respectively. The number of non-sulfonated units ($Y$) in sPEEK molecules was calculated from Eq. (2).

$$Y = \frac{W - M_s X}{M_{\mathrm{non}}} \tag{2}$$

where $W$ refers to the weight (g) of specimen, $M_s$ indicates the molecular weights of the sulfonated repeat unit, and $M_{\mathrm{non}}$ indicates the molecular weight of non-sulfonation repeat unit. The DS and IEC were calculated from Eqs. (3) and (4), as reported by Do et al. [28].

$$\mathrm{DS}(\%) = \frac{X}{X + Y} \tag{3}$$

$$\mathrm{IEC} = \frac{1000X}{W} \tag{4}$$

where $X$, $Y$ and $W$ are quantities explained above.

### 3.5. Fourier transform infrared (FT-IR) analysis

The Perkin-Elmer FT-IR Spectrometer (Model No. L1600300 Spectrum Two) was utilized to investigate the sulfonation process. The FT-IR data were recorded for various samples of sPEEK and sPEEK/c-CNT to study the changes that occurred as a result of the sulfonation process [29]. 1.0 mg of powdered sample was mixed with 100 mg potassium bromide (KBr) and was converted into a pellet using a KBr press. The spectrometer mentioned above was used to measure the spectrum for each pellet in the range of 400–4000 $cm^{-1}$.

### 3.6. Water uptake and swelling ratio

The sPEEK and sPEEK/c-CNT membranes were dried in an oven at 60 °C for 48 h and their weights were recorded. Samples were immersed in distilled water for 24 h at room temperature. Tissue paper was used to remove the surface moisture carefully and weights were recorded again [30,31]. Then, the percentage of water uptake was calculated from the Eq. (5) as given below:

$$\text{Water uptake } (\%) = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \tag{5}$$

where $W_{\mathrm{wet}}$ is the weight of the wet membrane and $W_{\mathrm{dry}}$ is the weight of the dry membrane.

For the measurement of swelling ratio, the membrane at first was dried it in an oven at 60 °C for 24 h and a piece of specific length was cut which was immersed in distilled water at room temperature for 24 h. Water and moisture from the surface were removed by using the tissue paper and the length was recorded again. The swelling ratio was calculated from Eq. (6):

$$\text{Swelling ration } (\%) = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \tag{6}$$

where $L_{\mathrm{wet}}$ is the length of the wet membrane and $L_{\mathrm{dry}}$ is the length of the dry membrane.

### 3.7. Proton conductivity measurements

The proton conductivity of the samples was measured by using a frequency response analyzer (FRA) Autolab model PGSTAT302 N [32,33]. The frequency was applied within the range of 0.1 to 10 kHz. The electrodes were typically connected in a four probe in the plane mode of conductivity cell for the measurement of conductivity and submerging the conducting cell in distilled water. The impedance of the membrane was obtained by electro-chemical fitting of Nyquist plot ($Z'$ vs. $Z''$). The proton conductivity of the specimens was calculated from the Eq. (7):

$$\sigma = \frac{L}{RTW} \tag{7}$$

where $\sigma$ (S/cm) is the proton conductivity, $L$ (cm) is the distance between two electrodes, $R$ (ohms) is the impedance, $T$ (cm) is the thickness of the membrane specimen, and $W$ (cm) is the width of the membrane specimen [34–37].

### 3.8. Thermal gravimetric analysis (TGA)

The thermal stability of the sPEEK and sPEEK/c-CNT membranes was analyzed using thermogravimetric analysis (TGA) using Perkin-Elmer TMA 4000 which is a uniquely designed thermomechanical analyzer (TMA) designed for optimal performance in measuring the coefficient of thermal expansion (CTE) in materials. TGA is known to be a method related to thermal study in which generally changes in the mass of materials are recorded by applying the heat from −20 to 900 °C under nitrogen atmosphere condition. The specimen was first dried in a vacuum oven at 80 °C to remove the moisture and the scan rate of the sample was kept at 10 °C/min.

### 3.9. Differential scanning calorimetry (DSC)

The DSC thermogram of sulfonated polymer, un-sulfonated polymers and composite membranes were studied using a Perkin-Elmer DSC. DSC 4000 offers dependable performance and quality results. This single-furnace, heat flux DSC is designed to run all routine applications and includes an easy-to-load vertical furnace that is resistant to oxygen and chemical corrosion. DSC measurements were performed over the temperature range of −90 to 350 °C at the heating rate of 10 °C/min under nitrogen atmosphere condition.

## 4. Results and discussions

### 4.1. Structural, morphological and topographical results

The effect of sulfonation on the crystal structure was investigated for PEEK, sPEEK and sPEEK/c-CNT nanocomposite membranes by using XRD. Fig. 1(a) shows XRD diffractogram of c-CNT, PEEK and sPEEK. It is clear from Fig. 1(a) that PEEK exhibits a semi-crystalline structure with sharp crystalline peaks at 2$\theta$ range at 18.6°, 20.6°, 22.5° and 28.7°corresponding to (110), (111), (200) and (211) planes respectively [38,39]. Also, XRD analysis shows intense peaks of c-CNT at 2$\theta$ =25.6° and 42.5° which is assigned to carbon nanotube (002) and (101) planes confirming the functionalization of CNT with carboxylic group c-CNT information as reported in literature [40]. Fig. 1(b) presents the powder XRD patterns of pristine sPEEK and sPEEK/c-CNT nanocomposite membranes. The presence of a broad peak at a 2$\theta$ value of 20° in the XRD pattern indicates a mixture of crystalline and amorphous components. As the concentration of c-CNT increases in the nanocomposite membrane, the broadening of the peak increases showing the increase in the amorphous nature of the membrane. Sulfonation introduces -$SO_3H$ group in PEEK altering the chair conformation and packing, thereby causing the loss in crystallinity [14,36,41]. Further, the presence of a peak at a 2$\theta$ value of 45° might be according to adding the filler (c-CNTs). The absence of

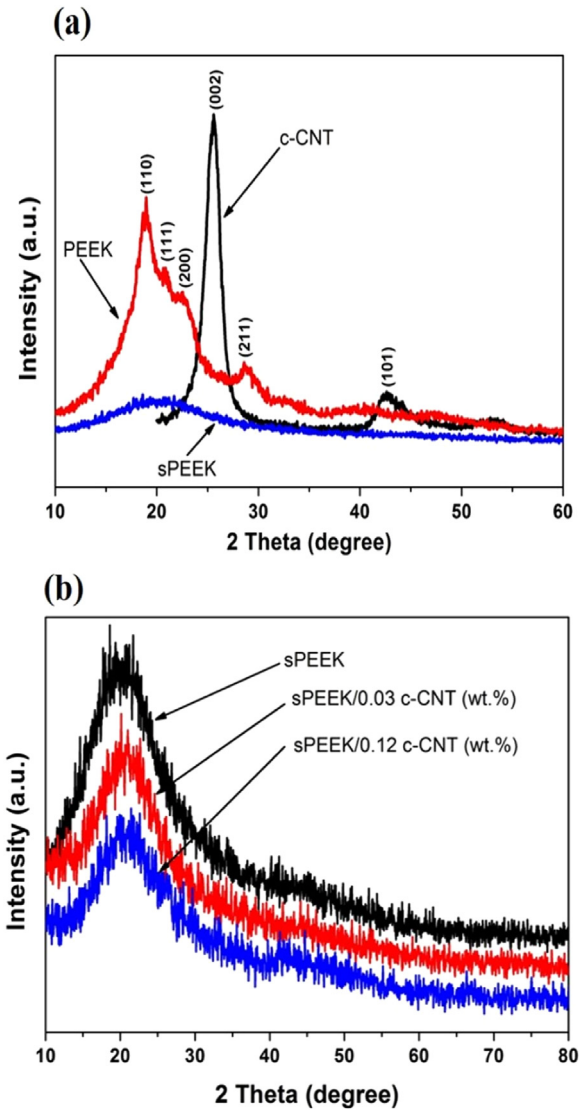


**Fig. 1.** XRD spectra of (a) c-CNT, PEEK and sPEEK samples, and (b) sPEEK, sPEEK/0.03 c-CNT (wt.%) and sPEEK/0.12 c-CNT (wt.%).

a crystalline peak in the nanocomposite membrane shows the good dispersion of c-CNT in the sPEEK polymer matrix. It is generally believed that the more amorphous nature of the nanocomposite membrane is desirable for higher water uptake and higher proton conductivity [42]. This inference is also corroborated by our water uptake and proton conductivity measurements discussed in the paper elsewhere.

SEM images exhibit the surface morphologies of the sPEEK and sPEEK/c-CNT nanocomposite membrane and revealed the incorporation of c-CNT due to intimate mixing of the component during membrane fabrication as shown in Fig. 2(a). The surface of the samples shows dense surfaces which referred to the proper incorporation of c-CNT in the sPEEK matrix [43–45]. It is also clear from the SEM image that the sPEEK/c-CNT surface becomes rugged and formed a knotty structure as shown in Fig. 2(a), which suggests that the modified CNTs with hydrophilic functional groups make the proper mixing of sPEEK and c-CNT. Further, the increased value of the filler (c-CNT) led to an increase of the roughness in the morphological surface [46]. The surface of sPEEK/c-CNT shows roughness value more than that of neat sPEEK indicating that increasing amount of c-CNT in the membrane may retain the molecules of the water, thereby increasing the proton conductivity [47,48]. It is obvious from the cross-section of SEM that c-CNT distributed in the sPEEK matrix is uniform. Fig. 2(b) shows the elementals

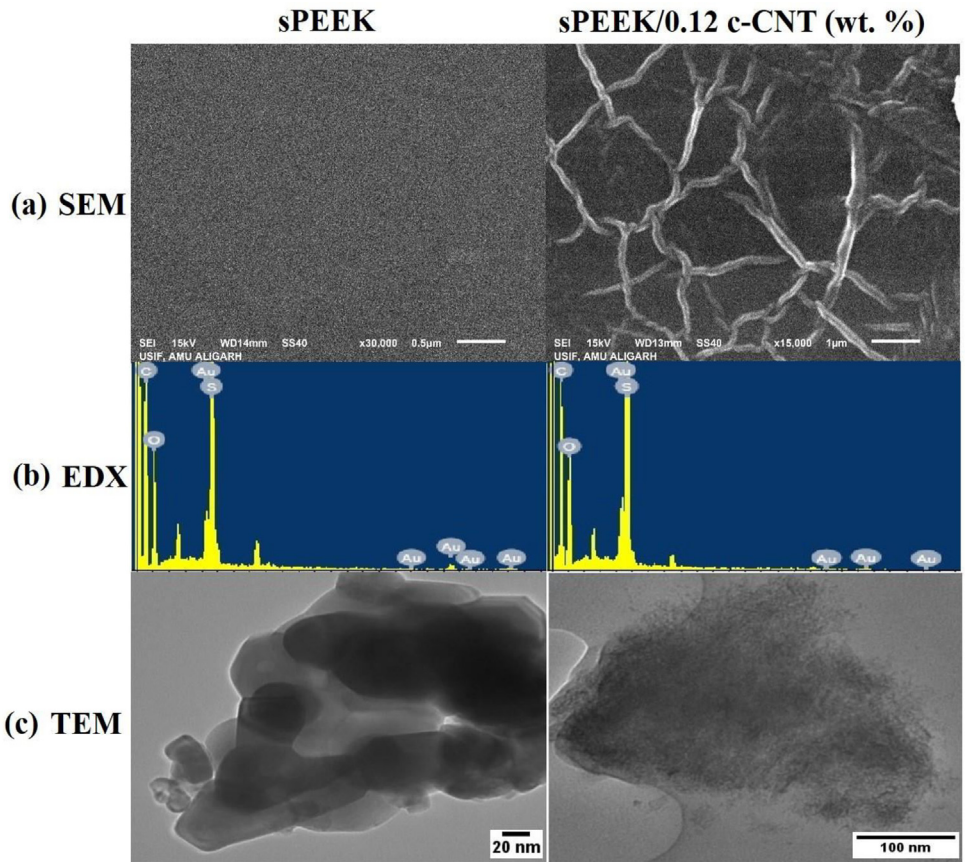


**Fig. 2.** (a) SEM, (b) EDX and (c) TEM of sPEEK and sPEEK/0.12 c-CNT (wt.%).

composition of the sPEEK and sPEEK/c-CNT nanocomposite membrane as revealed by EDX. Appearance of gold (Au) in the EDX analysis is due to the use of a thin layer of gold (gold sputter coating layer was done on the specimen).

Fig. 2(c) shows the TEM micrographs of the hydroxylated polymer and the acid-treated CNT (c-CNT). The morphology of the sPEEK and sPEEK/c-CNT nanocomposite membranes are difficult to recognize by TEM, due to the poor contrast of the polymer functional groups and low crystallinity [49,50].

### 4.2. Fourier transform infrared (FT-IR)

FT-IR spectroscopy was carried out to determine the effect of sulfonation in the synthesized sPEEK as well as sPEEK/c-CNT nanocom-

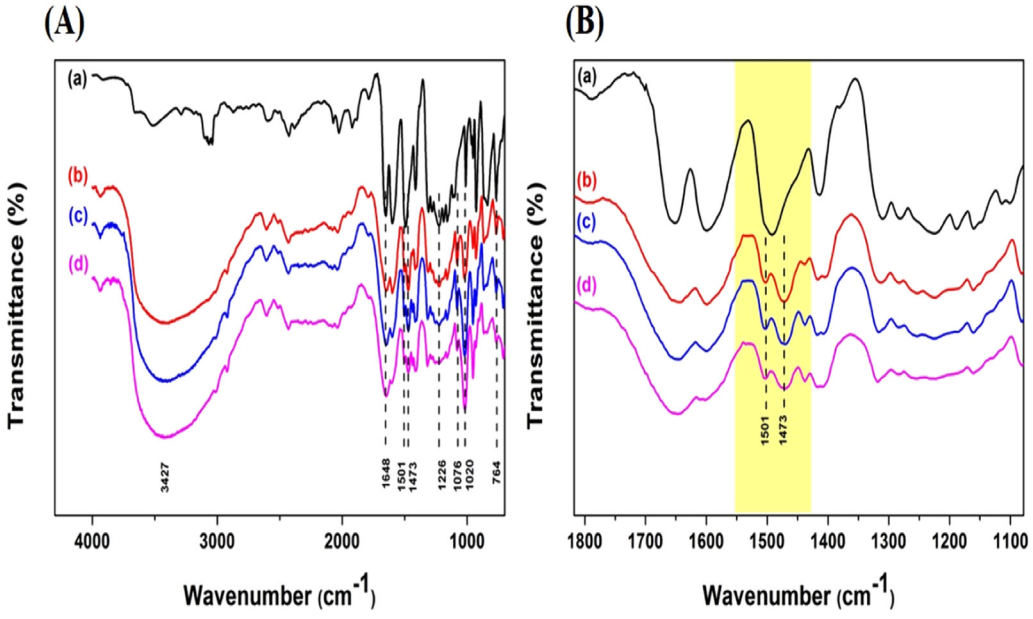


**Fig. 3.** (A) FT-IR spectra of (a) PEEK, (b) sPEEK, (c) sPEEK/0.03 c-CNT (wt.%) and (d) sPEEK/0.12 c-CNT (wt.%). (B) The effect of introduction of $-SO_3H$ groups on FT-IR peak.

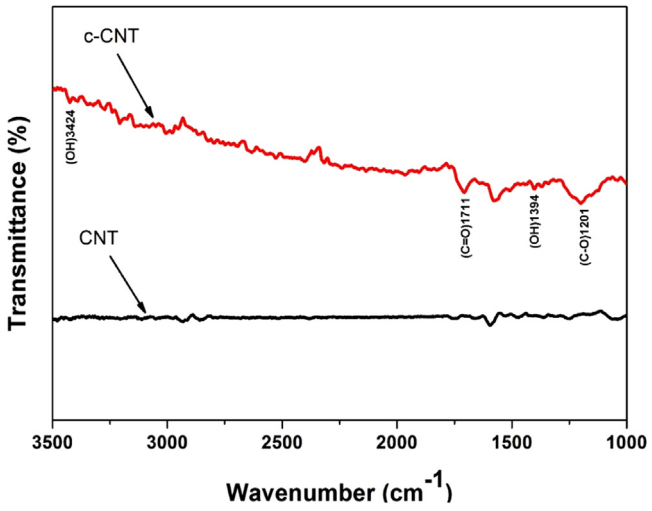


**Fig. 4.** FT-IR spectra of CNT and c-CNT.

posite membrane. Fig. 3(A) presents the FT-IR spectra of PEEK, sPEEK and sPEEK/c-CNT nanocomposite membrane. It shows a broad peak at 3427 $cm^{-1}$ which is associated with O–H vibration from sulfonic acid groups interacting with water molecules in the sPEEK as compared with PEEK spectra. The peaks around 1226, 1076, 1020 and 764 $cm^{-1}$ correspond to asymmetric stretching of O=S=O, the symmetric stretching vibration of O=S=O, stretching of S=O and stretching of S-O of the sulfonic acid group respectively. Also, the peak at 1648 $cm^{-1}$ is associated with the carbonyl group. The observed peak at 1482 $cm^{-1}$ in the PEEK due to aromatic C–C band was found to be splitted into two peaks at 1501 and 1473 $cm^{-1}$ in the sPEEK and sPEEK/c-CNT samples confirming the successful incorporation of sulfonic acid in the PEEK as shown in Fig. 3(B). These results are in good agreement with the results reported elsewhere [14,51–56]. The FT-IR spectrum of the functionalized CNT (c-CNT) is shown in Fig. 4. It shows an absorption peak at 3424 $cm^{-1}$ corresponding to the O–H functionality. The peak at 1711 $cm^{-1}$ is due to the C=O stretching of the carboxylic acid –COOH group and the peak at 1394 $cm^{-1}$ is associated with O–H bending deformation in COOH. The peak at 1201 $cm^{-1}$ is referred to C–O band stretching [29]. Observation of peaks due to the generation of –OH and –COOH groups confirm the functionalization of CNT.

### 4.3. Thermal properties

Fig. 5(a) shows the TGA curves of the c-CNTs, PEEK, sPEEK and sPEEK/c-CNT nanocomposite membranes. The curve of c-CNTs is almost thermally stable and showed a little weight loss in a temperature range of 0–550 °C [57,58]. The TGA curve for PEEK reveals high thermal stability up to 550 °C. The TGA curves for sPEEK, sPEEK/0.12 c-CNT (wt.%) and sPEEK/0.03 c-CNT (wt.%) exhibit three degradation stages. The first weight loss occurred at a temperature around 100 °C attributed to the evaporation of hydrated water present in the matrix of the membrane. The second step of the weight loss region lies in the range of 180–360 °C that can be assigned to the decomposition of acid groups. The final step indicates that weight loss region falls above 500 °C temperature and may be associated with the decomposition of sPEEK backbone chain and finally left only polymer residues (char) [59,60].

DSC measurements for PEEK, sPEEK and sPEEK/c-CNT nanocomposite membranes were carried out in nitrogen atmosphere condition with a heating rate of 10 °C/min. Fig. 5(b) shows the DSC curves for pristine sPEEK and sPEEK/c-CNT nanocomposite which exhibited broad endothermic signals with peaks centered in the whole range 40–80 °C. Sulfonation of PEEK imparts increased hygroscopic nature of polymer. The presence of endothermic peaks around 40–80 °C, in case of pristine sPEEK and sPEEK/c-CNT nanocomposites may be attributed to moisture loss from the samples. Increase in the sulfonic acid groups in polymer backbone led to absorb more water molecules which may also be confirmed by the findings showing increase in percent of water uptake with sulfonation [47,61]. The higher evaporation temperature in sPEEK composite membranes was thus because of the percentage of interactions of the water molecules with the sulfonic acid groups and also with the amount of c-CNT.

### 4.4. Effect of RSM-factors on ion exchange capacity (IEC)

The IEC of pristine sPEEK was measured to be 1.511 mmol/g. However, the value of IEC was found to increase with the increase in the content of c-CNT in sPEEK membrane and the highest value of IEC 1.6 mmol/g was obtained for sPEEK/0.12 c-CNT (wt.%) nanocomposite membrane as given in Table 4. The increase in the values of IEC with the increase in c-CNT may be due to increasing the number of carboxylic groups attaches in the shells of the CNT [47,62]. Fig. 6 depicts the 3D representation of response surfaces for IEC. Fig. 6 (a–c), show variation of IEC with respect to mixing temperature (factor B) and sPEEK concentration (factor C) at three levels of c-CNT (wt.%) i.e. 0.03, 0.065 and

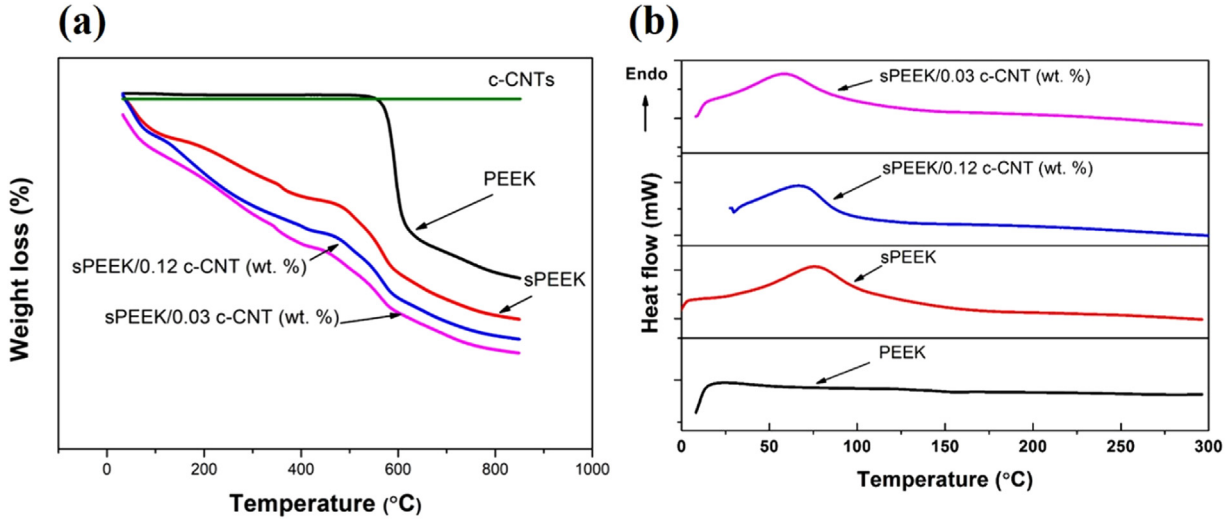


**Fig. 5.** (a) Thermal gravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC).

**Table 4**
Design of experiment and responses for sPEEK/c-CNT.

| | Factors | | | Responses | | | |
|---|---|---|---|---|---|---|---|
| Std | A:c-CNT (wt.%) | B: Mixing Temp ( ˚C) | C:sPEEK concentration (mg/mL) | Proton conductivity (mS/cm) | IEC (mmol/g) | Water uptake (%) | Swelling ratio (%) |
| 1 | 0.030 | 40.00 | 30.00 | 29.6 | 1.546 | 32.8 | 5.0 |
| 2 | 0.100 | 40.00 | 30.00 | 53.6 | 1.595 | 37.1 | 6.7 |
| 3 | 0.030 | 60.00 | 30.00 | 30.0 | 1.575 | 25.5 | 4.7 |
| 4 | 0.100 | 60.00 | 30.00 | 56.2 | 1.623 | 34.2 | 5.0 |
| 5 | 0.030 | 40.00 | 60.00 | 31.2 | 1.575 | 22.5 | 5.7 |
| 6 | 0.100 | 40.00 | 60.00 | 55.7 | 1.567 | 37.0 | 4.3 |
| 7 | 0.030 | 60.00 | 60.00 | 26.8 | 1.574 | 37.2 | 3.3 |
| 8 | 0.100 | 60.00 | 60.00 | 53.1 | 1.587 | 25.8 | 5.0 |
| 9 | 0.006 | 50.00 | 45.00 | 30.6 | 1.514 | 35.0 | 5.0 |
| 10 | 0.120 | 50.00 | 45.00 | 57.0 | 1.600 | 27.3 | 6.7 |
| 11 | 0.065 | 33.18 | 45.00 | 40.1 | 1.590 | 34.6 | 3.3 |
| 12 | 0.065 | 66.82 | 45.00 | 43.8 | 1.580 | 29.5 | 6.7 |
| 13 | 0.065 | 50.00 | 19.77 | 35.6 | 1.588 | 26.5 | 6.7 |
| 14 | 0.065 | 50.00 | 70.23 | 47.2 | 1.560 | 33.7 | 1.7 |
| 15 | 0.065 | 50.00 | 45.00 | 44.7 | 1.562 | 35.3 | 8.3 |
| 16 | 0.065 | 50.00 | 45.00 | 49.7 | 1.544 | 31.8 | 5.0 |
| 17 | 0.065 | 50.00 | 45.00 | 51.4 | 1.580 | 27.8 | 3.3 |
| 18 | 0.065 | 50.00 | 45.00 | 44.5 | 1.580 | 36.6 | 6.7 |
| 19 | 0.065 | 50.00 | 45.00 | 43.3 | 1.587 | 26.9 | 5.0 |
| 20 | 0.065 | 50.00 | 45.00 | 42.7 | 1.567 | 28.2 | 5.0 |

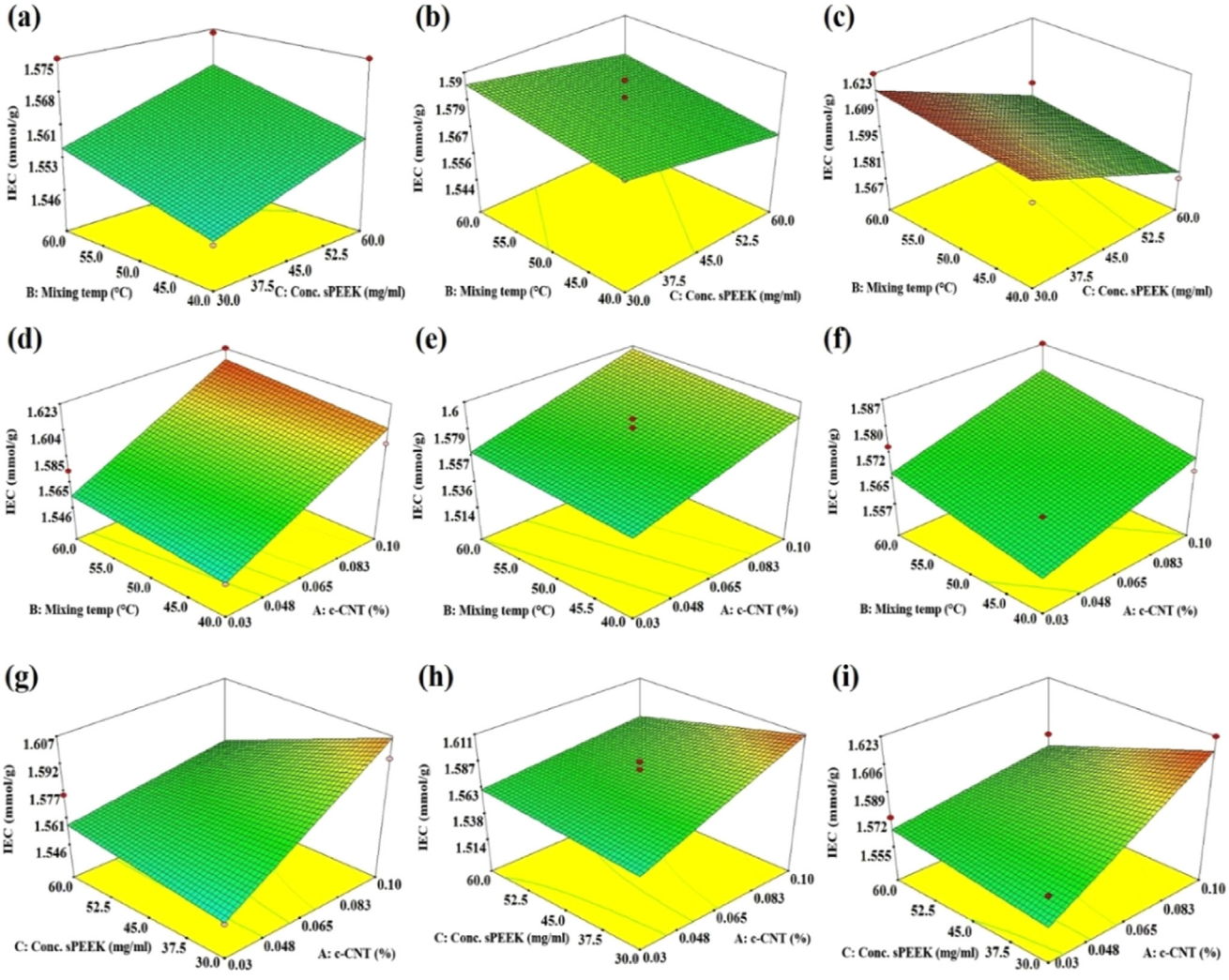


**Fig. 6.** 3D response surfaces for ion exchange capacity (IEC) (a–c) at 0.03, 0.065 and 0.1wt.% of c-CNT (factor A), (d–f) at 30, 45 and 60 mg/mL of sPEEK concentration (factor C) and (g–i) at 40, 50 and 60 ˚C of mixing temperature (factor B) respectively.

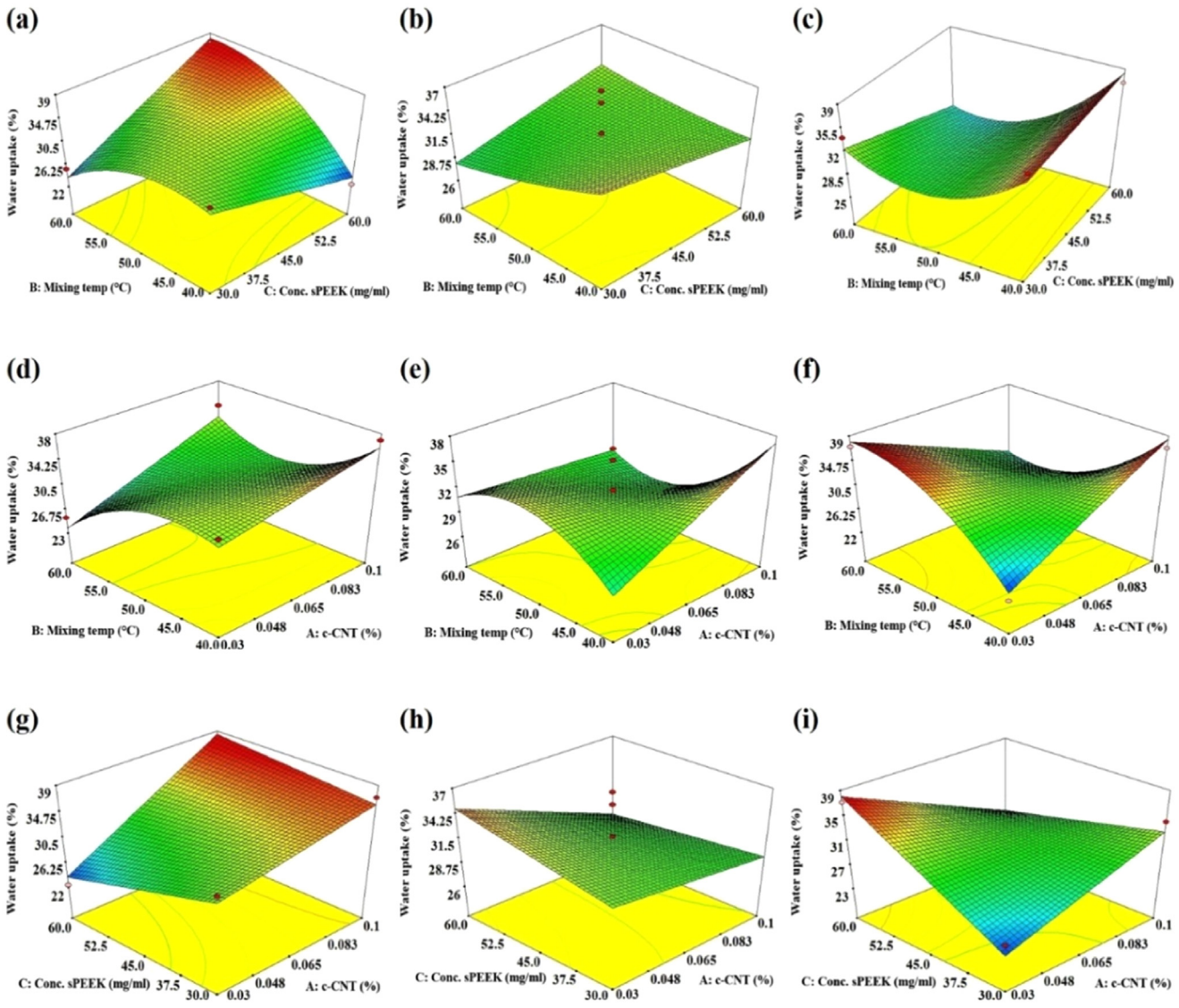


**Fig. 7.** 3D response surfaces for water uptake (a–c) at 0.03, 0.065 and 0.1wt.% of c-CNT (factor A), (d–f) at 30, 45 and 60 mg/mL of sPEEK concentration (factor C) and (g–i) at 40, 50 and 60 °C of mixing temperature (factor B) respectively.

0.1% respectively. It is clear from the figure that for a lower level of c-CNT (0.03%) the IEC value has been found to increase with the increase in mixing temperature (factor B). Further, IEC also increases with the increase of sPEEK concentration (factor C). For a higher level of c-CNT (i.e., 0.065 and 0.1%), the IEC value has been found to increase with the increase in mixing temperature (factor B). Also IEC decreases with the increase in sPEEK concentration (factor C) as shown in Fig. 6 (b and c). This may be due to the effect of reduction in the viscosity of sPEEK solution with higher loading level of c-CNT. Reduction in viscosity may help in better dispersion of nanoparticles (i.e., c-CNT) inside the sPEEK matrix. Fig. 6 (d–f) show the effect of IEC value on factors c-CNT (factor A) and mixing temperature (factor B) at sPEEK concentration 30, 45 and 60 mg/mL respectively. In general, IEC value has been found to decrease with the increase in sPEEK concentration (mg/mL). However, for lower and higher levels the IEC increase with increasing the mixing temperature (factor B) and also with increasing the c-CNT (wt.%) (factor A) that may be because of increase in the functional groups on CNT which were incorporated in the sPEEK matrix. Fig. 6 (g–i) exhibit variation in the IEC values as a function c-CNT (wt.%) (factor A) and sPEEK concentration (factor C) at mixing temperature 40, 50 and 60 °C respectively. IEC value has been found to increase with increase in c-CNT (wt.%) (facor A). At the low c-CNT (wt.%) (i.e., 0.03 %), IEC has been found slightly more with higher value of sPEEK concentration (factor C). At high c-CNT (wt.%), IEC decrease with increasing the sPEEK concentration (factor C). These observations are also seen in Fig. 6 (a–c).

### 4.5. Effect of RSM-factors on water uptake

Water uptake is one of the significant responses for sulfonated polymer membranes for fuel cells. It has been reported that mechanical stability of the membrane decreases at higher water uptake. Hence, stable water retention is required for fuel cell membranes. The water uptake for pristine sPEEK was found to be around 25.8%. The water uptake in all sPEEK/c-CNT samples was found to be higher than the value of water uptake for pristine sPEEK as depicted in Table 4. This increase in the percentage of water uptake in all sPEEK/c-CNT samples may be attributed to the number of sulfonic acid groups existed in the polymer backbone and hydrophilic groups on c-CNT [47,63]. The response surface for water uptake are shown in Fig. 7 (a–c) with respect to mixing temperature (factor B) and sPEEK concentration (factor C) at c-CNT (wt.%) 0.03%, 0.065% and 0.1%, respectively. Fig. 7(a) exhibits elliptic response of water uptake with mixing temperature for both levels

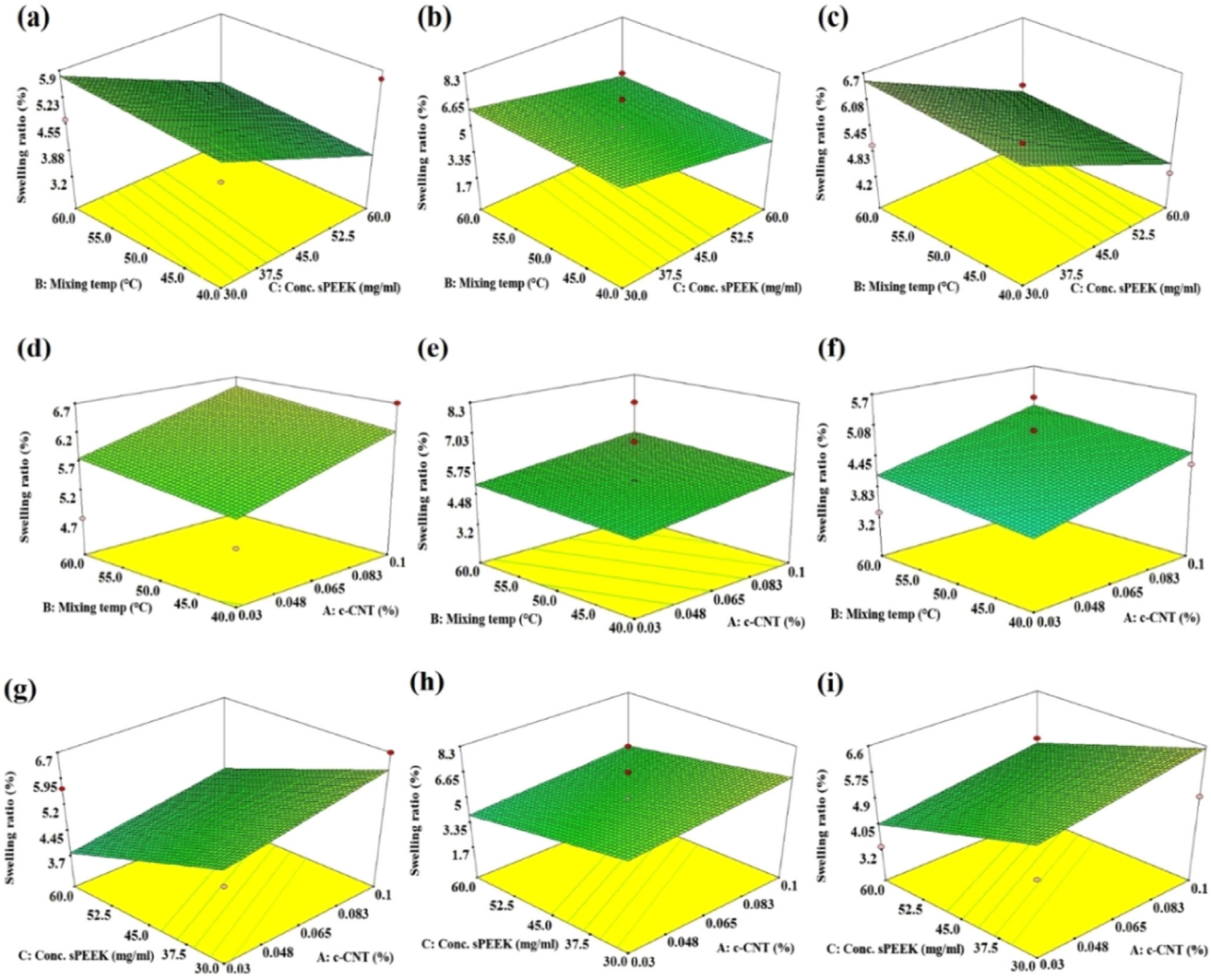


**Fig. 8.** 3D response surfaces for swelling ratio (a–c) at 0.03, 0.065 and 0.1 wt.% of c-CNT (factor A), (d–f) at 30, 45 and 60 mg/mL of sPEEK concentration (factor C) and (g–i) at 40, 50 and 60 °C of mixing temperature (factor B) respectively.

of sPEEK concentration (factor C). It also shows the opposite trend for water uptake corresponding to higher and lower levels of mixing temperature. Fig. 7(b) also exhibits a similar trend of water uptake with sPEEK concentration (factor C) as exhibited by Fig. 7(a). However, the variation of the water uptake with mixing temperature is similar but not so pronounced as shown in Fig. 7(a). Fig. 7(c) shows completely reversed response surface compared to Fig. 7(a). It may be concluded that increase in c-CNT from 0.03 to 0.1 wt.% reverse the surface response for water uptake with mixing temperature (factor B) and sPEEK concentration (factor C). Fig. 7 (d–f) exhibit the surface response of water uptake with the c-CNT (wt.%) (factor A) and mixing temperature (factor B) for three levels of sPEEK concentration (factor C) 30, 45 and 60 mg/mL. The variation of water uptake with mixing temperature (factor B) is elliptical for all the three levels of sPEEK concentration (mg/mL) as shown in Fig. 7 (d–f). However, the elliptical trend of water uptake with mixing temperature (factor B) get reversed for higher and lower levels of c-CNT (wt.%). Fig. 7 (g–i) exhibit variation of water uptake with c-CNT (factor A) and sPEEK concentration (factor C) for the three levels of mixing temperature (factor B) at 40, 50 and 60 °C respectively. These plots show a flat planer surface response for water uptake with c-CNT (wt.%) (factor A) and sPEEK concentration (factor C). Fig. 7(g) shows an increase in water uptake with increase in c-CNT (wt.%) (factor A) and a decrease in water uptake with an increase in sPEEK concentration (factor C). Fig. 7(h) shows the opposite surface trend compared to Fig. 7(g). Fig. 7(i) shows the surface response for water uptake closely coupled with the levels of factors c-CNT (wt.%) (factor A) and sPEEK concentration (factor C). It can be seen from Fig. 7(i) that by changing the levels of the above mentioned factors, the response for water uptake gets reversed.

### 4.6. *Effect of RSM-factors on swelling ratio*

Swelling ratio is also one of the significant responses for sulfonated polymer membranes for fuel cells. The swelling ratio of sPEEK and sPEEK/c-CNT membranes were determined by the measurement of the change in the length before and after hydration. The swelling ratio of pristine sPEEK membrane increased significantly with increasing c-CNT amount. The swelling ratio was found to be 3.3 and 6.7% for pristine sPEEK and sPEEK/0.12 c-CNTs (wt.%) respectively. It has been reported that mechanical stability of the membrane decreases with increase in swelling behavior of the electrolyte membranes. Therefore, stable moderate swelling ratio is required for fuel cell membranes.

The surface responses for swelling ratio are shown in Fig. 8(a–c) with respect to mixing temperature (factor B) and sPEEK concentration (factor C) at 0.03, 0.065 and 0.1 of c-CNT (wt.%) respectively. The swelling ratio has been found to decrease with the increase in the sPEEK concen-

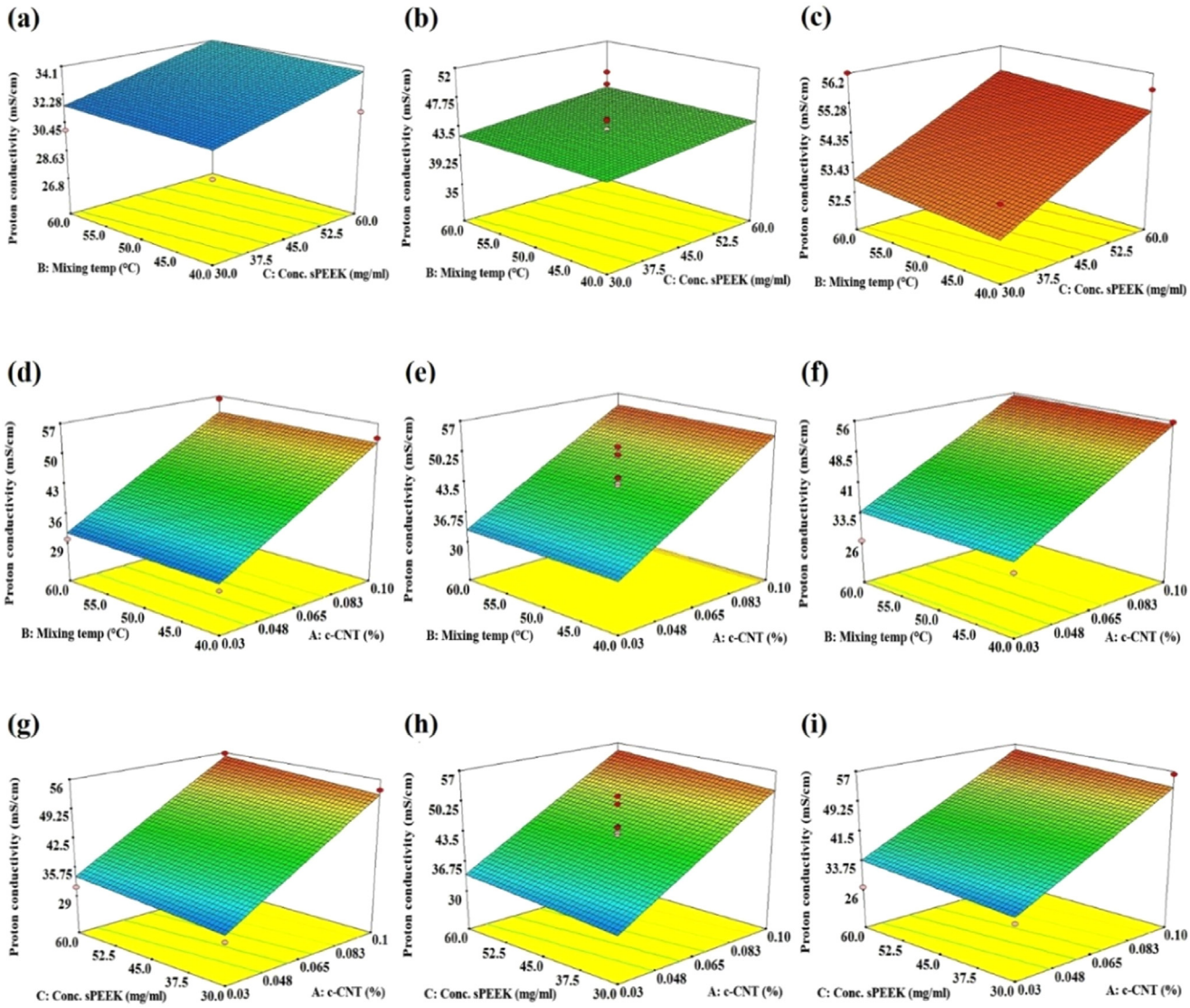


**Fig. 9.** 3D response surfaces for proton conductivity (a–c) at 0.03, 0.065 and 0.1 wt.% of c-CNT (factor A), (d– f) at 30, 45 and 60 mg/mL of sPEEK concentration (factor C) and (g–i) at 40, 50 and 60 °C of mixing temperature (factor B) respectively.

tration (factor C). Also the swelling ratio increases with the increase in the mixing temperature. Fig. 8 (d– f) show the variation of swelling ratio value with c-CNT (wt.%) (factor A) and mixing temperature (factor B) at sPEEK concentration at 30, 45 and 60 mg/mL, respectively. The swelling ratio has been found to increase with the increase of c-CNT (wt.%) (factor A) as well as mixing temperature (factor B). Fig. 8 (g–i) show the variation of swelling ratio with c-CNT (factor A) and sPEEK concentration (factor C) at mixing temperature 40, 50 and 60 °C respectively. The swelling ratio increased with the increase in the c-CNT (wt.%). It can be seen from the results that by incorporating c-CNT into the sPEEK matrix may slightly increase in the water uptake and the swelling behavior of the composite membranes as depicted in Table 4. The increase in water uptake and swelling ratio with an increase in the amount of c-CNT may be due to the interaction between the water and hydrophilic functional groups present in it [51].

### *4.7. Effect of RSM-factors on proton conductivity*

The proton conductivities of sPEEK and sPEEK/c-CNTs nanocomposite membranes were measured and are tabulated in Table 4. The proton conductivity for the pristine sPEEK specimen was found to be 23.9 mS/cm. The values of proton conductivities were found to increase with increase in c-CNT wt.%. Significantly high value of proton conductivity (57 mS/cm) was found for sPEEK/0.12 c-CNTs (wt.%). The surface response for proton conductivity are shown in Fig. 9(a–c) with respect to mixing temperature (factor B) and sPEEK concentration (factor C) at c-CNT 0.03, 0.065 and 0.1 wt.% respectively. The proton conductivity has been found to increase with increasing the sPEEK concentration [2]. It is also interesting to note from Fig. 9(a–c) that the proton conductivity is almost constant with respect to the mixing temperature. Fig. 9(d–f) show the proton conductivity value change with c-CNT (factor A) and mixing temperature (factor B) at sPEEK concentration at 30, 45 and 60 mg/mL respectively. Proton conductivity increases with the increase of c-CNT (wt.%) and is almost constant with the mixing temperature. Fig. 9 (g–i) show the proton conductivity with c-CNT (factor A) and sPEEK concentration (factor C) at 40, 50 and 60 °C respectively. The proton conductivity was found to be increased with increasing the c-CNT (wt.%) which may be attributed to the number of sulfonic acid groups that were attached in the polymer backbone and carboxylic groups on CNT. Also, proton conductivity has been found to increase with increasing the sPEEK concentration and may be due to good dispersion of c-CNT without agglomeration.

## 5. Conclusions

The sPEEK membranes were successfully prepared by sulfonation of poly-ether-ether-ketone. CNTs were treated with sulfuric acid and nitric acid to attach the functional groups onto the walls of CNT to enhance the interaction between the functionalized CNT and sPEEK matrix (sPEEK/c-CNT). The FT-IR analysis confirms the attachment of sulfonation (–$SO_3H$) groups onto the PEEK backbone. TGA and DSC were used to examine the thermal behavior of the synthesized nanocomposite membranes. The structural, morphological, and topographical behavior were investigated by using the XRD, SEM, EDX, and TEM. Various responses were effectively examined through the study of analysis of variance (ANOVA).

## Conflict of Interest

I hereby to certify that there is no conflict of interest regarding our paper.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cjac.2024.100365.

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