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ORIGINAL PAPER

Ionic liquid incorporated SPEEK/Chitosan solid polymer electrolytes: ionic conductivity and dielectric study

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Abstract

In this study, polymeric membranes composed of ionic liquid (IL), 1-ethyl-3-methylimidazolium tetrafluoroborate supported sulfonated poly(ether ether ketone) (SPEEK), and chitosan (CS) were prepared as novel promising solid polymer electrolytes (SPEs). First, the SPEEK polymer matrix was obtained by sulfonation of the PEEK polymer backbone. A composite membrane series (SPEEK/CS/IL-(1–4)) was created by adding CS at varying weight ratios according to the SPEEK. Structural, thermal, mechanical, and morphological characterizations were performed by FTIR, TGA, DMA, and SEM, respectively. Proton conductivity and dielectric measurements were performed over a wide temperature range to evaluate electrochemical properties. Composite membranes were stable for electrochemical processes at average temperatures. Storage modules have also improved with the addition of CS. All composite membranes showed ionic conductivities greater than 1×10^{-4} S.cm^{-1}, and the maximum conductivity was measured for SPEEK/CS/IL-4 as 9.87×10^{-3} S.cm^{-1}. Proton conductivity and dielectric tests showed that the SPEEK/CS/IL membrane series was presented as a novel SPE candidate.

Keywords Polymer electrolyte · Sulfonated poly (ether ether ketone) · Chitosan · Ionic liquid · Proton conductivity

Introduction

Solid polymer electrolytes (SPEs) have received great attention in electrochemical applications in recent years [1]. Limiting deficiencies such as corrosion, harmful liquid/gas leakage, and short circuit encountered in conventional liquid electrolytes have made the use of SPEs more widespread [2]. Polymer matrices can be shaped into the various size configuration, and SPEs can be prepared as thin films and layers with the desired flexibility. Moreover, polymer matrices can be easily functionalized with various organic/inorganic additives and processes [3, 4]. With these advantages, industrial and academic studies are increasingly focused on the use of superior SPEs in advanced electrochemical systems such as capacitors, sensors, electrochromic devices, fuel cells, and Li- and Na-ion batteries [3–7].

Polymer matrices such as polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), polyethylene oxide (PEO), poly(ether ether ketone) (PEEK), and polysulfone (PS) are commonly used in the preparation of SPEs [8]. Polymer matrices can be functionalized with various additives such as TiO_2, SiO_2, graphene oxide, and ionic salts to enhance ionic conductivity, thermal strength, and mechanical stability [8, 9]. In addition, processes such as chloromethylation and sulfonation may be needed as a pretreatment [10]. Sulfonated poly(ether ether ketone) (SPEEK) polymer matrix, developed to replace commercial Nafion membrane, which is essentially used in PEM fuel cells, is produced in this way by sulfonation of pure PEEK polymer [10, 11]. SPEEK polymer matrix is one of the most promising candidates as an alternative to commercial membrane electrolytes, with its high thermal stability and mechanical strength as well as being cheap. SPEEK membrane films are primarily preferred in electrochemical applications due to their outstanding properties such as high thermal stability, high water uptake capacity, excellent

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chemical and oxidative resistance, cost-effective and easy preparation, and long service life [10–13]. The degree of sulfonation (DS) has a significant effect on the proton conductivity and ionic mobility of SPEEK polymer electrolytes [14]. The DS changes with reaction time and acid concentration used in the sulfonation process [11, 14]. While high DS increases the ionic conductivity, it leads to a reduction in the mechanical strength of the polymer membranes because of its good swelling property [15]. For this reason, different ways are essential to keep both the conductivity and mechanical strength of SPEEK-based polymer electrolytes within certain limits depending on the field of application. The main approach is to blend the SPEEK polymer matrix with various polymers, crosslinking agents, hydrophobic materials, and several inorganic additives to provide mechanical strength with enhanced ionic conductivity [16, 17]. Bisht et al. studied the thermal and mechanical stability of the three-component hybrid structure of the SPEEK membrane matrix containing SiO_2, sulfonated SiO_2, and metal–organic framework (MOF-5) for PEM applications. They showed that the ionic and electrostatic interaction between the functional sulfonic acid groups of SiO_2 and MOF-5 improved the proton conductivity [18]. In another study, Parnian et al. synthesized and tested SPEEK-ceria nanocomposite membranes loaded with different ratios of cerium. The nanocomposite membranes also showed very high durability under the high stress [19]. In our previous studies, thermal, mechanical, and structural characterizations and dielectric performance of composite membranes produced by adding ionic liquids to the SPEEK polymer matrix were investigated. In these studies, it was reported that different ionic liquid additives improved ionic conductivity in addition to thermal and mechanical stability for high-temperature electrochemical applications [20, 21].

In recent years, many approaches have been presented on the development of cost-effective and environmentally friendly materials and polymeric membranes for electrochemical applications [22, 23]. Biomass-derived polymers have attracted great interest as polymer electrolyte. Chitosan (CS), a biopolymer that can be easily obtained from crab or shrimp shells, is also one of the important electrolyte candidates [24]. CS is hydrophilic and insoluble in water and alkaline environment. It is a potential electrolyte candidate in electrochemical applications as it is obtained with an easy production procedure, low cost, and allows various chemical modifications because of having the free hydroxyl and amine units in the backbone [24, 25]. Despite these superior properties, it also has limitations such as low proton conductivity and high swelling in its natural form, and modifications such as ionizing, crosslinking, or blending with other polymer matrices are needed to solve these problems [26]. Gil-Castell et al. synthesized CS/PVA blended electrolytes containing sulfosuccinic acid (SSA) as a crosslinker and sulfonation agent and glycerol as a plasticizer support. The resulting blended membranes exhibited efficient polyelectrolyte properties for direct ethanol fuel cells [27]. In another study, Wong et al. prepared CS/PVA composite membranes for fuel cell applications using sulfosuccinic acid (SSA) and 4-sulphthalic acid (SPTA) crosslinkers, and they reported the effects of different crosslinkers on membrane performance. The results showed that using SSA with the existence of sulfonic acid units was more efficient in crosslinking and membrane performance [28]. Ranjani et al. analyzed the performance of the composite membrane by adding the hygroscopic silica nanofiller to CS/sulfonated graphene oxide blends. The interaction between the components significantly increased the ion mobility and conductivity [29]. Vijayakumar et al. reported a series of cross-linked CS-based hybrid nanocomposite electrolytes made by utilizing polyaniline/nano silica (PAni/SiO_2) as inorganic filler. The CS-PAni/SiO_2 nanocomposites showed improved oxidative and mechanical properties. They reported that these nanocomposite membranes could be successfully employed as environmentally friendly polyelectrolytes in fuel cell applications [30].

In this study, the SPEEK/CS/IL-based membrane series was presented to the literature for the first time. Within the scope of the study, it was predicted that the IL in the composite structure will facilitate the separation of protons from the sulfonic acid groups, and the continuous hydrophilic channel formed by the interaction between SPEEK and CS will improve proton transfer. For this purpose, IL, 1-ethyl-3-methylimidazolium tetrafluoroborate, was incorporated to the SPEEK polymer matrix in moles equal to the sulfonic acid units in SPEEK, and then SPEEK/CS/IL composite membrane series was prepared by adding CS at different weight ratios to the SPEEK structure. Composite blend electrolytes were obtained by the solution casting method. Structural, thermal, mechanical, and morphological characterizations of SPEEK/CS/IL composites formed by the addition of CS were performed by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM) analysis, respectively. AC/DC conductivity (σ_{ac}/σ_{dc}) and dielectric properties (ε', ε'') of polymer electrolyte membranes were discussed in detail, and their usability in electrochemical applications was evaluated.

Materials and method

Materials

Chitosan (CS) and sulfuric acid (H_2SO_4, 95–98 wt.%) were purchased from Merck. Poly(ether ether ketone) (PEEK) was received from Röchling Sustaplast SE & Co.Kg and was dried before sulfonation (24 h, at 65 ℃). Silver (I) oxide (Ag_2O, ≥ 99.99%), 1-ethyl-3-methylimidazolium bromide ($C_6H_{11}BrN_2$, ≥ 97.0%) tetrafluoroboric acid solution (48 wt.% in H_2O), and N,N-dimethylformamide (DMF, anhydrous, 99.8%) were obtained from Aldrich. Sodium chloride (NaCl, ≥ 99.5%) and sodium hydroxide (NaOH, ACS reagent, ≥ 97.0%) were received from Merck and used as received.

Preparation of 1-ethyl-3-methylimidazolium tetrafluoroborate (IL)

Tetrafluoroboric acid solution was added dropwise (30 min) onto silver (I) oxide, which was mixed as a slurry of a certain amount of distilled water. The reactor containing the mixture was covered with aluminum foil to prevent photodegradation effects, and the mixture was stirred until a clear solution was obtained. Subsequently, 1-ethyl-3-methylimidazolium bromide was added to the homogeneous mixture at an equimolar ratio to other reactants and stirred at room temperature for 4 h. Silver bromide (AgBr) precipitates were removed by filtration with filter paper. The liquid mixture was placed in a vacuum rotary evaporator at 80 ℃, and 1-ethyl-3-methylimidazolium tetrafluoroborate (IL) was obtained in the yellow oily phase [20]. [Yield: 98.4%, 1H-NMR: 9.13 (s, 1H), 7.54 (t, 1H), 7.79 (t, 1H), 4.01 (q, 2H), 3.91 (s, 1H), 1.44 (t, 3H)].

Preparation of sulfonated poly(ether ether ketone) (SPEEK)

A certain amount of weighed PEEK was ground and put into 10 ml of sulfuric acid. The sulfonation process was carried out by mixing at 80 ℃ for 1 h. After 1 h, the dark red viscous mixture was slowly dropped into 1 L of cold water–ice mixture. SPEEK structures precipitated in the form of drops. In order to remove the excess acid in the structure, it was washed several times with distilled water and dried at 65 ℃ for 48 h. The degree of sulfonation (DS) and ion exchange capacity (IEC) of the obtained SPEEK polymer matrix were determined by analytical methods and found to be 30% and 0.94, respectively [20].

Preparation of composite membranes (SPEEK/CS/IL-(1–4))

SPEEK/CS/IL-1, SPEEK/CS/IL-2, SPEEK/CS/IL-3, SPEEK/CS/IL-4, and SPEEK/IL composite membranes were prepared by solution casting method. CS-doped membranes, SPEEK/CS/IL-1, SPEEK/CS/IL-2, SPEEK/CS/IL-3, and SPEEK/CS/IL-4 were prepared with a weight ratio (SPEEK:CS) of 50:50, 60:40, 70:30, and 80:20, respectively. Firstly, a particular amount of SPEEK was weighed and dissolved in DMF. IL was added equimolar to the sulfonic acid groups in the weighed amount for each membrane mixture and mixed for 2 h. On the other hand, a particular amount of CS for each composite membrane was weighed and dissolved in 30 ml acetic acid solution (5%), and each CS set was kept in the refrigerator for 24 h. Finally, the SPEEK/IL and CS mixtures formed by weighing for each composite membrane were mixed for 6 h. Each membrane solution was poured into glass petri dishes to remove solvents and incubated at 40 °C for 48 h. Composite membranes were obtained in the form of films by peeling off the petri dishes. The chemical structure of SPEEK/CS/IL composite electrolytes and possible interactions of components are presented in Scheme 1.

Prepared membranes and their compositions are shown in Table 1.

Characterization

The ion exchange capacity (IEC) of the SPEEK polymer matrix was calculated. For IEC determination, 0.05–0.1 g

Scheme 1 Chemical interaction in SPEEK/CS/IL composite electrolytes

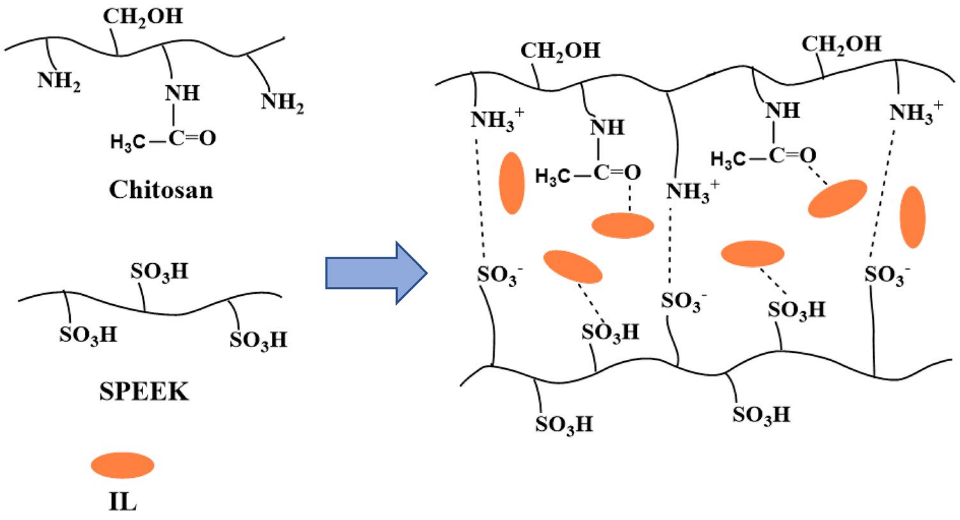

Table 1 SPEEK/CS/IL composite membranes and their compositions

Sample	Mole ratio (HSO_3:IL)	Weight ratio (SPEEK:CS)
SPEEK/CS/IL-1	1	50:50
SPEEK/CS/IL-2	1	60:40
SPEEK/CS/IL-3	1	70:30
SPEEK/CS/IL-4	1	80:20
SPEEK/IL	1	100:0

of SPEEK was added to 20 mL of saturated NaCl solution at 50 ℃ for 48 h in order to allow the displacement of H^+ and Na^+ ions in the sulfonic acid groups. Then, the solution was titrated with 0.1 N NaOH, and the IEC value was calculated by the following equation:

$$\mathrm{IEC} = \left(\mathrm{V}_{\mathrm{NaOH}} \times \mathrm{N}_{\mathrm{NaOH}}\right)/\mathrm{W}_{\mathrm{p}} \qquad (1)$$

(V_{NaOH} = NaOH consumption; N_{NaOH} = NaOH normality; W_p = dry weight of membrane or polymer after ion exchange).

After the IEC determination, the DS value of SPEEK was determined by using the following formula [31]:

$$\mathrm{DS}(\%) = [(288 \times \mathrm{IEC})/(1000 - 103 \times \mathrm{IEC})] \times 100 \qquad (2)$$

where 288 $gmol^{-1}$ is the mass of the unit of the initial polymer (PEEK), and 103 $gmol^{-1}$ is the molar mass of the SO_3Na group. As mentioned before, the IEC and DS values of the SPEEK polymer matrix were calculated as 0.94 and 30%, respectively.

Fourier transform infrared spectroscopy (FTIR) measurements were performed for the structural characterization of the composite electrolyte series. Analyses were performed with ATR unit integrated Perkin Elmer Spectrum 100 instrument at a wavenumber range of 650–4000 cm^{-1} and at room temperature. Scanning electron microscopy (SEM) morphological characterizations of polymer electrolyte membranes were performed with a Carl Zeiss 300VP instrument. Thermogravimetric analyses (TGA) were performed to determine the temperature resistance and thermal behavior of the polymer electrolyte membrane series. TGA analyses were performed under nitrogen atmosphere with SEIKO TG/DTA 6300 device with a heating rate of 10 ℃/min in the temperature range of 25–800 ℃. Mechanical tests of the membranes were performed by dynamic mechanical analysis (DMA). DMA analyses were performed with SEIKO DMS 6100 instrument at a heating rate of 2 ℃/min and in tension mode. Proton conductivity (σ) and dielectric tests (dielectric constant (ε'), imaginary part of dielectric permittivity (ε")) were carried out by Agilent 4284A LCR Meter instrument in the frequency range of 20 Hz–1 MHz and in the temperature range of 310–400 K.

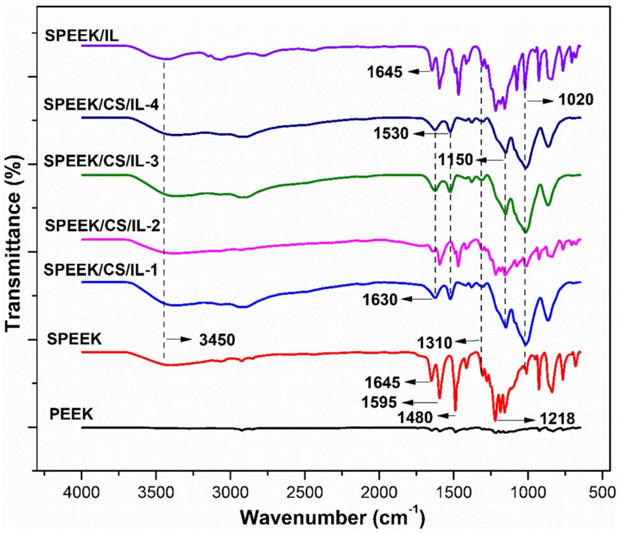

Fig. 1 FTIR spectra of PEEK, SPEEK, SPEEK/IL, and SPEEK/CS/IL electrolytes

Results and discussion

Characterization of electrolytes

SPEEK, SPEEK/IL, and SPEEK/CS/IL-(1–4) composite electrolytes were characterized by FTIR spectroscopy to confirm the sulfonation process and chemical interaction of SPEEK/IL and CS. The FTIR spectra of the samples are shown in Fig. 1.

The peak corresponding to the O–H stretching vibration in sulfonated polymer electrolyte structures was strongly observed at 3450 cm^{-1}. The presence of sulfonic acid groups in the SPEEK membrane matrix was further evidenced by the vibrations at 1020 and 1218 cm^{-1}, corresponding to S–O and asymmetrical O = S = O tension bands. The vibration observed at 1150 cm^{-1} indicates the symmetrical NH_3 + deformation in the SPEEK/CS structure. Additionally, the peak observed at 1150 cm^{-1} was also attributed to the imidazole groups of the IL structure. The vibrations arising from the carbonyl groups in the SPEEK matrix were seen at 1645 cm^{-1}, while the 1480 and 1595 cm^{-1} peaks were attributed to the aromatic groups in the SPEEK structure. For SPEEK/CS/IL electrolytes, new broad peaks were observed at 1530 and 1630 cm^{-1}, and they attributed to the presence of O = C-NHR and NH_2 of CS, respectively [20, 32].

Thermal strength is one of the basic criteria sought in some application areas of solid polymer electrolytes to be used in electrochemical applications is thermal stability. For this purpose, the thermal behavior of PEEK, SPEEK, SPEEK/IL, and SPEEK/CS/IL-(1–4) membranes were investigated by TGA analyses in the nitrogen atmosphere at a temperature range of 25–800 ℃. TGA curves are shown in Fig. 2.

As shown in the figure, pure PEEK membrane showed single polymer main chain degradation behavior, while SPEEK/CS/IL composite membranes showed three degradation behaviors. For pure PEEK, the single thermal degradation phase starting at 550 ℃ corresponds to the decomposition of the polymer main chain [33]. Initial weight loss for composite polymer electrolytes was observed at about 100 ℃ due to the evaporation of adsorbed moisture in the polymers. The second weight loss zones of the SPEEK, SPEEK/IL, and SPEEK/CS/IL composite membranes occurred at the temperature range of 150–250 ℃ due to the sulfonic acid groups [33, 34]. Thermal stability is slightly lower in CS-doped composite electrolytes. The main reason for this is the increase in the side group degradations present with the addition of both IL and CS. In SPEEK/CS/IL composites, the first decomposition in the temperature range of 40–100 ℃ corresponds to the evaporation of water. Subsequently, multiple degradation steps between 150 and 300 ℃ are attributed to the degradation of the amino and hydroxyl side chains in the SPEEK and CS. Finally, the degradation step that appears between 300 and 550 ℃ also proves the CS polymer backbone degradation in composite structures.

Morphological images of PEEK, SPEEK, and SPEEK/CS/IL-4 membranes were obtained by SEM analysis and presented in Fig. 3.

PEEK polymer film has a homogeneous and dense surface structure before sulfonation (Fig. 3a) [20]. The sulfonic acid groups attached to the polymer backbone after sulfonation caused the distances and branching between the polymer chains. Therefore, the surface morphology of the SPEEK polymer matrix is more irregular (Fig. 3b). While PEEK does not exhibit ionic conductivity in its pure form, the sulfonic acid groups included in the polymer backbone both provide active conduction due to the functional ion charge and increase mobility [20]. As seen in Fig. 3c, the composite polymer electrolyte obtained by the addition of IL and CS showed a dense and homogeneous morphology. With the interaction of active ends in CS and IL structures and sulfonic acid groups in SPEEK, branching and gaps between polymer matrix were eliminated.

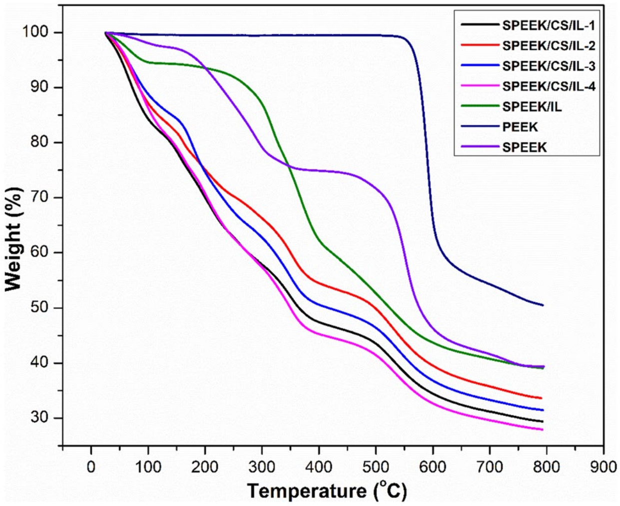

Fig. 2 TGA curves of PEEK, SPEEK, SPEEK/IL, and SPEEK/CS/IL electrolytes

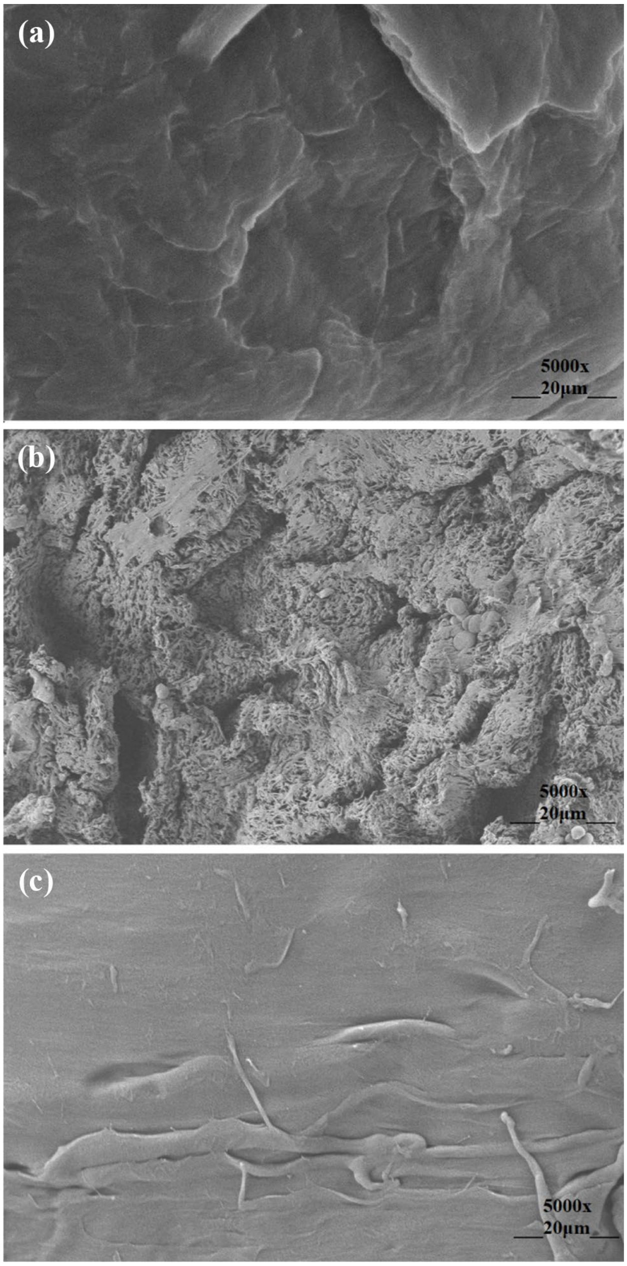

Fig. 3 SEM micrographs of **a** PEEK, **b** SPEEK, and **c** SPEEK/CS/IL-4 electrolytes [20]

Polymer electrolyte membranes should also show superior mechanical properties in electrochemical processes. Mechanical properties of solid polymer electrolytes prepared within the scope of the study were evaluated with DMA. For this purpose, the storage (E') modulus of SPEEK and SPEEK/CS/IL-(1–4) composite membranes were analyzed, and the DMA plots are given in Fig. 4.

As seen in the figure, the storage modulus of the composite electrolytes was plotted as a function of temperature. After reaching the maximum storage (E') modulus with the increase in temperature, the storage (E') modulus of all electrolytes decreased, as transitions from a glassy to rubbery state occurred. Due to the plasticizing effect of the presence of ionic liquid in the SPEEK/IL membrane, the storage (E') modulus was considerably reduced [20, 21]. On the contrary, composite electrolytes formed by the addition of CS showed high storage (E') modulus values. This is due to the fact that crosslinking in SPEEK/CS/IL-(1–4) electrolytes creates a denser and harder network structure [35].

Proton conductivity

The ionic conductivity of SPEEK/CS/IL composite membranes was measured with ac impedance up to 1 MHz at various temperatures under an anhydrous atmosphere. The samples were sandwiched between two electrodes in a temperature-controlled cell. The ionic conductivity (σ) is essentially described by following Eq. (3):

$$\sigma = \frac{d}{RA} \tag{3}$$

where d represents the thickness, R is the bulk resistance of the sample, and A is the electrode contact area.

In general, proton conductivity takes place by two mechanisms: Grotthuss and vehicular. In the Grotthuss mechanism, the proton jumps from one ionic region to the other, while the proton is transferred by a charge carrier in the vehicular mechanism. The anhydrous proton conductivities of the SPEEK/CS/IL-4 membrane as a function of frequency at various temperatures are portrayed in Fig. 5.

The proton conductivity of composite membranes reduced with improving temperature in an anhydrous environment as in previous studies [35, 36]. This may be explained by the evaporation of water retained in both Il and the polymer matrix as the temperature rises. It causes a decrease in conductivity since the presence of the mobile phase, i.e., water, is absent or rather limited at higher temperatures. Under these conditions, $-SO_3H$ groups in the SPEEK do not make an appreciable contribution to conductivity or become almost immobile in the anhydrous environment. From Fig. 6, it can be readily confirmed that the successful addition of ILs to a SPEEK/CS host matrix has been made.

The incorporation of ILs leads to an improvement of more than 10 times in ionic conductivity compared to the polymer matrix, which is primarily attributed to having a high ionic charge in the composite membranes. Accordingly, polymer chain mobility as well as ionic mobility increases, which enables the formation of proton transport pathways inside the composite membranes [37]. In addition, ionic liquids may produce an environment that helps proton transport in composite membranes as water in hydrated polymer electrolyte membranes [38].

An increasing amount of ionic liquid facilitates the dissociation of protons from the sulfonic acid groups of SPEEK leading to an enhancement in proton conductivity. All composite membranes display ionic conductivities greater than 1×10^{-4} S.cm^{-1}, surpassing that of pristine chitosan (CS),

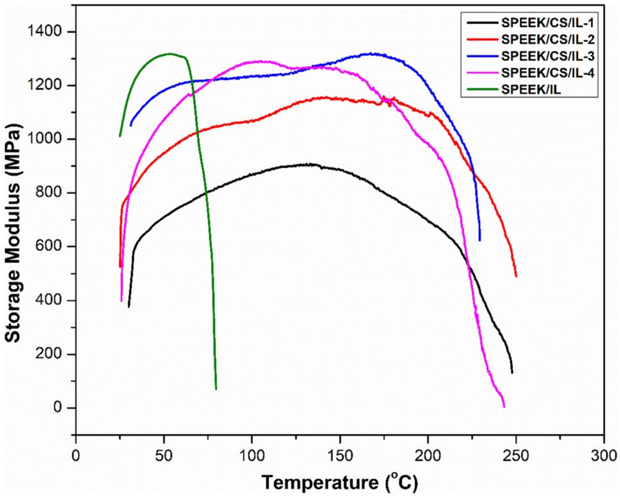

Fig. 4 DMA graphs of SPEEK/IL and SPEEK/CS/IL-(1–4) electrolytes

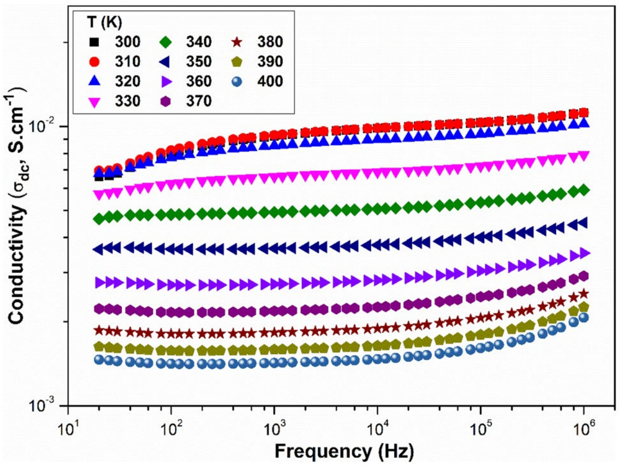

Fig. 5 The frequency-dependent ac conductivity of SPEEK/CS/IL-4 composite membrane at various temperatures

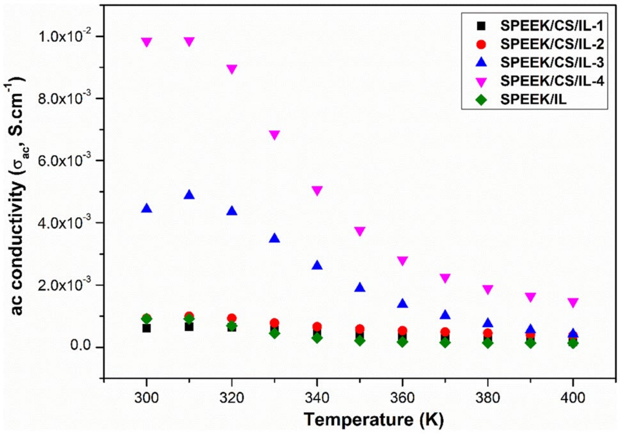

Fig. 6 Temperature-dependent ac conductivity of SPEEK/CS/IL composite membranes

SPEEK, and CS-SPEEK composite membranes as reported in previous studies [39–42]. The highest conductivity was measured as 9.87×10^{-3} S.cm^{-1} for the SPEEK/CS/IL-4 composite membrane, while the SPEEK/CS/IL-1 membrane exhibits the lowest ionic conductivity of 1.70×10^{-4} S.cm^{-1}. The -OH group on SPEEK can offer additional conduction area for proton transfer, and the interaction between CS and SPEEK ensures the formation of a continuous hydrophilic channel, allowing proton transfer to occur via diffusion mechanism. Moreover, electrostatic interactions among SPEEK, chitosan, and IL result in the development of various ions such as $-\mathrm{OH}^-$, $-\mathrm{NH}_3^-$, and heteropoly anions in composite membranes. The movement of the proton takes place through ionic and hydrogen bonds by jumping between functional groups. Accordingly, the proton conductivities in these membranes can occur by both vehicular and Grotthuss mechanisms. Figure 6 indicates that the increase in the chitosan content has a negative effect on the proton conductivity, and accordingly, the conductivity decreases. In composite membranes, amino groups ($-\mathrm{NH}_2$) in CS interact with the sulfonic groups ($-\mathrm{SO}_3\mathrm{H}$) in SPEEK to form $-\mathrm{NH}_3$ leading to a crosslinking-like structure [43, 44]. The decrease in conductivity of composite membranes having SPEEK as a result of the crosslinking has already been reported [35, 45, 46]. With increasing the number of $-\mathrm{NH}_2$ species (consumed amount of sulfonic acid groups), the number of $-\mathrm{SO}_3\mathrm{H}$ species decreases, which plays a significant role in the conduction mechanism. As explained earlier, proton transfer between ionic clusters composed of polar groups such as $-\mathrm{SO}_3\mathrm{H}$ contributes significantly to conductivity. Accordingly, the number of ionic clusters decreases as the number of $-\mathrm{SO}_3\mathrm{H}$ species decreases with an increase in chitosan content. Therefore, the reduction of $-\mathrm{SO}_3\mathrm{H}$ species in the membranes may restrict the mobility of protons causing a decline in proton conductivity. Temperature-dependent conductivity is mainly described with the dc conductivity (σ_{dc}) by using the following Arrhenius relation Eq. (4):

$$\log \sigma_{dc} = \log \sigma_0 - \frac{E_a}{k_B T} \tag{4}$$

where σ_{dc} represents the dc conductivity, σ_0 is the pre-exponential factor, E_a is the activation energy, and k_B is the Boltzmann constant (8.617×10^{-5} eV.K^{-1}). The activation energy or smallest energy necessary for proton transfer is achieved from the slope of the log σ(T) versus 1/T plot in Fig. 7.

The highest activation energy is obtained as 35.76 kJ.mol^{-1} for SPEEK/CS/IL-3 composite membrane, whereas SPEEK/CS/IL-4 composite membrane possessing the highest IL and lowest CS content displays lower activation energy as 30.03 kJ.mol^{-1}. Having a low energy barrier also supports the formation of a continuous network for proton conduction. The ionic conductivity follows the nearly identical trend with temperature for all membranes. The presence of curved shape at low temperatures and linearity at high temperatures indicates that the charge transfer processes are more dominating at lower temperatures, whereas the diffusion of the ionic species is leading at higher temperatures. Additionally, the curves show that there is no phase transition in the membranes within the studied temperature range suggesting no dynamic conformational change in the polymer matrix and ion transport principally occur via the conduction path formed by the lattice structure of the SPEEK and CS chains. The general trend for dc conductivity is an increase with increasing temperature due to structural loose and an increase of water and ionic mobility at low temperatures. Therefore, a positive temperature-conductivity dependence is observed. When the temperature is further increased, amino groups ($-\mathrm{NH}_2$) and sulfonic groups ($-\mathrm{SO}_3\mathrm{H}$)) interact in composite membranes to form $-\mathrm{NH}_3$ to form a crosslinking-like

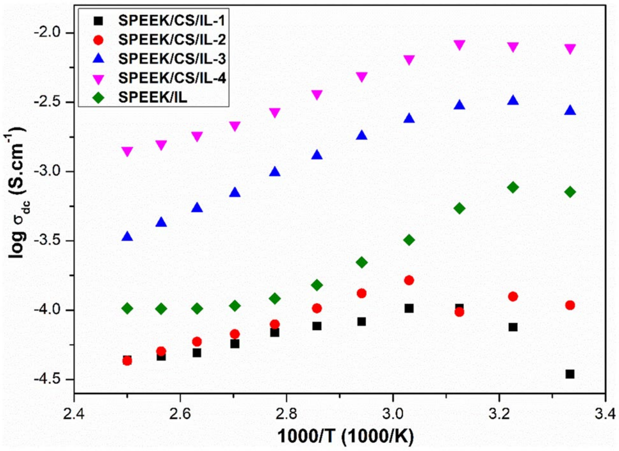

Fig. 7 Variation of the ionic conductivity of the SPEEK/CS/IL composite membranes with the inverse of temperature

structure with the increase in the evaporation rate of water [43, 44]. Accordingly, the conductivity of SPEEK composite membranes decreases due to crosslinking as reported in previous studies [35, 45, 46].

Dielectric studies

The evaluation of dielectric behavior is a significant way to study the ion–polymer interaction and conduction process of polymer composites. Due to the polarization phenomena, dielectric materials become electrically polarized under the electric field.

Figures 8a, b display the frequency-dependent variations of dielectric constant (ε') and dielectric loss (ε") of SPEEK/CS/IL composite membranes at room temperature (300 K). The dielectric constant of composite membranes increases with the addition of ionic liquids, and maximum values are observed for SPEEK/CS/IL-4. This represents the contribution of Maxwell–Wegner ionic conduction and electrode polarization resulting from the presence of –SO_3H and –NH_2 polar groups in the SPEEK/CS/IL composite membranes. The considerable decrease in dielectric constant of SPEEK/IL membrane (possessing the highest amount of IL and no CS) compared to SPEEK/CS/IL-4 suggests that the hopping of ILs does not contribute a significant effect on the conductivity since there are no sufficient free ILs for charge carriers. IL behaves as a plasticizer; therefore, increasing IL content in the polymer matrix enables the alignment of the electric dipoles and subsequently improves the dielectric constant [47]. In the case of SPEEK/CS/IL-4, the interaction between –SO_3H and –NH_2 polar groups leads to an improvement in charge carrier concentration (IL), facilitating the orientation of dipoles and accordingly enhancing the dielectric constants.

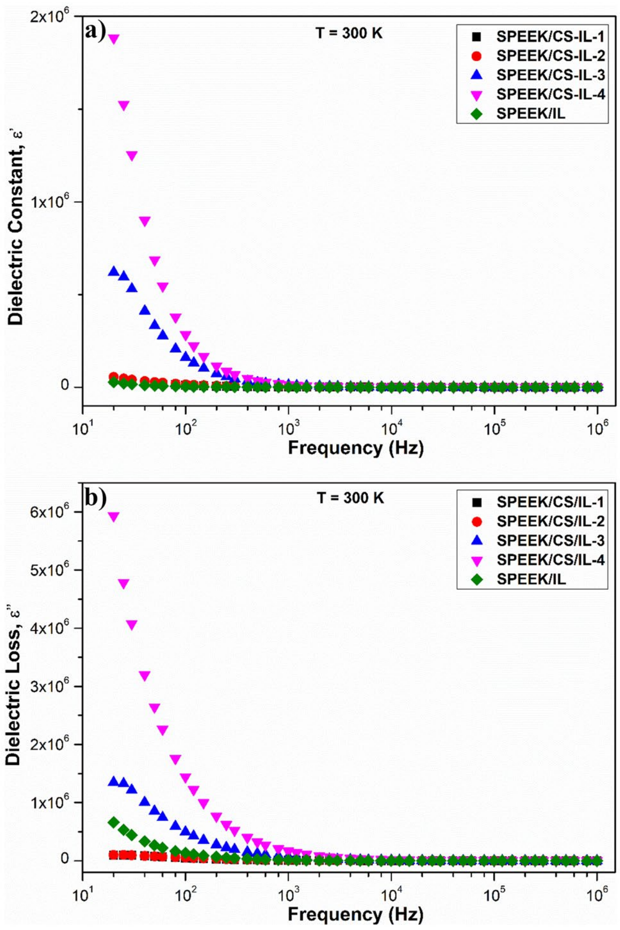

Fig. 8 Variation of **a** dielectric constant and **b** dielectric loss of SPEEK/CS/IL composite membranes with frequency at room temperature (300 K)

For all composite membranes from Fig. 8a, the observation of high dielectric constants in the low-frequency domain verifies the existence of non-Debye behavior owing to the contribution of charge gathering at the electrolyte–electrode interface.

The dielectric constants decrease regularly with increasing frequency, and it exhibits virtually frequency-independent behavior at higher frequency region. At lower frequencies, the charge carrier dipoles have adequate time to align in the direction of the employed electric field causing higher ε' values [48, 49].

The dielectric loss factor (ε") depends on the features of dipolar relaxation, and it is appropriate to evaluate the strength and frequency of relaxation. Figure 8b shows the dielectric loss factors. It is clear that the magnitude of the bulk relaxation rises noticeably as the amount of IL increases, and accordingly, the dielectric loss increases with the inverse of the frequency (ω^{-1}), which is a result of a typical behavior to be expected from the ionic conductivity. The dielectric relaxation height moves to a higher frequency field with a rise of IL concentration, which signifies the decline of relaxation time and the decrease in dielectric loss is essentially due to the restriction of charge carriers' mobility in the polymer blend matrix.

The temperature-dependent dielectric constant (ε') for SPEEK/CS/IL-4 membrane between 300 and 400 K is shown in Fig. 9a. The sharp exponential decline in dielectric constants especially at low temperatures and at low-frequency zone whereas demonstrating a relatively slight decrease at higher temperatures might be assigned to the rearrangement of polar groups (– SO_3H and –NH_2). An inverse correlation with temperature may suggest restriction of the mobility of the polymer chains due to the removal of water and crosslinking to some extent with an increase in temperature, which causes particularly immobilized ions. In addition, the contribution of space charge polarization consequences in fewer dipoles that aid in orientation with the applied field [50, 51]. As mentioned before, no phase transition was observed in the temperature range studied; however, it is expected to see a substantial increase in dielectric constant ε' around the transition region since the dipoles are more easily oriented with the increase in temperature

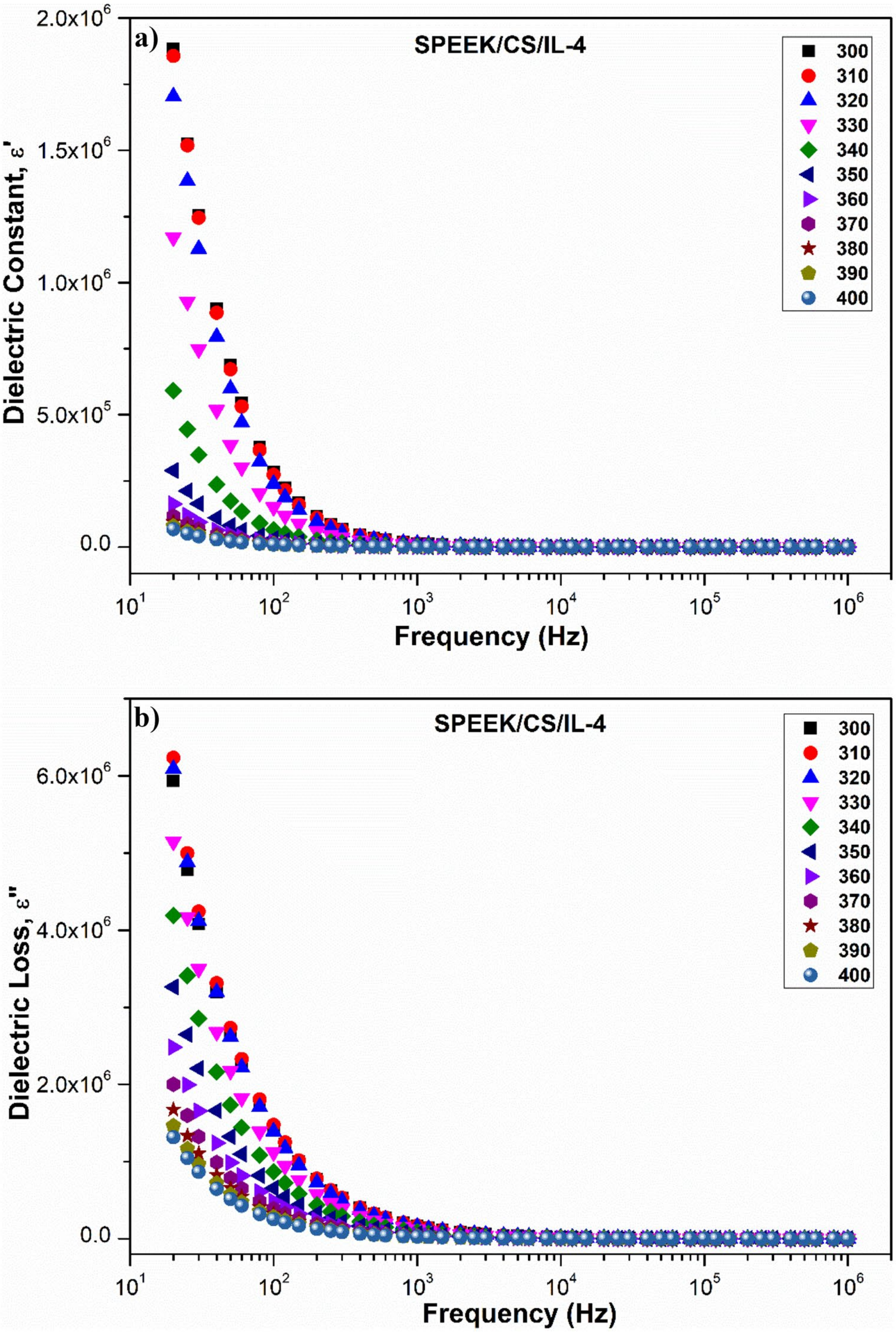

Fig. 9 Variation of **a** dielectric constant and **b** dielectric loss of SPEEK/CS/IL-4 composite membrane with temperature

[48, 52]. The increase in dielectric constant can be also assigned to the presence of different crystalline characters of polymer matrix producing interphases between SPEEK and CS which behaves as hopping centers for charge carriers. While increasing frequency, the dielectric constant declines sharply, and at a higher frequency, it becomes nearly constant, which may suggest failing of the orientational polarization.

Figure 9b illustrates the dielectric loss (ε") of the SPEEK/CS/IL-4 membrane measured in the frequency range of 20 Hz–3 MHz at various temperatures. The samples exhibit a highest dielectric loss at a low frequency that becomes more considerable at lower temperatures. The dielectric loss decreases linearly with frequency, which can be justified by dc conductivity relating to the equation: $\varepsilon''_{dc} = \sigma_{dc}(\omega C_o)$ (σ_{dc} is the dc conductivity, and C_o is the vacuum capacitance)

[53]. It possibly indicates the dependence of the conduction process on the temperature in cooperation with the nature of reorganization, i.e., structural diffusion. The temperature dependency of the capacitive response of membranes predominates over the nature of the rearrangement of polar groups (−SO_3H and –NH_2). Additionally, the conductivity relaxation is more remarkable than other dielectric relaxations for the studied temperature and frequency interval as $\varepsilon''_{\mathrm{conduct}} > > \varepsilon''_{\mathrm{relax}}$ [54, 55].

The first relaxation curvature is possibly caused by free charge carriers produced at the electrode- electrolyte interface. Since the charge carriers show a thermally activated behavior, the dielectric loss curves move to a higher frequency. The dielectric loss shows a linear decrease with temperatures, and it is more pronounced at low temperatures. This may be due to the evaporation of trapped water in parallel with the increase in temperature as stated in the previous sections, restraining random interactions of ions, shorter relaxation time, and higher frequency relaxation. As presumed, once rearrangement of the polar groups (−SO_3H and –NH_2) is accomplished, the dielectric losses curve reaches an almost constant value at high frequencies.

Conclusion

In the present study, SPEEK/CH/IL composite membranes were produced and analyzed for electrochemical processes. First, the SPEEK polymer matrix was obtained via the sulfonation of the PEEK polymer. Then, the degree of sulfonation (DS) and ion exchange capacity (IEC) of the SPEEK polymer matrix were calculated using analytical methods and found to be 30% and 0.94, respectively. IL was taken equimolar to the sulfonic acid groups on the SPEEK polymer matrix. Then, for each membrane, CS biopolymer was added in varying proportions according to the amount of SPEEK, and SPEEK/CH/IL membrane series was obtained by the solution cast method. Structural, thermal, mechanical, and morphological characterizations were performed by FTIR, TGA, DMA, and SEM analysis, respectively. The chemical compositions of the SPEEK polymer matrix, SPEEK/IL, and composite membranes were verified by FTIR analysis. All composite membranes display ionic conductivities higher than 1×10^{-4} S.cm^{-1}, and the highest proton conductivity was observed for SPEEK/CS/IL-4 as 9.87×10^{-3} S.cm^{-1}. SPEEK/CS/IL-4 sample exhibited approximately 20 times higher ionic conductivity value compared to SPEEK/IL composite membranes in our previously published work (SPEEK-30 × 2IM demonstrated ionic conductivity as 5.45×10^{-4} S.cm^{-1}). The −OH group on SPEEK may support further conduction location for proton transfer, and the interaction between CS and SPEEK produced a permanent hydrophilic path, which permits the proton transfer to occur through the diffusion mechanism. Moreover, electrostatic interactions among CS, SPEEK, and IL resulted in the development of various ions such as $-OH^-$, $-NH_3^-$, and heteropoly anions in composite membranes. The proton transfer took place through ionic and hydrogen bonds by jumping between functional groups. In the case of SPEEK/CS/IL-4, the interaction between –SO_3H and –NH_2 polar groups led to an increase in the amount of charge carrier (IL), which facilitated the orientation of dipoles and accordingly improved the dielectric constants. While all thermomechanical analysis, conductivity, and dielectric measurements are evaluated, SPEEK/CS/IL-4 composite electrolyte can be offered as a novel proton conductive membrane for electrochemical processes.

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