



Effect of deep eutectic solvent in proton conduction and thermal behaviour of chitosan-based membrane

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ARTICLE INFO

Article history:

Received 7 June 2018

Received in revised form 16 August 2018

Accepted 18 August 2018

Available online 20 August 2018

Keywords:

Deep eutectic solvent (DES)

Chitosan-CMC biocomposite

Polymer electrolyte membrane (PEM)

Fuel cell

ABSTRACT

This work aims to study the effect of choline chloride (ChCl) and urea based deep eutectic solvent (DES) on the proton conduction and thermal properties of chitosan-carboxymethylcellulose (Chitosan-CMC) membrane. Chitosan-CMC biocomposites were prepared in different ratios of 5:95, 10:90, 25:75, 50:50 and 75:25 with DES and was characterised. This study showed a positive improvement the proton conductivity without excessive swelling using DES in comparison with those without DES, with a slight trade-off on the thermal stability. The sample corresponding to 50 wt% of chitosan showed the highest proton conductivity of 1.57×10^{-2} S/cm, which was slightly lower compared to Nafion-117 membrane (8.6×10^{-2} S/cm). The study revealed the blend film with 75 wt% of chitosan with the presence of DES has a potential for polymer electrolyte membrane (PEM) with a low but sufficient water uptake of 49.4% to avoid structural disintegration despite a lower proton conductivity obtained.

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1. Introduction

Chitosan-based membrane has recently been explored as the potential polymer exchange membrane for low-temperature fuel cell applications owing to its advantages of (1) possessing the hydrophilic groups of hydroxyl, primary amine and ether bonded on its backbone that allows chemical modification to facilitate proton transport, (2) low cost owing to its abundance in nature and (3) environmental benign material. Numerous methods have been investigated through chemical modification to prepare chitosan membrane such as sulphonation on amine sites or hydroxyl sites, phosphorylation, quaternisation and chemical cross-linking. The results have shown that chitosan-based membranes are feasible to be tuned to allow proton conduction. Nonetheless, the low mechanical stability in pure chitosan membrane requires further modification to it to ensure its practical usage in fuel cell. Composite it with compatible polymers is one of the methods which would improve the membrane properties. One of the polymers which retains some special characteristics such as biodegradability, hydrophilicity, broad chemical modification capacity, and the formation of versatile semicrystalline

fiber morphologies is carboxymethyl cellulose (CMC) [1]. Its chemical structure is similar to cellulose, with the advantage of possessing the carboxymethyl groups in place of hydroxyl groups that is easily soluble in water.

Blending of both biopolymers offers a modification for both amino groups and hydroxyls groups of CMC and chitosan. Through cross-linking between both biopolymers, it promotes significant change in physical properties (such as mechanical strength) [2]. Each individual polymer's chains loses its ability to slide past each other and forming a close packing structure. Subsequently, the hydroxyl groups of both natural polymers reduced due to the polymerisation and result in decreased hydrophilic behavior and reduce membrane swelling. Nonetheless, such composite membrane possesses another drawback that it shows brittleness in the film without the use of additive. Kolhe and Kannan [3] reported that chitosan-based membrane is brittle and has a high degree of swelling. Consequently, it leads to an excessively high level of water uptake (causes increase in fragility) within the membrane boundary which makes it less durable as a film.

Herein, we propose the use of plasticiser additive to address the aforementioned issue. In practice, plasticiser shows its advantage in improving the flexibility of a polymeric film as it can act as an intermediate between the intermolecular polymer chains. It induces a shift in the amorphous elastomeric phase (regarded as the high conducting phase in polymer electrolytes) [4]. The addition of plasticiser was able to display a promising increment in flexibility of polymeric segment and

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release of mobile charge carries due to the ion dissolution effect [5]. For instance, Singh et al. [6] reported the use of polyethylene glycol (PEG) as plasticiser into polyethylene oxide (PEO) matrix to reduce crystallinity and hence produced more flexible film. For a promising replacement of Nafion membrane, it is crucial to obtain a film which is stable and flexible with good tolerance to water uptake as well as similar proton conductivity. In fact, various plasticisers have been investigated for applications in commercial products with polymeric films, sheets and coats.

To suit the application for proton exchange membrane, conventional hydrophilic plasticisers such as water and ionic liquids is foreseen to take significant role in improving the film flexibility and provide higher thermal stability of new composite materials [7]. Interestingly, a newly emerged ionic based compounds in recent years, named deep eutectic solvent (DES) which is considered as green solvent have been extensively studied on its usage which are found similar to ionic liquids. DES is a mixture of hydrogen bond donor with simple salt to produce liquid which exhibits physicochemical properties similar to ionic liquids (ILs) [8]. In recent years, the integration of DES has been intensively studied for various applications including electrolytes for lithium-ion batteries [9], anolyte for hybrid redox flow batteries [10], crustacean waste extraction solvent [11] and solvent for synthesizing multi-substituted cyclohex-1,3-dienamines [12]. The use of DES as plasticiser was studied by Zdanowicz et al. [13], where they revealed ChCl based DES is one of the potential candidates to decrease the polymer chain interaction and bind them together. Based on the work of Leron et al. [14], a mixture of ChCl and urea, at the molar ratio of 1:2 will hold an optimum melting point of 12 °C. As a result, the mixture of DES possesses characteristics such as high thermal stability, low vapor pressure and low melting point, which satisfied the criteria of a plasticiser. This ChCl:urea DES shows to possess similar functional groups to 1-alkyl-3-methylimidazolium chloride ([AMIM][Cl]) ionic liquid, which the latter was found to have effectively plasticised film from starch derivatives [13]. Additionally, ChCl based DES plasticiser was also reported to be the best due to its strong interaction between —OH groups of polysaccharide chains [14,15]. In evidence, Wang et al. [16] presented a related study on ChCl:urea plasticiser for cellulose films. The group reported a gain in elongation at break with the incorporation of ChCl:urea plasticiser as comparison to pure cellulose film (ratio of ChCl:urea to deionised water at 0.01:1 = 25.92% ± 0.25, while pure cellulose film = 2.22% ± 0.42). Aside from that, a report from Souza et al. [17] also revealed a potential of using ChCl: citric acid (CA) based DES as a plasticiser for chitosan film. Besides that, Ma et al. [18] also addressed an interesting effect with the use of plasticiser that contained amide groups. The group reported with an improvement in mechanical properties was believed to have attributed to the hydrogen bonds formation between plasticiser and starch molecules, and thus we expected similar outcome through the uses of ChCl:urea DES as potential plasticiser towards chitosan-CMC membrane.

To the best of knowledge no work has been reported with the incorporation of deep eutectic solvent into the polymeric blend film for fuel cell applications. Therefore, the objective of this work is to serve as a preliminary study through investigating the effect of deep eutectic solvent as a potential plasticiser while also evaluates the proton conducting and thermal behaviour of chitosan-CMC membrane to reveal its potential for fuel cell applications.

2. Experimental

2.1. Materials

Chitosan powder (low-molecular weight) having a viscosity of 20–300 cP and carboxymethyl cellulose (CMC) were obtained from Sigma-Aldrich, Malaysia. Choline chloride (ChCl), urea (99.5%) and acetic acid were procured from Merck, Malaysia. Deionised water (Thermo Scientific, Barnstead 50,129,887 Smart2Pure 6 l/h UV/UF) was used as

solvent for CMC and water uptake testing medium with a pH level measured at 6.80 (Mettler Toledo, Delta 320 pH meter).

2.2. Synthesizing deep eutectic solvent (DES)

The mixture of ChCl and urea based DES was prepared according to the procedure described by Abbott et al. [19] Both ChCl and urea were measured with a molar ratio of 1:2 and were poured gently into 100 ml DURAN® laboratory bottle. The solutions were purged with nitrogen and subsequently sealed with parafilm in the bottles to prevent any moisture absorption. Later, the mixture was heated with continuous stirring at 90 °C and 600 rpm on a magnetic hot plate stirrer until a colorless homogeneous liquid was obtained. The final transparent viscous liquid was stored for further usage.

2.3. Dissolution of biopolymers

The dissolutions of chitosan and carboxymethyl cellulose (CMC) in 0.1 M of acetic acid and deionised water were performed separately. 1 wt% of chitosan was added to 100 ml of 0.1 M acetic acid solution in 100 ml DURAN laboratory bottle under nitrogen purge. The solution was heated at 47 °C with continuous stirring at 300 RPM for 24 h. At the end of the dissolution, a clear solution of chitosan was obtained. Similarly, CMC solution was prepared by dissolving 1 wt% of CMC in a basis of 100 ml of distilled water at room temperature. The solution was later homogenised by stirring it at 500 RPM for 4 h.

2.4. Preparation of chitosan-carboxymethyl cellulose (CMC) blend film

The preparation of chitosan-CMC blend film was performed by mixing both chitosan (1 wt%) and CMC (1 wt%) as described in Section 2.3 under gentle stirring at room temperature. Different proportion of both dissolved polysaccharide solutions were mixed with the chitosan to CMC ratio of 5:95, 10:90, 25:75, 50:50 and 75:25 respectively. The procedure for preparation of blend film was conducted accordingly as described by Kuzmina et al. [20]. The blended solution of 50 ml in different proportion was casted on a glass petri dish, while the temperature of the oven was set to 60 °C. Besides that, a pure chitosan film was fabricated using the above mentioned procedure and used

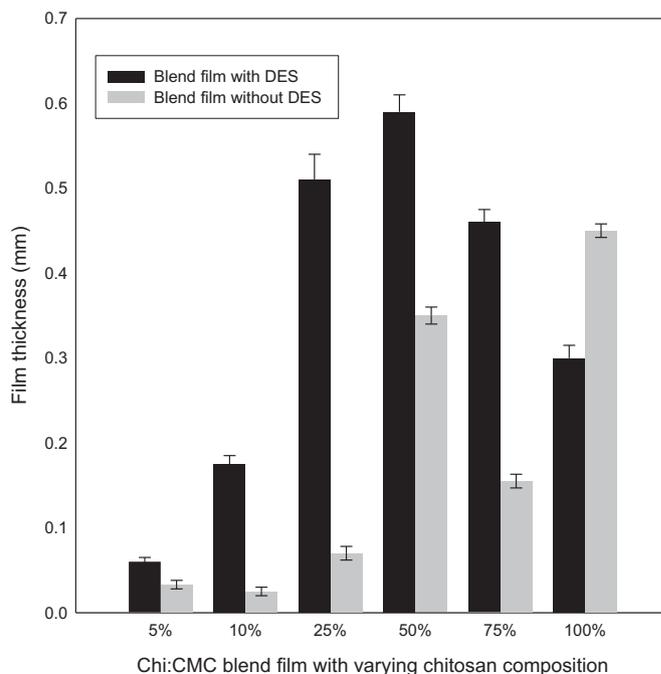


Fig. 1. Thickness of chitosan:CMC blend films with varying chitosan composition.

as a control. The polymeric blend film formed within the petri dish was rinsed several times with distilled water to remove the excess solvent. The thickness of chitosan–CMC blend films produced were measured with a micron scaled film thickness gauge (Dial Thickness Gauge 0–10 mm 0.01 mm leather paper measuring instrument tester A9).

2.5. Scanning electron microscope (SEM) analysis

The morphology of the biocomposite films were analysed using field emission scanning electron microscope (FESEM, FEI Quanta 400) under an accelerating voltage of 20 kV.

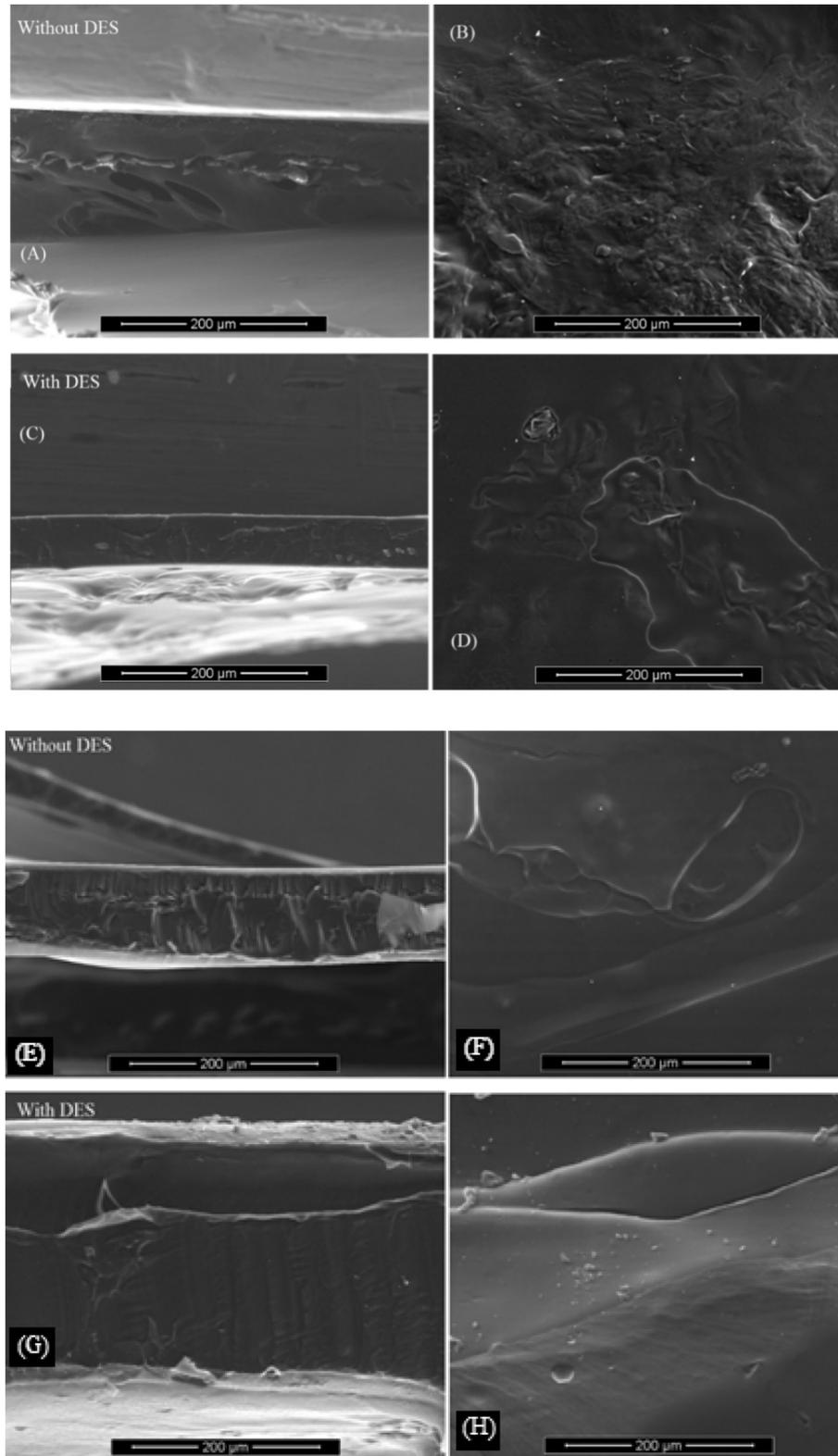


Fig. 2. Blend film with 10 wt% chitosan; without DES: (A) cross-sectional view, (B) surface morphology; with DES: (C) cross-sectional view, (D) surface morphology and blend film with 75 wt% chitosan; without DES (E) cross-sectional view, (F) surface morphology; with DES: (G) cross-sectional view, (H) surface morphology.

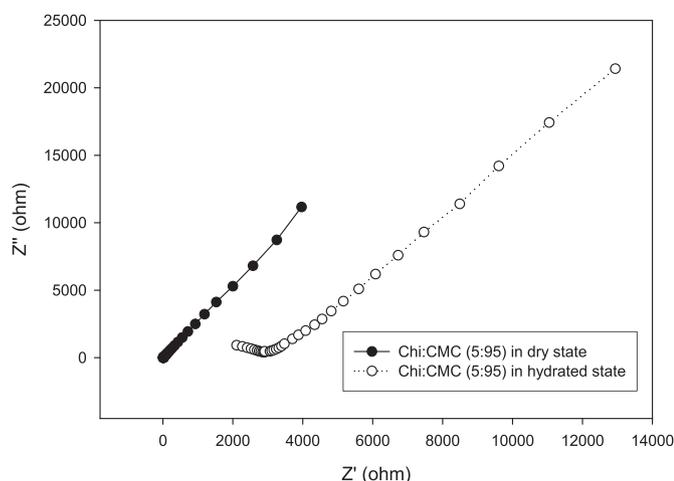


Fig. 4. Nyquist plot of chitosan:CMC (5:95) with DES in dry and hydrated state.

smoother and more homogeneous structure than that without DES, which did not depict any clear orientation [24]. This finding is also consistent with our visual observation, the film without DES showed severe polymer agglomeration and shrinking. This can be attributed to the tendency of polymers to form intramolecular hydrogen bonding between chitosan and CMC polymer. With the increase in chitosan content, as shown in Fig. 2F and H, the films are shown to be more homogeneous with little or no agglomerations. This result were in good agreement with Stefanescu et al. [25] who reported that the increase in chitosan concentration reduced the voids and thus results in more compact and smoother film structure.

On the aspect of chemical bonding in the blend film with DES, FTIR analysis was employed. Fig. 3 depicts the spectra of chitosan-CMC blend film with DES. In particular, all the polymeric blend films do possess three common characteristic peaks in the range of 1000 to 1200 cm^{-1} , 1200 to 1700 cm^{-1} and 3200 to 3400 cm^{-1} . The characteristic peak in the range of 1000 to 1200 cm^{-1} shows the presence of glycoside bond, which indicates the formation of C—O—C bonds arose from the intermolecular bonding between two monosaccharides [26]. Besides that, characteristic peak in the range of 1200 to 1700 cm^{-1} shows the existence of both amino (N—H) and carboxyl (C=O) groups from chitosan and CMC respectively. Lastly, characteristic peak of 3200 to 3400 cm^{-1} indicated the hydroxyl (O—H) group of the polymeric blend film. The comparison of all the blend films shows the presence of characteristic peaks reported for the interaction between chitosan and CMC. According to Yu et al. [27], the characteristics peak of amino groups characteristic peak of amino groups (1200 to 1700 cm^{-1}) will become sharper while the band of OH⁻ groups will become weaker (3200 to 3400 cm^{-1}) due to the formation of intermolecular interaction between biocomposite polymers. It was further observed that the band of O—H group was weakened with an increasing amount of chitosan in the polymeric blend film, possibly attributed to the formation of hydrogen bonding between chitosan and DES or CMC, which can be correlated with the XRD spectra in the latter section. This shows a correlation with

the SEM micrographs in which with increase in chitosan content, the tendency of polymeric agglomeration within the film was reduced. Hence, it is deduced that higher chitosan concentration will improve the structural stability of the polymeric blend film due to the reduction in hydrophilic properties [28].

The results were correlated with the proton conductivity test using impedance method. Fig. 4 demonstrated the Nyquist plots for Chi:CMC (5:95) sample with DES. Two main regions were detected on Nyquist plot for dry composite film, a partial arc in the high frequency zone which corresponded to the conduction process through the bulk of blend film [29]; a linear line in the low frequency regions. This linearity was attributed to the solid electrolyte-electrode interface, resulted from the resistance obtained from the stainless-steel electrodes sandwiched the blend film. In hydrated state, the partial arc disappeared. This linear region was apparent as the film acted like a common conductor that was attributed to the availability of freely move ions in the hydrated state. The proton conductivities of the samples were calculated from the resistance obtained from the electrochemical circuit fitting of Nyquist plots and were tabulated in Table 1. Interestingly, without DES the films were not able retain its original form upon immersing into water; the films underwent dissociation and hence not able to record any valuable data. As CMC is a water-soluble cellulose derivative, it appears to be easily dissolved likely due to the weak bonding sites with chitosan in the film structure. Hence, it is observed herein that DES has played a vital role in maintaining the film structure, through the strong ionic interaction of its oppositely charged ions with the polymeric chains, and increase the segmental mobility [30], which concurrently enhanced the proton conductivity of the blend film. It is deduced here that DES has played a role as a plasticiser with the ability to improve polymer chains flexibility and preventing the polymer in the solid form from dissolution in water. A study by Ma et al. [18] reported that C—O group of starch formed hydrogen bond interactions with glycerol or formamide used as a plasticiser. The plasticising effect of DES can be attributed to the hydrogen bond interactions between the C—O group of chitosan or CMC with urea in DES. In dry state, the contribution of DES is positive towards the proton conductivity of the films. The results obtained on the film with DES was shown to possess comparable proton conductivity with that reported by Wan et al. [31] studied on hydroxyethyl and hydroxypropyl chitosan membranes even after hydration. The group reported an optimum proton conductivity of $1.4 \times 10^{-3}\text{ S/cm}$ (after hydration) with 35 ml of 2-chloroethanol used in hydroxyethylation of chitosan. The relatively high proton conductivity in our study could be attributed to the existence of plasticiser. It assists the blend film in decreasing the crystallinity while promoting amorphous phases for ion transport. However, it was worth noting that the film with weight ratio of 25:75 appeared to be in gel form in room conditions likely due to the inability of DES to be embedded successfully into the polymeric chain of chitosan and CMC composites. Hence, proton conductivity could not be determined. Upon increasing the chitosan content to 50 wt%, the proton conductivity has increased and showed detrimental effect with further chitosan content increased to 75 wt%. This is correlated to the water uptake results observed between 50:50 and 75:25 samples, as shown in Fig. 5. Apparently, 75:25 samples with DES has a reduction in water uptake of 43%. This contradict the results

Table 1

Proton conductivities of samples under dry and hydrated states.

Sample	Conductivity, S/cm (With DES)		Conductivity, S/cm (without DES)	
	Dry state	Hydrated state	dry state	Hydrated state
Chitosan:CMC (5:95)	1.24×10^{-5}	1.31×10^{-4}	1.46×10^{-6}	Dissociate
Chitosan:CMC (10:90)	7.08×10^{-4}	1.68×10^{-3}	Dissociate	Dissociate
Chitosan:CMC (25:75)	Dissociate	Dissociate	1.19×10^{-4}	Dissociate
Chitosan:CMC (50:50)	2.00×10^{-3}	1.57×10^{-2}	Dissociate	Dissociate
Chitosan:CMC (75:25)	2.47×10^{-3}	4.44×10^{-3}	6.22×10^{-5}	Dissociate
Pure chitosan	2.29×10^{-3}	7.42×10^{-3}	Dissociate	Dissociate

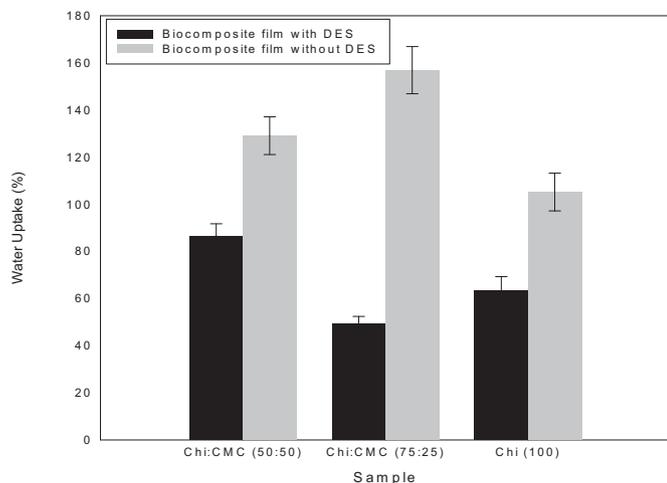


Fig. 5. Water uptake of samples.

obtained on samples without DES in which increase in water uptake was observed with increased chitosan content. It can be inferred that DES has excessively suppressed the hydrophilic sites for water absorption specifically on chitosan polymer, and therefore reduce the mobility of proton in the membrane.

In particular, both 50:50 and 75:25 with DES samples were then subjected to elevated temperatures (from 25 to 80 °C) to define the correlation between proton conductivity and temperature which presented in Fig. 6. The plotted data was further used for the estimation of activation energy (E_a), the minimum energy required for the proton transport across the membrane via the Arrhenius equation in Eq. (3) [32]:

$$\ln \sigma = -\frac{1000E_a}{RT} \quad (3)$$

where σ is the proton conductivity, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), E_a is the activation energy value in kJ/mol, and T is the absolute temperature (K).

Accordingly, E_a values for both samples were estimated through the slopes of the plots with an expression of $-E_a/R$. 50:50 with DES sample had arguably better heat management that proton conductivity increase with temperature which obeyed the Arrhenius rule. Nonetheless, the intrinsic properties of low thermal stability in biopolymer had certainly played an important role in which a drop in proton conductivity at 80 °C was observed [33]. Furthermore, the reported activation value of

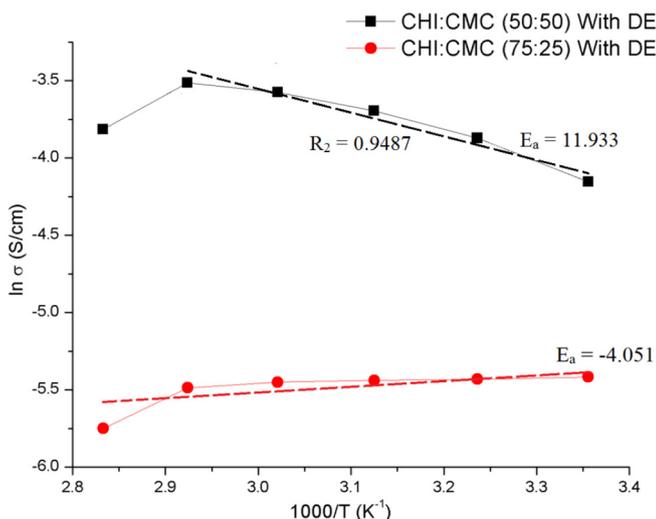


Fig. 6. Arrhenius plots for chitosan-CMC blend films.

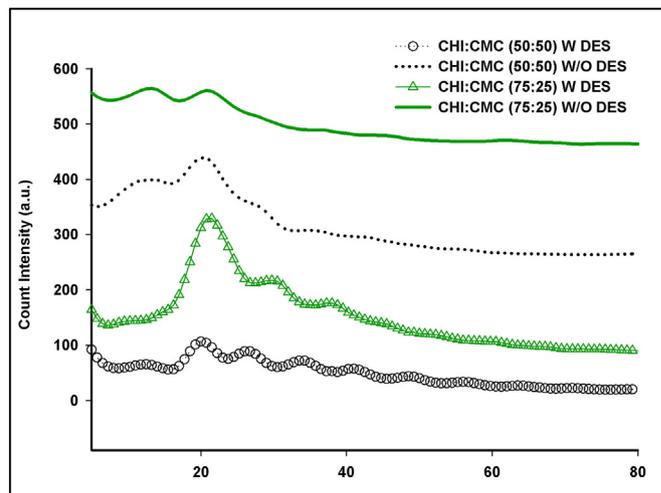


Fig. 7. XRD patterns of the chitosan-CMC blend films.

11.933 kJ/mol for 50:50 sample was shown comparable to Nafion 117 membrane (5.453 kJ/mol) [32] which was ideally showed as a good proton conductor in replacement to conventional Nafion membrane. In contrast, the sample with the ratio of 75:25 showed a gradual reduction in the proton conductivity exhibited with temperature which could probably due to the weak intermolecular interaction and low hydrolytic stability due to the much higher water uptake compared to that of 50:50 ratio. This shows that composition of polymers in the blend films showed significant influence on the properties of the film and further tuning on the composition is required to achieve the desired PEM. Besides that, the obtained activation energy also revealed the probable proton transport mechanism occurrence within the electrolyte membrane. According to Hara et al., activation energy valued between range of 9.6 and 38.5 kJ/mol suggested the dominance of Grotthuss mechanism [34]. For that, the synthesised 50:50 sample was shown dominance in proton diffusion by the Grotthuss mechanism.

The increase in proton conductivity due to the presence of DES can be correlated with the crystallinity of the films. It was suggested that higher degree of crystallinity indicates greater packing arrangement in polymer chains and hence less polymeric segment flexibility [35]. Fig. 7 depicts the XRD patterns for chitosan-CMC blend films with and without the incorporation of DES. In this study, the focal point lies within the region of 2 theta of 0–30° in which the crystalline peak of both CMC ($2\theta = 10^\circ$ and 20°) and chitosan ($2\theta = 12^\circ, 21^\circ, 23^\circ$ and 26°) are bounded [36,37]. XRD shows the evident that the blend film without DES shows the presence of crystalline peak of chitosan at $2\theta = 12.9^\circ$ (1 1 0) [36]. The intensity

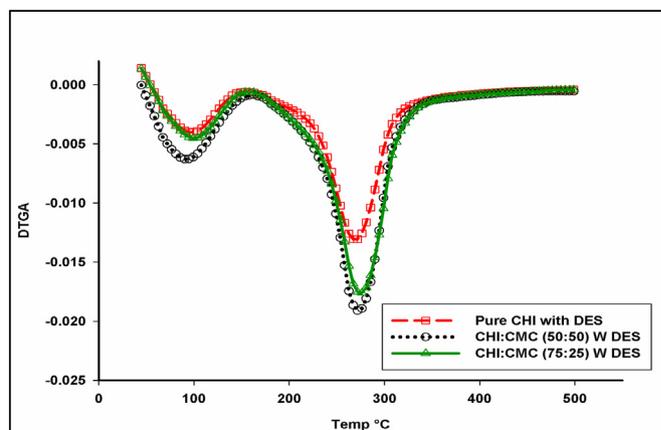


Fig. 8. TG thermal curve of chitosan-CMC blend films with DES.

Table 2

Degradation temperature of the chitosan-CMC blend films with DES.

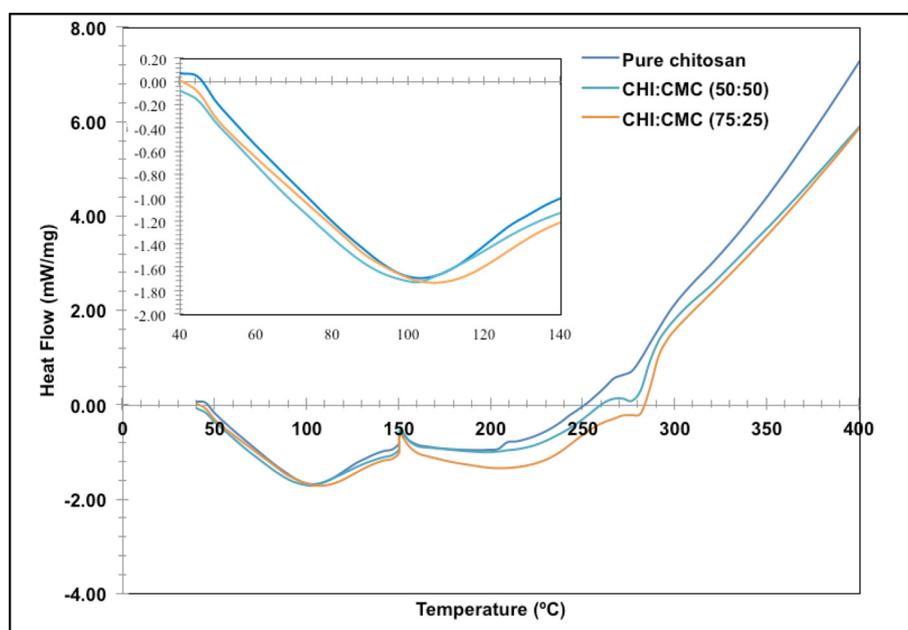
Samples	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)	Max T _{deg} (°C)	Remaining weight (%)
Pure chitosan with DES	88.3	112.5	271.6	267.3	27.5
CHI:CMC (75:25) with DES	88.3	112.5	271.6	273.8	18.05
CHI:CMC (50:50) with DES	73.8	93.16	266.8	271.8	16.15

of this peak increases with the increase in the amount of chitosan present in the blend film. This phenomenon may be attributed to the repolymerisation of chitosan after film drying due to usage of non-common solvent for biocomposite membrane preparation. Interestingly, with the addition of DES, this peak diminished owing to the fact that the hydrogen bonding between amino groups and hydroxyl groups in the chitosan was broken by complexation, resulting in higher amorphous level in the blend film [36]. The removal of internal hydrogen bonds of the polymer also allows us to explain on the higher flexibility of the film with addition of DES in comparison with that without which shows brittleness of the film. These results further confirm the role of DES in acting as the plasticiser through the formation of intermolecular hydrogen bonding with the biocomposite film that has successfully reduce the swelling effect of the composite film as well as to improve the film conductivity. In summary, blend film containing 50 wt% of chitosan shows the highest proton conductivity under hydrated state with a value of 1.57×10^{-2} S/cm, which was slightly lower compared to Nafion-117 membrane (8.6×10^{-2} S/cm) (despite others reported with a lower order of magnitude) [28]. Therefore, chitosan-based membrane can be potentially used as proton exchange membrane with the inclusion of DES as plasticiser.

The effect of the addition of DES on the thermal stability behaviour of the pure chitosan and chitosan-CMC blend films are demonstrated in Fig. 8 and Table 2. From the DTGA thermogram in Fig. 8, a two-step weight loss was visualised for all films. All films exhibit an initial weight loss around 50 °C that is mainly attributed to the evaporation of water and solvent bounded to the polymeric structure by hydroxyl and amine groups [38]. The high reduction in weight in the first step of weight loss could be possibly attributed to the relatively high water uptake of the film compared to Nafion membrane and thus expected a

high moisture content captured by the blend film in the ambient environment. A second step weight loss begins at 150–160 °C and reaches to maximum at 280–290 °C. In case of pure chitosan with DES, the second stage degradation occurs due to the depolymerisation of chitosan chain. Besides that, it is interesting that addition of DES deteriorates the thermal stability of membrane whereby pure chitosan (low molecular weight) was reported with a decomposition temperature of 313.3 °C [39]. Accordingly, this might prompted to the effect of ChC:urea DES whereby a decomposition temperature of 189.6 °C was reported by Delgado-Mellado et al. [40]. Furthermore, the thermogram also indicates that addition of 25% CMC resulted in increasing thermal decomposition temperature, indicating more stability of the blend film. This increase in thermal decomposition temperatures might be related to the improved intermolecular interaction arising due to coordinating nature of the ions in DES.

However, as the CMC concentration was increased to 50%, the maximum degradation temperature of the blend reduced slightly due to the domination of cellulose ethers degradation of CMC. The lower thermal stability of CMC is also evident from the early mass loss at different stages presented in Table 2. Moreover, with further increases in the temperature, random scission of macromolecules predominates, and the major degradation of the compound occurs through decomposition (thermal and oxidative), and disposal of other volatile compounds. Similar results were reported by Fadzallah et al. [41] for polymer electrolyte membrane prepared by chitosan-oxalic acid blend. Considerably high water uptake in the current blend films has possibly reduce the hydrolytic and thermal stability of the blend film despite improved in the proton conductivity and film forming ability with the presence of DES. Despite the earlier thermal degradation observed with the blend films owing to high moisture content, it is expected that further tuning on

**Fig. 9.** DSC thermogram of chitosan:CMC blend films with DES.

the chemical functional groups of the polymers would ensure its durability as a proton exchange membrane to be used in low temperature fuel cell systems such as direct methanol fuel cell operates at ambient conditions.

The potential application of this blend film with the presence of DES is further explained in DSC analysis. An interrelationship between glass transition temperature, T_g and ionic conductivity is demonstrated in this work. Fig. 9 presents the DSC thermogram for chitosan-CMC blend films. All the blend films with DES (Fig. 9) show a broad endothermic peak at 100 °C and a weaker peak at 200 °C. The first peak was attributed to the glass transition of the ionic clusters [42]. As for the second peak, it denotes the dissociation of the polymer blend film [43]. The ionic clusters here referred as the proton transfer sites of chitosan-CMC blend film; a point within the specified ranges indicated the changes in polymeric blend film from rubbery state to glass state without phase changes [44]. Above 250 °C, the films are dissociated due to thermal degradation that is in good correlation with the TG analysis depicted in Fig. 8 [45]. It is of our interest to examine on the transition temperature, T_g of the film with DES in comparison to that on the commercial Nafion-117 membrane. Although, our DSC curve doesn't show a good baseline to determine the T_g value, it is still valid to estimate that this value falls between 70 and 90 °C, gives a lower T_g value than Nafion-117 membrane recorded at 125 °C in the as-received state [46]. The inset of Fig. 8 shows that an increase in the chitosan amount has further shifted the T_g to a higher value, indicating a reduction in the ion mobility in the polymer matrix. Jung et al. [46] reported that with reduced water content in the polymer matrix, the glass transition temperature would shift to a higher value. This is consistent with results obtained on the reduction in water uptake with increase in chitosan content as report in Fig. 5, restricting the mobility of the ionic transport within the polymer matrix. Interestingly, they have shown that the shift in the T_g value was due to the plasticising effect of water. With increase water absorption, the T_g is shown to decrease. Hence, it is appropriate to tell that the addition of DES as plasticiser has played its role in increasing the T_g of the films that is beneficial to be applied as proton exchange membrane.

Based on the study of transition temperature for Nafion-TiO₂ composite, Matos et al. [47] reported two similar effects within the ranges of 110 °C for first peak and 210 °C for the second one. A negative shift in both peaks was observed in our study while compared to the results obtained by Matos et al. [47] indicating higher thermal degradation stability of the polymeric film. Thus, it can be concluded that DES shows a positive effect in enhancing proton conductivity and thermal stability of Chitosan-CMC blend film that can be potentially applied as proton exchange membrane.

4. Conclusion

The ChCl:urea-based DES is a potential plasticiser for chitosan-CMC blend film which can promote proton conductivity and film stability to prevent film dissociation in water. 50 wt% chitosan blend film with the incorporation of DES has shown to be highest in proton conductivity (1.57×10^{-2} S/cm) and was found comparable to the commercial Nafion-117 membrane (8.6×10^{-2} S/cm), following the Arrhenius rule. Furthermore, the water uptake for blend film with 75 wt% of chitosan (49.4%) was sufficiently low to avoid structural disintegration despite a lower proton conductivity obtained. Besides that, The polymeric blend film with DES acted as plasticiser possessed higher thermal degradation stability than the reported results of Nafion-TiO₂ composite membrane. Thus, this study has shown potential of constructing a novel fuel cell membrane with DES as plasticiser. Further studies of this particular work can focus on optimising the ratio of chitosan to CMC and chemical modification of the polymers to further improve the hydrolytic and thermal stability of the blend film to achieve the desired properties used in fuel cells.

Acknowledgment

This work is financially supported by the Universiti Kebangsaan Malaysia (UKM) through University Research Grants (GGPM-2017-043). The authors acknowledge Center for Research and Instrumentation Management (CRIM) of UKM for the support given.

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