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Research Article

### Ionic Conductivity and Conduction Mechanism of Biodegradable Dual Polysaccharides Blend Electrolytes

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#### ABSTRACT

Polymer blending is a promising method used to enhance the ionic conductivity as well as improving mechanical strength and thermal stability of biodegradable dual polysaccharides blend electrolytes (PBEs). PBEs containing carboxymethyl cellulose-chitosan doped ammonium nitrate (AN) has been successfully prepared using the conventional solution casting technique. This research aimed to explore the ionic conductivity and conduction mechanism of prepared PBE films via electrical impedance spectroscopy and transference number measurement. The enhancement of ionic conductivity of PBE films is influenced by the addition of AN concentration. The maximum ionic conductivity is achieved at 40 wt.% AN of  $(1.03 \pm 0.13) \times 10^{-3} \text{ Scm}^{-1}$ . The ionic conductivity also is affected by temperature and followed the Arrhenius law where  $R_2 \sim 1$ . The charge transport of the most conductive PBE film is identified to be dominated by ions. Jonscher's universal power law was employed to obtain the exponent  $n$ . Thus, revealed that the conduction mechanism in the most conductive SBE film can be represented by quantum mechanical tunneling model.

**Keywords:** Biodegradable, dual polysaccharides, blend electrolytes, ionic conductivity

#### INTRODUCTION

Natural based biodegradable polymers have attracted much attention due to potential application as solid biopolymer electrolytes in low energy density batteries, [1,2] as proton exchange membranes in fuel cells, [3-5] and for biomedical applications [6,7]. Solid biopolymer electrolytes preparation for energy storage involves dissolution of ionic salt into the polymer matrix. In this system, the ionic conductivity is ascribed to proton mobility ( $\text{H}^+$ ) which originated from proton salts such as

ammonium salts. The increase of ionic conductivity is due to the freely move of charge carriers without the presence of blocking phase. In contrast, the decrease of ionic conductivity may result from the blockage of the cation in the polymer blends [8].

Blending is an effective method for polymer modification which can endow polymers with enhanced properties. It is the easiest method to associate different polymers together, cheaper than developing new polymers, improved property-cost performance and advantageous method to obtain

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new structural materials. Ionic conductivity was believed to increase with blending two polymers together [9]. According to Zakaria *et al.*, [10] the miscibility of polymer blends is the key factor which led to the increase of ionic conductivity. The miscible of polymer blends showed no phase separation between the two polymers.

Carboxymethyl cellulose (CMC) and chitosan are naturally abundant polymers that have been utilized as proton conducting polymers for many years due to their desirable attributes such as renewable, biodegradable, biofunctional, non-toxic, environmentally/ecologically friendly materials and were reported to have strong antibacterial activities [11,12]. CMC can be found vastly in plants from wood to renewable agricultural waste or biomass feedstock resources, [13] whereas chitosan was extracted from the external skeleton (shell) of marine crustaceans such as shrimp shells, crab shells and fungal mycelia [14] CMC is a linear anionic polysaccharide of anhydroglucose units linked by C-1 and C-4 ether bonds known as  $\beta$ -1,4 glycosidic linkages with extensive intramolecular hydrogen bonding, a cellulose derivative prepared from alkaline cellulose and chloroacetic acid by etherification and usually used as its sodium salt (cellulose gum) [15]. It is widely used in many industrial sectors including food, textiles, paper, adhesives, paints, pharmaceuticals, cosmetics, mineral processing and more recently as reducing/stabilizing agent in preparation of silver nanoparticles [16]. Chitosan, the second most abundant polysaccharide found in nature after cellulose is a linear cationic polysaccharide consists of (1,4)-linked 2-amino-deoxy- $\beta$ -d-glucan, is a deacetylated derivative of chitin [17]. Chitosan is insoluble in either water or organic solvents. It can be dissolved in hydrochloric acid and aqueous organic acids such as formic, acetic, oxalic, and lactic acids. The solubility of chitosan depends on the concentration and type of acid. In the pharmaceutical industry, the CMC/chitosan blend has been utilized as a stomach drug delivery due to its mucoadhesive and swellable properties [18]. Due to the superior characteristics of these biodegradable dual polysaccharides, the present work has been proposed. To date, no report has been made on the investigation of CMC/Chitosan biopolymer blends doped ammonium nitrate (AN) salt for proton battery application.

Thus, this work aims to prepare biodegradable dual polysaccharides blend electrolytes based CMC/chitosan-AN via solution casting technique. Physical characterization was carried out using electrical impedance spectroscopy and transference number measurement to investigate the ionic conductivity and conduction mechanism of PBE films.

## 2. Experimental:

### Preparation of PBE films:

CMC powder (average MW = 90,000; DS = 0.7; purity > 99.9%), chitosan powder, AN salt (purity 99%) and acetic acid were purchased from Acros Organics, W.A. Hammond Drierite Company Ltd., Sigma Aldrich and Merck, respectively. All materials were used as received. 1% acetic acid solution was employed in preparation of PBE due to chitosan insoluble in water. Solution casting technique was applied to obtain PBE film with varied amount of AN salt concentration (10, 20, 30, 40 and 50 wt.%  $\text{NH}_4\text{NO}_3$ ). A varied amount of AN were weighted and added into 2:1 weight ratio of CMC: Chitosan solution. The mixture solution was stirred continuously at room temperature until complete dissolution was achieved. The final PBE solution then was casted into petri dishes and left to dry to form final solid film.

### Characterization techniques:

Impedance spectroscopy measurement was performed to determine the ionic conductivity of PBE films over a wide range of frequencies and temperatures. The measurements were carried out with an electrical impedance spectroscopy (EIS) HIOKI 3532-50 LCR Hi Tester interfaced to a personal computer in 50-1M Hz frequency range at temperature of 303 - 353K. A 2 cm diameter of round piece of electrolyte film was pressed between two stainless steel (SS) electrodes of sample holder and placed in a temperature controlled MEMMERT oven.

Transference number measurement (TNM) was carried out using direct current (dc) polarization technique by monitoring the polarization current as a function of time. The current decays gradually with the time and approaches steady state (saturated). This technique employed PBE film sandwiched between two stainless steel blocking electrodes connected to the voltage source (1.5V) and True RMS Multimeter UT803 in the configuration cell of SS/PBE film/SS. The measurement focuses mainly to obtain the transference (transport) numbers of charge carrier in PBE system.

## Results and Discussion

PBE films are transparent, flexible and light yellowish in colour is shown in Figure 1.

### Ionic conductivity:

Figure 2 depicts the salt concentration-dependent ionic conductivity of PBE films obtained at ambient temperature, 303K. The dc ionic conductivity,  $\sigma_{dc}$  ( $\text{Scm}^{-1}$ ) can be expressed as,

$$\sigma_{dc} = t / (Rb * A) \quad (1)$$

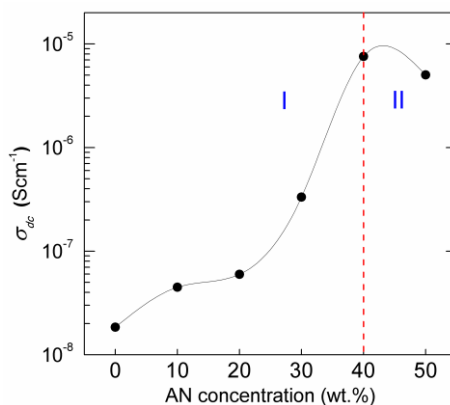
where  $t$  (cm) is the thickness of PBE film measured using a digital micrometer,  $R_b$  ( $\Omega$ ) is the

bulk resistance calculated from the intercept of high frequency semicircle or the low frequency spike on the  $Z_r$ -axis of Cole-Cole plots, and  $A$  ( $\text{cm}^2$ ) is the area of electrolyte-electrodes contact. From the figure, the ionic conductivity arises gradually with the increment of AN concentration. In Region I, the neat CMC/Chitosan film (0wt.% AN) shows the lowest ionic conductivity of  $(1.79 \pm 0.01) \times 10^{-8} \text{ Scm}^{-1}$ . The highest ionic conductivity was achieved at  $(1.03 \pm 0.13) \times 10^{-5} \text{ Scm}^{-1}$  with the addition of optimum AN concentration of 40wt.%. At AN concentration greater than 40wt.%, the ionic

conductivity was found to slightly drop to  $(5.03 \pm 0.02) \times 10^{-6} \text{ Scm}^{-1}$  (Region II). The enhancement of ionic conductivity with the addition of AN concentration in Region I is attributed to the increment of the number of mobile ions and its mobility [19]. At optimum AN concentration, the highest ionic conductivity was achieved as a result of overcrowded of ions are formed (dissociation of ions) and hence creating aggregation of ions [20]. This cause the decline of ionic conductivity at 50 wt.% AN in Region II.



**Fig. 1:** Yellowish-translucent PBE film obtained via solution casting technique.



**Fig. 2:** Salt-dependent dc ionic conductivity of PBE films at ambient temperature.

In order to investigate the effect of temperature on dc ionic conductivity of the PBE film, temperature dependence ionic conductivity measurement has been carried out on the highest ionic conductivity sample (PBE film containing 40 wt.% AN) as denoted in Figure 3(a). The corresponding Cole-Cole plot is illustrated in Figure 3(b). The linear variation of  $\log \sigma_{dc}$  vs.  $1000/T$  plot suggests the Arrhenius-thermally assisted behavior of ionic conductivity as expressed by,

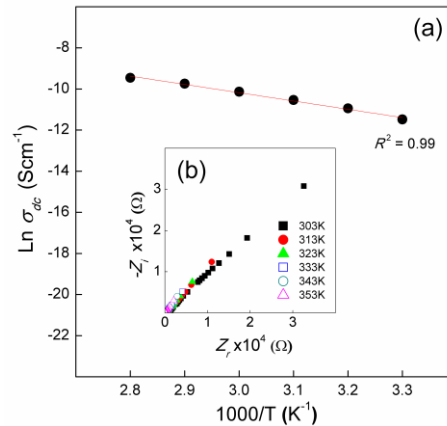
$$\sigma_{dc} = \sigma_0 \exp(-E_a / (k_b * T)) \quad (2)$$

$\sigma_0$  is the pre-exponential factor,  $E_a$  is the activation energy,  $k_b$  is the Boltzmann constant and  $T$  is the absolute temperature. The regression value,  $R^2$

obtained from linear fit of Arrhenius plot is found close to unity ( $R^2 \sim 1$ ) and do not show any abrupt jump with temperature indicating there is no phase transition in the PBE film structures within the specific temperature range. The ionic conductivity was enhanced from  $(1.03 \pm 0.13) \times 10^{-5} \text{ Scm}^{-1}$  (303K) to  $(1.44 \pm 0.01) \times 10^{-4} \text{ Scm}^{-1}$  (353K). The enhancement of ionic conductivity with the temperature can be interpreted as a hopping mechanism being assisted by local structural relaxations and segmental motions of the polymer electrolytes [21]. Kumar *et al.* [22] reported that the changes of ionic conductivity with temperature in polymer electrolytes are attributed to the segmental (i.e.

polymer chain) motion resulted in an increase in the free volume of the system as the temperature increases. The segmental motion allows the ions to hop from one site to another, or provides a pathway

for ions to move. Thus, the free volume around the polymer chains caused the ion to move faster and subsequently driven the segmental motion of polymer chains to increase the ionic conductivity.



**Fig. 3:** (a) Plot of temperature dependence of dc ionic conductivity, and (b) corresponding Nyquist plots for the highest conducting sample (PBE film containing 40wt.% AN) at selected temperatures. (Note: Straight line is the linear fit).

#### Conduction mechanism:

Jonscher's universal power law stated that the total ac conductivity of polymer electrolyte is equivalent to the sum of dc conductivity,  $\sigma_{dc}$  and ac conductivity,  $\sigma_{ac}$  through the relation, [23]

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac} \quad (3)$$

where

$$\sigma_{ac} = A \omega^n = \varepsilon_0 \varepsilon_i \omega$$

Consolidating equation (3) gives the following equations,

$$\ln \varepsilon_i = \ln(A/\varepsilon_0) + (n-1) \ln \omega \quad (4)$$

and,

$$\ln \sigma_{ac} = \ln A + (n) \ln \omega \quad (5)$$

by substituting  $\varepsilon_i = \varepsilon_r \tan \delta$ .

Here,  $A$  is a parameter dependent on the temperature (pre-exponential factor),  $\omega = 2\pi f$  ( $f$  = frequency),  $n$  is the power law exponent in the range of ( $0 < n < 1$ ),  $\varepsilon_i$  is the dielectric loss, and  $\varepsilon_0$  is the permittivity of free space =  $8.85 \times 10^{-12} \text{ Fm}^{-1}$ .

The values of  $n$  can be determined either from the gradients of  $\ln \varepsilon_i$  vs.  $\ln \omega$  or  $\ln \sigma_{ac}$  vs.  $\ln \omega$  plots as shown in Figure 4(a) and (b), respectively. Dielectric loss in Figure 4(c) showed that PBE film exhibited electrode polarization effects at lower frequency region and inherited non-Debye behaviour [24].

Fig. 5 displays the variation of power law exponent  $s$  over temperature for PBE film containing 40wt.% AN obtained based on plots of (a)  $\ln \varepsilon_i$  vs.  $\ln \omega$  and, (b)  $\ln \sigma_{ac}$  vs.  $\ln \omega$ , respectively. From both plots, it can be observed that the exponent  $n$  is almost equal to 0.4 and independent of the temperature. Thus, the frequency dependence of this system can be explained by quantum mechanical tunneling model. According to Shukur *et al.* [25] and

Buraidah & Arof, [26] conduction mechanism of QMT is due to the polarons (i.e. the protons and their stress field) are able to tunnel through the potential barrier that exists between two possible complexation sites. This result also has been found similar to the CMC-chitosan- $\text{NH}_4\text{Br}$  system as reported by Hafiza & Isa [27].

#### Transport numbers:

In polymer-ammonium salt system, proton ( $\text{H}^+$ ) was identified as charge species that responsible for ionic conduction to take place which was originated from ammonium ion,  $\text{NH}_4^+$ [28,29]. The transport numbers ( $t^+$ ) or also known as transference numbers are equivalent to the total contribution of ionic and electronic in solid electrolytes. For pure ionic

conductor,  $t_{ion}^+ = 1$ , whereas pure electronic

conductor,  $t_{ele}^+ = 1$ . However, for mixed conductor,

$t^+ = t_{ion}^+ + t_{ele}^+ = 1$ . Linford & Hackwood [30] stated that in polymer electrolyte systems, electron

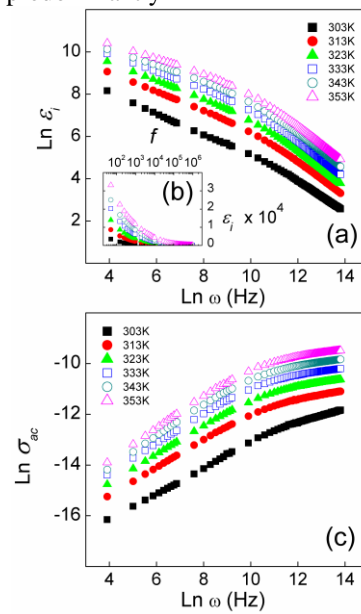
conduction can be negligible using dc polarization technique. Based on Figure 6, the ionic transport

numbers,  $t_{ion}^+$  at room temperature for PBE film containing 40wt.% AN was calculated from the plot of normalized polarization current against time using the relation,

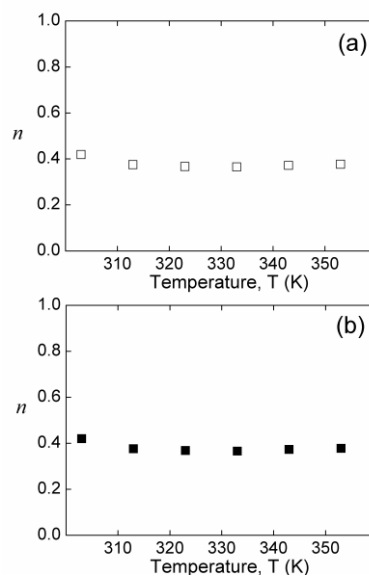
$$t_{ion}^+ = \frac{I_i - I_f}{I_f} = 1 - t_{ele}^+ \quad (6)$$

where  $I_i$  is the initial current and  $I_f$  is the final

residual current. The plot in Figure 6 suggests that the charge transport in PBE system is predominantly due to ions.



**Fig. 4:** Plots of (a)  $\text{Ln } \varepsilon_i$  vs.  $\text{Ln } \omega$ , (b)  $\text{Ln } \sigma_{ac}$  vs.  $\text{Ln } \omega$  and, (c) dielectric loss,  $\varepsilon_i$  vs. frequency,  $f$  for BPE film containing 40wt.% AN at selected temperatures.

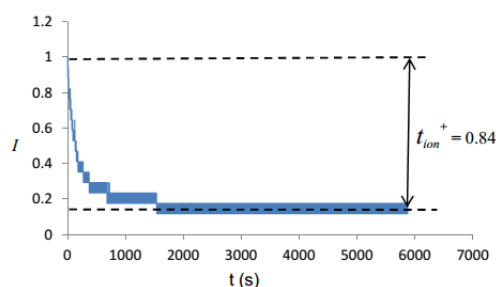


**Fig. 5:** Exponent  $n$  against temperature for PBE film containing 40wt.% AN obtained based on plots of (a)  $\text{Ln } \varepsilon_i$  vs.  $\text{Ln } \omega$  and, (b)  $\text{Ln } \sigma_{ac}$  vs.  $\text{Ln } \omega$ , respectively.

#### 4. Conclusion:

Yellowish-translucent biodegradable dual polysaccharides blend electrolytes based CMC/chitosan-ammonium nitrate has been successfully prepared via solution casting technique. The most conductive PBE film exhibited the ionic conductivity of  $\sim 10^{-5} \text{ Scm}^{-1}$  (40wt.% AN) at 303K.

The ionic conductivity was increased one magnitude order to  $\sim 10^{-4} \text{ Scm}^{-1}$  at 353K. The conduction mechanism in PBE film was analyzed and can be represented by the quantum mechanical tunneling model. The charge transport in PBE film was identified and has been observed to be predominantly by ions.



**Fig. 6:** Normalized polarization current,  $I$  vs. time,  $t$  for PBE film containing 40wt.% AN ( $t_{ion}^+ = 0.84$ ).

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### Authors' Contribution:

K.H. Kamarudin and M.S.A. Rani contributed equally to this work.

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There is no conflict of interest.

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