

Electrical Properties of Starch/Chitosan-Nh₄no₃ Polymer Electrolyte

A.S.A. Khiar, A.K. Arof

Abstract—Starch/chitosan blend have been prepared via the solution casting technique. Ionic conductivity for the system was conducted over a wide range of frequency between 50 Hz-1 MHz and at temperatures between 303 K and 373 K. Sample with 35 wt% of NH₄NO₃ shows the highest conductivity of $3.89 \pm 0.79 \times 10^{-5} \text{ Scm}^{-1}$ at room temperature. Conductivity-temperature relationship suggests that samples are Arrhenian. Power law exponent was obtained through dielectric loss variation and the trend suggests that the conduction mechanism of the ions can be represented by the correlated barrier hopping (CBH) model.

Keywords—starch, chitosan, permittivity, power exponent law

I. INTRODUCTION

THE research on solid polymer electrolytes (SPE) goes way back to 1975 when Wright [1], found the ionic conduction in Polyethylene-based electrolyte. Since then, many works have been done to increase ionic conductivity of SPE for application in high-energy density batteries [2]. Ideally, SPE should have good ionic conductivity of 10^{-3} to 10^{-2} Scm^{-1} . There are many methods that have been suggested to enhance ionic conductivity in SPE which include polymer blending, co-polymer grafting and addition of plasticizer or ceramic. The method used depends on the materials used in developing the SPE. Polymer blending is a well-used technique whenever modification of properties is required, because it uses conventional technology at low cost. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend [3].

Starch is a semi-crystalline polymers that composed of two repeating unit of 1,4- α -D-glucopyranosyl: amylose and amylopectin. It is renewable and biodegradable polymers which usually are stored as granule in plants. Starch easily dissolves in water, however the molded articles prepared from starch and water was transparent, brittle and sensitive to atmospheric moisture [4]. Therefore, blending two or more dissimilar natural polymers has shown potential to overcome these difficulties. Many works have shown that when starch was blend with chitosan, the mechanical strength of the blend increases and the crystallinity suppresses [5-6]. Furthermore, starch-chitosan blends exhibits good film forming property due to the presence of high density of amino groups and

hydroxyl groups and inter and intra molecular hydrogen bond [7]. The present work reports the electrical properties of films from starch-chitosan blends which have been doped with ammonium nitrate (NH₄NO₃). Dielectric data were calculated from the relevant equations, which make use of experimentally obtained impedance data. Using Jonsher's Power Law, the conduction mechanism of the samples was investigated.

II. MATERIALS AND METHODS

A. Sample Preparation

Commercially available tapioca starch and chitosan (Fluka) was used to prepare the samples using solution casting method. Starch solution was prepared by dispersing different weight of tapioca starch in 50ml distilled water solutions, which were then heated on a hotplate and maintain at 90°C for 30 min under gentle stirring, to complete the starch gelatinization, while chitosan solution was prepared by dissolving different weight of chitosan in 50 ml of acetic acid solution (Ajax Chemical, 1%, v/v). The starch and chitosan solution were then mixed in different percentage (w/w) to form the blend polymer. In this present work, the ratio of starch to chitosan (25:75) was used for further works as it shows the least crystalline structure. NH₄NO₃ was then added at different weight percent of the total solid weight in solution to the mixture of starch-chitosan. The mixtures were stirred continuously and then cast onto plastic petri dish and left to dry at room temperature. Dried films were conditioned at room temperature in vacuum aspiration for 24 h prior to testing.

B. Impedance Measurements

Impedance spectroscopy measurements were used to determine the electrolyte conductivity and its frequency behavior. The impedance was measured with a HIOKI 3531-01 LCR Hi-Tester that has been interfaced to a computer. This bridge has been set to measure the impedance and phase angle from 50 Hz to 1 MHz. The software controlling the measurements also calculates the real and imaginary impedance. A plot of negative imaginary impedance versus real impedance on a graph with horizontal and vertical axes having the same scales will give a semicircle if the sample exhibits Debye characteristics. From the complex impedance plot, the bulk resistance, R_b can be obtained and the electrical conductivity, σ of the sample can be calculated from:

$$\sigma = \frac{l}{R_b A} \quad (1)$$

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Here l and A is the thickness and area of the samples, respectively. A Mitutoyo digital gauge was used to measure the thickness of the polymer films. The conductivity measurement for each sample was also carried out at temperatures from 303 K to 373 K.

The complex permittivity of a system is defined by:

$$\varepsilon^* = \varepsilon_R + i\varepsilon_I \quad (2)$$

where ε_R is dielectric constant (the real part of complex permittivity) and ε_I is dielectric loss (the imaginary part of complex permittivity). Using the measured impedance values, the dielectric constant and dielectric loss can be calculated from the equations:

$$\varepsilon_R = \frac{Z_I}{\omega C_0(Z_R^2 + Z_I^2)} \quad (3)$$

$$\varepsilon_I = \frac{Z_R}{\omega C_0(Z_R^2 + Z_I^2)} \quad (4)$$

Here Z_I and Z_R are the real and imaginary part of complex permittivity, $C_0 = \varepsilon_0 A/t$, where ε_0 is the permittivity of free space, A is the electrolyte-electrode contact, t is thickness of the samples and $\omega = 2\pi f$, f being the frequency in Hz. The ratio of ε_R and ε_I gives loss tangent, $\tan \delta$.

III. RESULTS AND DISCUSSION

A. Conductivity Studies

The conductivity of the blends with different composition of salt at room temperature is illustrated in Fig. 1. The plot shows that the increase in conductivity is almost gradual with addition of NH_4NO_3 . From previous work [8], the maximum conductivity of $2.83 \times 10^{-5} \text{ Scm}^{-1}$ was achieved for samples with composition of 25 wt% NH_4NO_3 . However, in this study, a maximum conductivity is observed for samples with composition of 35 wt% NH_4NO_3 at $(3.89 \pm 0.78) \times 10^{-5} \text{ Scm}^{-1}$. This shows that when starch was blend with chitosan, the conductivity value increases.

There are various factors that influences ionic conductivity; the number of charge carriers, ionic mobility as well as the availability of a connecting polar domain as the conduction pathway [9]. In this present work, the increase in conductivity could be attributed to the increment of charge carriers, while the decline in conductivity value could simple be explain by the formation of ions pairs producing neutral species which reduces number of free ions that in turn decreases conductivity.

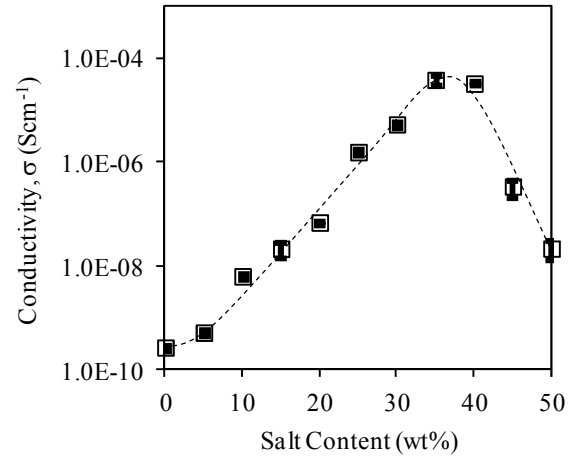


Fig. 1 The room temperature ionic conductivity of starch-chitosan blend with various amount of NH_4NO_3

The temperature-dependent ionic conductivity measurements were taken to analyze the mechanism of ionic conduction in polymer electrolytes. Fig. 2 shows the plot of $\log \sigma$ versus $10^3/T$ for selected samples in the system. A linear variation observed from this plot suggests that samples are Arrhenian. This linear relation also suggests that no phase transition occurred in the polymer matrix or domain formed by addition of NH_4NO_3 . The increase in conductivity with temperature in solid polymer electrolyte is attributed to segmental motion which facilitates faster ionic movement [10].

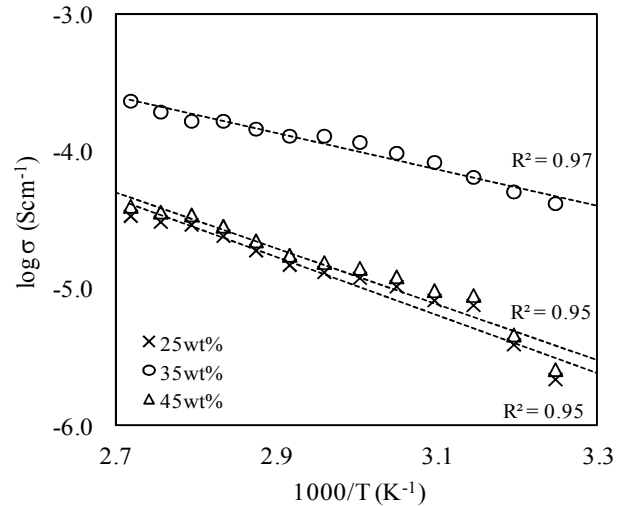


Fig. 2 Temperature-dependent of ionic conductivity, R^2 is the regression value.

B. Dielectric Studies

Conductivity behavior of polymer electrolyte can best be described through dielectric studies. Dielectric constant, ε_R , charge carriers, n and the dissociation energy, U are related according to the equations:

$$n = n_o \exp(-U / \varepsilon_R kT) \quad (5)$$

From this equation, an increase in dielectric constant will result in the increase number of charge carriers.

The salt concentration dependence of the dielectric constant at selected frequencies is shown in Fig. 3. The graph follows almost the same trend as the conductivity plot shown in Fig. 1. This further confirms that the increase in conductivity is mainly due to the increase number of charge carriers. The decrement in dielectric constant after 35wt% of NH_4NO_3 is attributed to reassociation of ions in which decreases the number density of mobile ions. The reassociated ions may be neutral aggregates that do not contribute to conductivity or larger size ion aggregates with reduced mobility [11].

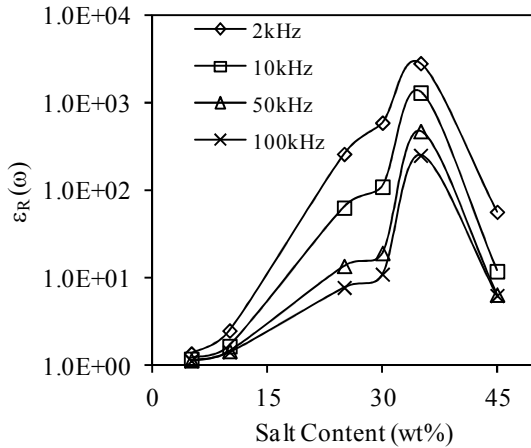


Fig. 3 Salt concentration dependence for selected samples of dielectric constant $\epsilon_R(\omega)$ at selected frequencies.

Fig.4 depicts the frequency dependence of lost tangent for selected samples at ambient temperature. For maximum dielectric loss ($\tan \delta_{\max}$) at a particular frequency, the absorption peak is described by:

$$\tau\omega = 1 \tag{6}$$

Here τ is the relaxation time, ω is the angular velocity with $\omega=2\pi f$, f is the frequency value corresponding to maximum $\tan \delta$ in Hz.

Relaxation time occurs as a result of ionic charges carriers within the polymer material to obey the change in the direction of the applied field. It is observed from Fig. 4, that the peak frequency shifted towards higher frequency as the salt concentration increases. The shift of the peak towards higher frequency suggests quicker relaxation time. As discussed earlier, the increase in ionic conductivity is due to the enhancement the number of carrier ions. Thus, the relatively fast segmental motion coupled with mobile ions enhances the transport properties of the sample which explains the decrease in relaxation time with conductivity as depicted in Fig. 5 [12].

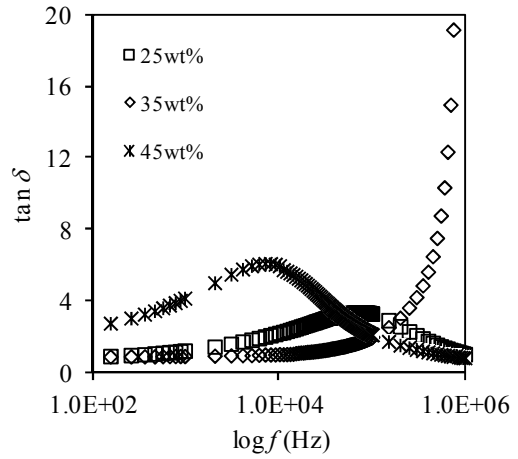


Fig. 4 Variation of $\tan \delta$ with frequency for selected samples

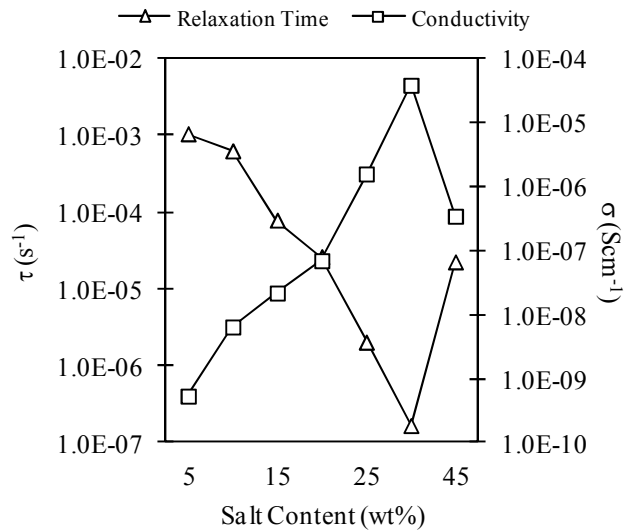


Fig. 5 Variation of relaxation time and conductivity as a function of salt concentration

C. Frequency dependent conductivity

Fig. 6 shows the typical frequency dependent conductivity plot for the highest conducting sample at different temperatures. The spectra consist of two well-defined regions, a low-frequency dispersive region due to electrode polarization effects and the plateau representing the dc conductivity. It is observed that the dc conductivity increases with increase in temperature which suggests that the free volume around the polymer chain causes the increase in mobility of ions, polymer segments and hence the conductivity [13].

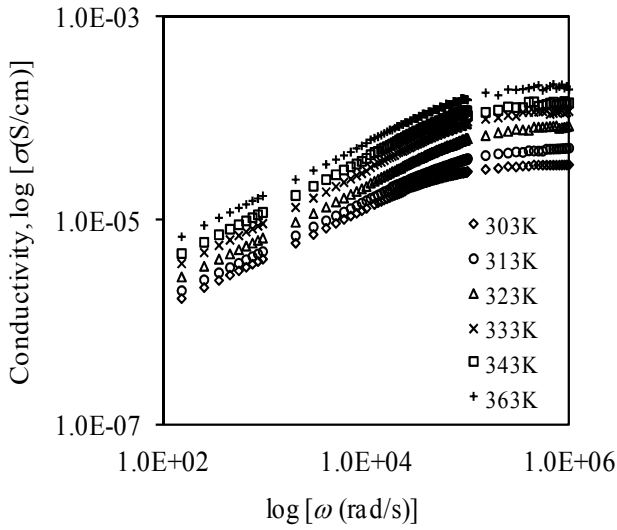


Fig.6 Frequency dependence of AC conductivity for the highest conducting sample at selected temperatures

The phenomenon of ac conductivity, $\sigma(\omega)$, can be analyzed using Jonscher's Universal Power Law (UPL) and is found to vary with angular frequency, ω from:

$$\sigma_{\omega} = \sigma_{dc} + A\omega^s \quad (7)$$

where $\sigma(\omega)$ is the measured AC conductivity, σ_{dc} is the frequency independent DC conductivity which is a thermally activated quantity, A is the pre-factor that depends on temperature and composition, s is the frequency exponent in the range $0 < s < 1$ and ω is the angular frequency. Hence,

$$\sigma_{ac} = A\omega^s \quad (8)$$

Where the ac conductivity can be obtained from dielectric loss, ϵ_l at every frequency according to:

$$\sigma_{ac} = \epsilon_o \epsilon_l \omega \quad (9)$$

Equating (8) and (9),

$$A\omega^s = \epsilon_o \epsilon_l \omega \quad (10)$$

Gives:

$$\epsilon_l = \frac{A}{\epsilon_o} \omega^{s-1} \quad (11)$$

Or

$$\ln \epsilon_l = \ln \frac{A}{\epsilon_o} + (s-1) \ln \omega \quad (12)$$

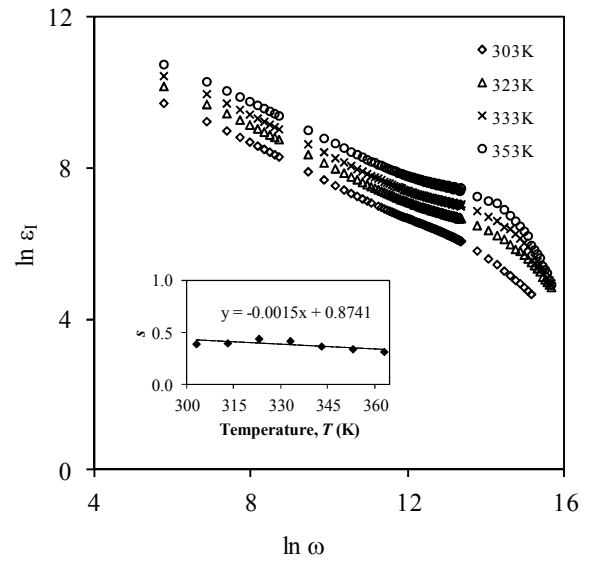


Fig. 7 $\ln \epsilon_l$ versus $\ln \omega$ at selected temperatures for highest conducting sample. The inset figure shows the plot s versus temperature for the present system

Since polaronic conductor exhibits similar behavior as the ionic conductor [14], conduction mechanism models in polaronic conductor could also be used to explain conduction mechanism in ionic conductor. The value of s was obtained from the slope of $\ln \epsilon_l$ vs. $\ln \omega$ at higher frequency region where there is minimal space charge polarization. Fig. 7 depicts the variation of s at different temperatures. From the plot, s was found to decrease with the increase in temperature. This implies that the conductivity mechanism of the present system follows the Correlated Barrier Hopping (CBH) model. The plot can be fitted to the equation, $s = -0.0015T + 0.8741$. From the fitting equation, it can be deduced that when $s \rightarrow \pm 1$ when $T \rightarrow 0$.

IV. CONCLUSION

Starch-chitosan blends with composition of 25:75 have been chosen as the host polymer for the preparation of polymer electrolyte. The conductivity and dielectric behavior of Starch-chitosan- NH_4NO_3 have been studied as a function of frequency at ambient and elevated temperature. The highest conductivity at ambient appeared to be $3.89 \pm 0.79 \times 10^{-5} \text{ Scm}^{-1}$. The trend of dielectric constant, ϵ_r , as a function of salt composition suggest that the increase in conductivity is mainly due to the increase of number of charge carriers. Conduction mechanism of the system has been established from the study of ac conductivity and can be represented by the correlated barrier hopping (CBH) model when exponent, $s \rightarrow 1$, as temperature, $T \rightarrow 0$.

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