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Preparation and Characterization of Solid Polymer Electrolyte Based on Carboxymethyl Chitosan, Ammonia Nitrate and Ethylene Carbonate

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Abstract: Research is conducted that related to the preparation and characterization of solid polymer electrolyte based on carboxymethyl chitosan, ammonia nitrate and ethylene carbonate. The potential of carboxymethyl chitosan as a green polymer electrolyte has been explored. Chitosan is a natural biopolymer which can be obtained from partially deacetylated derivative of chitin. Chitosan react with monochloroacetic acid to form carboxymethyl chitosan. The solid films were prepared by solution casting technique with ammonia nitrate and ethylene carbonate. Characterization of carboxymethyl chitosan – 30% wt. ammonia nitrate – ethylene carbonate at the weight percentage of different plasticizers were carried out by using infrared spectroscopy analysis (FTIR) analysis in order to study the changes in functional groups and structural of carboxymethyl chitosan. The changes in shifting of wavenumbers confirmed that there is an interaction between the ion of ammonia nitrate and ethylene carbonate. Scanning electron microscope are used to study the morphology of the film samples. Morphological observation determine whether the blends were homogenous and no phase separation occurred. The presence of amorfus and crystalline structure of the film samples can be determined by X- ray diffraction. The conductivity in the film samples can be calculated through electron impedance spectroscopy (EIS). Solid polymer electrolyte based on carboxymethyl chitosan as host polymer and ammonium nitrate (NH_4NO_3) as a complexing salt and ethylene carbonate were prepared by solution casting technique. The highest ionic conductivity value achieved by carboxymethyl chitosan – 30% wt. ammonia nitrate salt – 25% wt. ethylene carbonate in room temperature was 3.86×10^{-3} S cm^{-1} which characterized by AC impedance spectroscopic analysis.

Keywords: Polymer

Introduction

Synthetic polymers are polymers made from human using chemicals. Most synthetic polymers are non-biodegradable polymer where synthetic polymers are not easy to decompose. When plastic materials are burned, releases of toxic gases will occur and cause depletion of ozone layer. This causes environmental pollution to occur. This situation has prompted researchers to find solutions to address this problem. Fossil fuel pollution on the environment has resulted in the production of environmentally friendly based products. The use of biodegradable polymers such as natural polymers derived from living things as environmentally friendly materials has grown rapidly to address environmental pollution problems (Luc Averous & Eric Pollet 2012). Materials with independent ions and capable of forming conductive electrical materials are known as electrolytes. The main function of the electrolyte is acting as a medium for transfer of charge occurs between electrons (Rahman et al. 2011). According to Stephen et al. (2006), the polymer electrolyte is known as a membrane having a charge carrier which is comparable to conventional liquid electrolytes. Among the materials that can be used for the production of electrolyte membranes is the polymer in which the polymer is known as polymer electrolyte. The ionic conductivity of a polymer electrolyte is very important for the purpose of its use in an electronic device. Polymers with electron-contributors are suitable as the main polymer (Anon 2005). Electrolyte polymeric materials should have properties such as good mechanical strength, good electrode interaction, and good conductivity values (Agrawal & Pandey 2008). Fenton et al. (1973) was among the first researchers to discover the potential of polymer to be applied as an electrolyte in an electrochemical device system.

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Studies on polyethylene oxide using lithium salts have been applied in solid electrolyte polymers especially for battery use in 1979 (Agrawal & Pandey 2008). The very high ionic conductivity properties of the solid electrolytic polymers (SPE) systems have attracted considerable attention as the most suitable option for fabricating full solid state electrochemical devices, ie batteries, detectors and fuel cells (Reddy et al. 2002). This condition led to the development of the study involving electrolyte polymers. Solid polymer electrolytes are a solution capable of electrifying the electrons in which the solution contains salts that are soluble in the polymer matrix. Solid polymer electrolytes used in comparison with liquid electrolytes have some unresolved weaknesses such as toxic liquids that cause flammable and leakage due to corrosion caused by the reaction between strong solvent and container (Armand et al 1978). In addition, solid polymer electrolyte has low volatility, high energy density and easy to form (Rahman et al. 2011). The development of polymer electrolytes was initiated by Fenton et al. (1973) found that poly-poly (ethylene oxide) polymer film (PEO) thin film can be used as a condensing material after dissolving it with lithium salts in the polymer matrix. However, Fenton and Wright faced a low ionic conductivity problem at room temperature during the conduct of electrolyte polymer studies in 1973. One of the steps to improve the ionic conductivity value is the addition of plasticizers and polymeric materials such as polyvinylalkohol. The addition of plasticizers allows the movement of polymer chains to be more flexible and increases the value of conductivity. The use of plasticizers is an efficient and effective way in which plasticizers can reduce crystalline properties and enhance amorphous properties in composite electrolyte polymers (Ramesh & Ong 2010).

Addition of salt such as lithium also helps to improve ionic conductivity (Rahman et al. 2011). In this study, natural polymeric materials such as chitosan have been used to produce carboxymethyl chitosan. Chitosan is a biodegradable material in which chitosan is easily disposed off and does not pollute the environment. Chitosan has a hydroxyl and amine functional group where these functional groups have isolated electrons and are suitable for the preparation of solid electrolyte polymers (Yahya et al. 2003). The addition of salt to the carboxymethyl chitosan helps increase ionic conductivity in the electrolyte. Ammonia nitrate has low lattice energy in which the decomposition of salts and solubility in polymer matrices is easier in electrolytes. The choice of ethylene carbonate as a plasticizer is better than polypropylene carbonate plasticizers because ethylene carbonates have a high dielectric constant and a high boiling temperature range compared to polypropylene carbonate (Ramesh & Ong 2010).

Method

Preparation of membrane

Carboxymethyl chitosan had been prepared according to Sun et al.'s method. In order to prepare polymer electrolyte film, carboxymethyl chitosan was dissolved in 1% acetic acid solution and was continuously stirred with a magnetic bar for 24 hours. Various weight percentage of ethylene carbonate with 30% wt. NH_4NO_3 were dissolved separately in 1% acetic acid solution before added in to the dissolved carboxymethyl chitosan solution. The solutions were further stirred for 24 hours to achieve a homogenous mixture. The solution was cast on petri dishes and allowed it to dried completely at room temperature until a film was obtained. The samples were stored in a desiccator for further use.

Sample characterization

The alternating current (AC) impedance measurement was carried out using a high frequency response analyzer (HFRA; Solartron 1260, Schlumberger) and an electrochemical interface (SI 1286) in the frequency range of 1Hz–10 MHz with 10 mV amplitude at room temperature. The polymer electrolyte was sandwiched between the stainless steel blocking electrodes with a contact surface area of 2.0 cm^2. The bulk resistance (R_b) was determined from the equivalent circuit analysis by using the Zview analyzer software. Transference number of electrolytes films were determined by the application of D.C. potential (0.1 V) across the sample using stainless steel electrodes at 303K using Zive mp2 multichannel electrochemical workstation. X-ray diffraction model D5000 Siemens was used to determine the amorphous and crystalline properties of the prepared samples. The data was collected in the range of diffraction angle 2θ from 3° to 35° at the rate of 0.05 s^{-1} at room temperature.

Results and Discussion

FTIR analysis

The existence of various groups working on chitosan allows chitosan to be used in the development of composite materials. The chitosan mixes based on the polymer electrolytes have been used in electrochemical devices such as solar cells. Infra-red spectroscopy is used to verify the complexity and ionization mechanisms (Kadir et al. 2010). This is because absorption peaks identified in the infra-red vibrational environment will give different frequency values for specific bonding types (Pavia et al. 2001). The interactions between cations and anions interacting in a polymer electrolyte matrix can be detected through changes in wave numbers in functional groups that interact besides the emergence of new peaks. The polymer mixture of carboxymethyl chitosan binder doped with ammonia nitrate and ethylene carbonate plasticizers will show a waveform shift in the amine and hydroxyl functional groups (Kadir et al. 2010).

Figure 1 shows the FTIR sample carboxymethyl chitosan-30% wt. ammonia nitrate - ethylene carbonate at the weight percentage of different plasticizers. Peaks highlighted after blending are the emergence of C = O peaks at the 1775cm^{-1} and 1807cm^{-1} waves confirmed that there was an interaction between ethylene carbonate and the host polymer. Peak (C = O) without the addition of ethylene carbonate plasticizer gives peak at wave number 1772cm^{-1}. Peak C = O decreases and goes to 1720cm^{-1} wave number when plasticizer is added at 10% wt., 15% wt. , 20% wt. and 25% wt. The peak of C = O on the 1775 cm^{-1} and 1807cm^{-1} wave numbers was also observed to 1773cm^{-1} and 1802 cm^{-1} and the peak of this C = O was increasingly widening after the addition of ammonia nitrate salt. This indicates that no chemical reaction which occurs between the plastics packet and the plastics, and between the plastics and the plasticizers only act physically with the polymer (Alias et al. 2005).

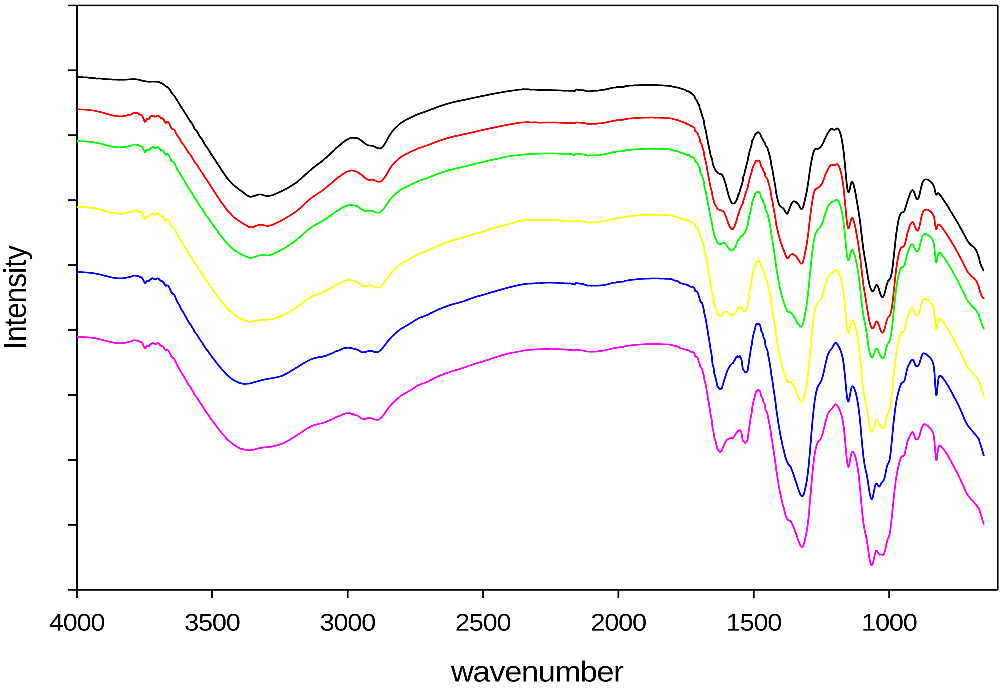

Figure 1. FTIR Analysis carboxymethyl chitosan - 30% wt. ammonia nitrate - ethylene carbonate at the weight percentage of different plasticizers

X-ray Diffraction Analysis

Determination of structural and crystalline crystalline properties can be determined by analyzing the X-ray diffraction by observing the presence of amorphous and crystalline phase in the polymer electrolyte film. The amorphous phase shows the intensity of the peaks that are increasingly horizontal while the crystalline phase shows sharp peaks that have high intensities (Wang et.al 2006). Figure 2 shows diffractogram of carboxymethyl chitosan – 30% wt. ammonia nitrate – ethylene carbonate at the weight percentage of different plasticizers. With the addition of ammonia nitrate salt of 30 wt.% and different weight percentages of ethylene carbonate, the high-peaked prime peaks are reduced and almost invisible. From this study, the semi-crystalline phase that exists in carboxymethyl chitosan has decreased and is increasingly amorphous with the addition of salt and ethylene carbonate at optimum levels. High-density reducer and widening of the hump shows the structure of semi-crystalline carboxymethyl chitosan has changed to amorphous due to the presence of salts allowing polymer chain movement occurs in polymer electrolyte systems (Shin et al.2002).

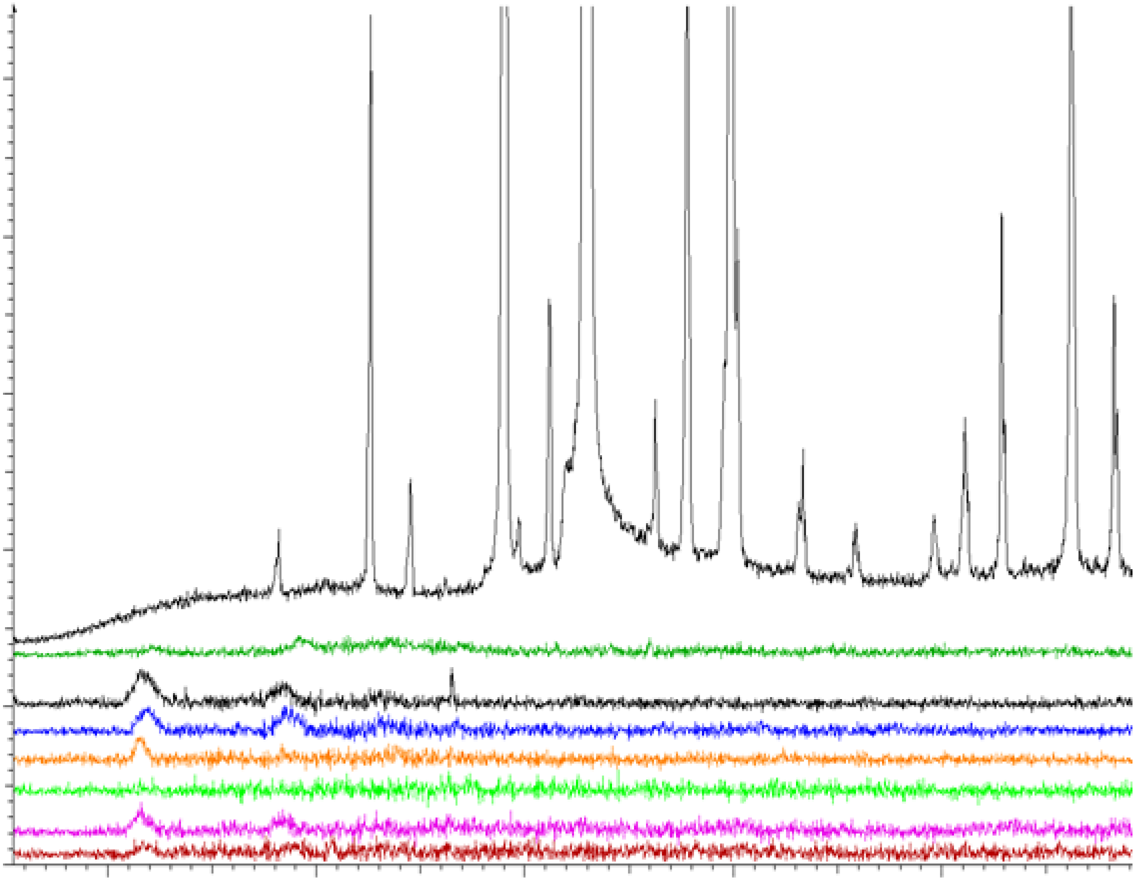

Figure 2: XRD Analysis carboxymethyl chitosan - 30% wt. ammonia nitrate - ethylene carbonate at the weight percentage of different plasticizers

Ionic Conductivity Analysis

The complex impedance plot shows that there are semi-circular areas within the frequency range which will contribute to the conductivity of polymer electrolytes (Jacob et al. 1997, Rajendran et al. 2002, Su'ait et al. 2009) while linear linear areas are contributed by electrode effects in low frequency range (Kim et al. 1999, Rajendran et al. 2002, Su'ait et al. 2009). The conductivity of the carboxymethyl chitosan sample with the addition of 30% wt. salt ammonia nitrate is 1.60 $x10^{-3}$ Scm^{-1}. The ionic conductivity showed an increase to 3.63 $x10^{-3}$ Scm^{-1} with an addition of 10% bt. ethylene carbonate plasticizers. The increase in ionic conductivity occurs due to the presence of NH_4^+ which serves as a charge carrier in the electrolyte system. The optimum conductivity, 3.86 x 10^{-3} Scm^{-1} obtained by adding 25% wt. ethylene carbonate plasticizers. The conductivity values are gradually increased with the addition of plasticizers to the optimum conductivity achieved at the weight of the plasticizer percentage by 25% wt. This indicates that the polymer electrolyte system of carboxymethyl chitosan dough and 30% wt. salts of ammonia nitrate with the presence of ethylene carbonate plasticizers produce higher ionic conductivity than without ethylene carbonate. The increase in the conductivity of ions with the addition of plasticizers is due to the high acidity dielectric constant which can increase the number of moving ions by weakening the koulombic force between cation and salt anion (Mohamed et al. 2008). Hence, more NH_4^+ ions can be produced and the solubility of salts into the system can also be improved. Additionally, an increase in ion conductivity occurs when the reduction of electrolyte polymer viscosity occurs after the addition of the material plasticizers and thus facilitating charge carriers to the electrolyte system (Ahmad et al. 2006, Idris et al. 2001, Wang & Kim 2007). This increase was due to the composition of the ammonia nitrate salt decomposed into ion species NH_4^+ and NO_3^-. There are various factors that affect ionic conductivity such as the number of charge carriers and ionic movement. The existence of a charge carrier species occurs when an ionization occurs which helps to increase the value of the ionic conductivity (Wang et al.2006). According to reports (Buraidah et al. 2009; Choi & Shin 1996; Subban 2003), an initial increase in conductivity was due to an increase in the number of car ions after the addition of plastic materials. The plasticizer, ethylene carbonate acts as an agent in which the process of decomposition of the salt occurs more easily.

Scanning Electron Microscope Analysis

Morphological examination on the surface of the polymer electrolytic film was performed to see the effect of plasticizer on surface morphology and topographic texture of the sample. Figure 3 shows the SEM micrograph of carboxymethyl chitosan sample -30% wt. ammonia nitrate - ethylene carbonate on addition (a) 0% wt. (b) 10% wt. (c) 15% wt. (d) 20% wt. (e) 25% wt. (f) 30% wt. (g) 35% wt. ethylene carbonate plasticizer. Based on the pictures, it is found that the distribution of plasticizers in the carboxymethyl chitosan matrix is uneven but gives a smoother surface compared to the carboxymethyl chitosan surface of 30% wt. ammonia nitrate without addition of ethylene carbonate. The addition of ethylene carbonate plasticizers also reveals darker areas where phase separation occurs between polymer and ethylene carbonate matrices. Figure 3(e) shows the smoothest, uniform and homogeneous surfaces as compared to the other percent weight of ethylene carbonate. A homogeneous surface is usually associated with a reduction in the crystallization phase and an increase in the amorphous phase. The increase in the movement of ions in polymer electrolytes usually occurs in the amorphous phase and causes an increase in ionic conductivity. The ions move freely in the electrolyte with a smooth surface and this leads to the increased ionic conductivity of the polymer electrolyte (Mobarak et al. 2012). However, high concentrations of salt will affect the ionic species for aggregation and associate with each other (Ahmad et al. 2010: Wickham et al. 2007). This will lead to a reduction in the number of species and the mobility of the ion inhibit the migration of ions in the polymer chain segment. Low conductivity of the polymer electrolytic system will occur due to the digression of polymer chain process travel in polymer electrolyte systems (Su'ait et al. 2011).

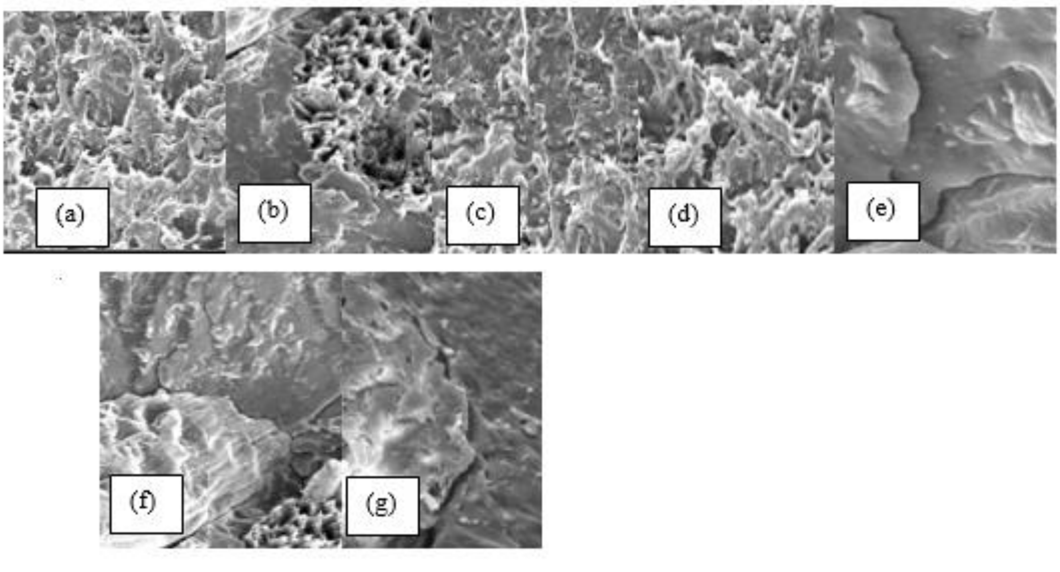

Figure 3: SEM Analysis carboxymethyl chitosan - 30% wt. ammonia nitrate - ethylene carbonate at the weight percentage of different plasticizers

Conclusion

This study was carried out for the preparation and characterization of polymer electrolytes based on the carboxymethyl chitosan blend of chitosan, ammonia nitrate and ethylene carbonate. Solid polymer electrolytes based on the carboxymethyl chitosan mix, ammonia nitrate at 30% wt. of the composition and ethylene carbonate at different ratios are provided. The effect of different percentage of ethylene carbonate weight ratio and ammonia nitrate doped salt on composition of 30% wt. by weight on the properties of ion conductivity, chemical interactions and morphological surfaces of solid polymeric electrolyte film was successfully analyzed.

In this study, the effect of the addition of ethylene carbonate plasticizers was shown to indicate the overall ionic conductivity. The increase in the ratio of ethylene carbonate plasticizers in the carboxymethyl blend of chitosan-ammonia nitrate contributes to an increase in the value of the ionic conductivity to the optimum level. However, ionic conductivity decreases after one optimum and this occurs due to the recrystallization of ammonia nitrate salt as evidenced in the x-ray diffraction analysis. The addition of low-quantity plasticizers has the ability to reduce the cohesion between the withdrawal of the polymer bond. The plasticizer with a small molecular size compared with the polymer molecule is easier to dissolve to the polymer matrix and the formation of the attraction between the plasticizer and the bonding segment will occur. The reduction of cohesion power between polymer bonds will occur when the attraction occurs and thus increases the segment mobility and ionic conductivity in solid electrolyte polymers. The ionic species will decompose from the ammonia nitrate salt composition when the salts are dissolved in the polymer matrix. When ion decomposition occurs, the charge carrier species will exist and help to increase the value of the ionic conductivity.

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