Characterization of Biopolymer Blend-based on Alginate and Poly (vinyl Alcohol) as an Application for Polymer Host in Polymer Electrolyte

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Abstract. In the present work, alginate (Alg) blend with polyvinyl alcohol (PVA) with various compositions were prepared by using solution casting method. The intermolecular interaction occurred in the polymer blends were investigated via Fourier Transform Infrared (FTIR) spectroscopy. Electrical impedance spectroscopy was used to determine the conductivity values of the blends. The conductivity value of Alg-PVA polymer blend was found to be optimum at 7.52 x 10^{-8} \text{S/cm} for composition with 70:30 of Alg:PVA. Based on the findings, it is believed that the Alg-PVA blend is a promising candidate to be act as polymer host materials for application in polymer electrolyte system.

Keywords: polymer blend, hydrogen bonding, FTIR analysis, alginate.

1. Introduction
Generally, polymer electrolyte (PE) was known as linear macromolecular chains which contains a large amount of charged when dissolved in suitable solvent. It is also played important role in electrochemical devices such as solar cell, batteries, fuel cell and supercapacitor [1]. However, most commercialized PE were prepared based liquid state and using non-biodegradable materials which are not safe to environment and humankind. Recently, PE has gained many interests among researchers due to their promising properties that can be used as a powerful platform to achieve high efficiency for energy storage devices. Numerous reports have been made on the application of petroleum-based polymer or biodegradable polymer-based throughout the advancement of solid polymer electrolyte. However, the application of petroleum-based polymer can give drawbacks such as costly, decreasing resources of petroleum, and can raise problems in the environment.

Owing to the abundant in nature and eco-friendly, biopolymer materials have been a new interest to researchers to study comprehensively as a polymer electrolyte system using the biodegradable materials. Several biodegradable polymers such as chitosan [2], agarose [3], carboxymethyl cellulose [4], carrageenan [5], and sodium alginate [6] has been reported which have potential to be act as host polymer in the preparation of polymer electrolytes. Alginate can be obtained by extraction in the cell wall of marine brown algae and is a polysaccharide which comprised of linear chain of (1,4)-\beta-D-mannuronic acid and (1,3)-\alpha-L-guluronic acid [7]. The properties of alginate (Alg) includes water-soluble, rigid chain of molecules, and good film forming ability and it is has been widely being studied...
in the application of biomedical such as drug carriers [8]. In addition, some of the crucial properties that are needed for the polymer to act as a successful host include the availability of atoms in the polymer to donate its electrons to form bonds with the cations of the salts. This will allow the polymer to dissolve the salt through the interaction. Other than that, a flexible polymer chain is desired for the solvation of the cations into the polymer to be effective. In addition, the glass transition temperature of the polymer should be lower so that the cohesive energy density is also low. to ensure effective solvation of the cations in the salt and have low glass transition temperature to ensure low cohesive energy density [9].

In order to improve the physicochemical properties of the individual polymer, incorporation with other polymer has been done as an alternative method which this method is known as the blending method. It is said that the compatibility between the polymer molecules regulated by intermolecular interactions has an influence on the properties of the blends [10]. From the previous report, the addition of Alg into poly (ethylene oxide) (PEO) proved that there are intermolecular interactions occurred between the polymers and improved the mechanical properties of the blend corresponding to those Alg and PEO thus, enhanced the electrochemical properties of polymer electrolytes when introduced with ionic dopant [11]. Numerous studies on polymer blend has been reported including chitosan-methylcellulose (CS-MC) [12], chitosan-agarose [13], and poly (vinyl alcohol)-poly (methyl methacrylate) (PVA-PMMA) [14]. Incorporation of biopolymers is promising owing to its characteristics which are renewable, no toxicity, and easy to prepare.

Although biopolymers have shown good biocompatibility characteristics, but it has lower mechanical properties compared to the synthetic polymers. Therefore, blending of natural with synthetic polymers has been an interesting way to improve the properties while maintaining the biocompatibility. Tremendous studies has been reported based on natural and synthetic polymer blending including carboxymethyl cellulose-poly(vinyl alcohol) (CMC-PVA) [15, 16], sodium alginate-poly (ethylene oxide) [11], and chitosan-poly (vinyl alcohol) (CS-PVA) [17]. Polyvinyl alcohol (PVA) is a polymer and has hydroxyl groups attached to the carbon chain backbone present in the molecule which the hydroxyl groups can be the source of hydrogen bonding in the polymer blends as it regulates the miscibility between the polymer molecules [18].

This present study is mainly focus on the preparation and characterization of Alg incorporated with PVA using the blending technique to produce the polymer blend. The structural and conduction properties of Alg-PVA are examined using Fourier Transform Infrared (FTIR) spectroscopy, and Electrical Impedance Spectroscopy (EIS) analysis.

2. Experimental

2.1. Preparation of Alg-PVA film
Alg (molecular weight: 216.12 g/mol) and partially hydrolyzed PVA ~85% (molecular weight: 70000) were obtained from Sigma Aldrich and Merck Schuchardt, respectively and used as received. Solution casting technique was used to prepare the Alg-PVA polymer blend [15, 19]. Alg-PVA with different ratios of composition was dissolved in distilled water. Table 1 illustrates the composition of Alg-PVA polymer blend. The mixture was stirred until homogenous and completely dissolved. The solution is then was casted into several petri dishes before drying it in oven for about 6-8 hours at 60°C. The sample was then stored in desiccator for further drying to ensure all the solvent left in the samples has been evaporated.

| Table 1. Composition of Alg-PVA blend |
|-------------------------------------|
| Sample label | Alg (wt. %) | PVA (wt. %) |
|---------------|-------------|-------------|
| AP0           | 100         | 0           |
| AP1           | 90          | 10          |
| AP2           | 80          | 20          |
2.2. Characterization of Alg-PVA film

2.2.1. Fourier Transform Infrared (FTIR) Spectroscopy. The structural properties and complexation occur between Alg-PVA in the polymer blend was observed using Thermo Scientific Nicolet iS5 FT-IR spectrometer in the frequency range of 4000 cm\(^{-1}\) to 700 cm\(^{-1}\) by attenuated total reflection (ATR) technique. The resolution used to obtain the IR spectra is 4 cm\(^{-1}\).

2.2.2. Electrical Impedance Spectroscopy (EIS). The conductivity of the samples was measured by using HIOKI 3532-50 LCR HITESTER in frequency ranges of 50 Hz to 1 MHz at ambient temperature. The sample was sandwiched between two stainless steel electrodes. The conductivity value of the samples can be calculated based on the equation:

\[
\sigma = \frac{t}{R_b A}
\]

where \(t\) is the thickness of the thin film, \(R_b\) is the bulk resistance, and \(A\) is the area of the electrode.

3. Results and discussions

3.1. FTIR spectroscopy

FTIR study is important in this present work as to obtained information on the composition of the blend along with interaction of the two polymers that may be occur due to the hydrogen bonding or formation of complexes in the blend. The FTIR spectra of raw Alg, raw PVA, and Alg-PVA polymer blends are shown in Figure 1a-c. From the observation, it can be seen that the position of some peaks in the polymer blends has been slightly shifted while having an akin to their individual polymer.

From figure 1a, the characteristic bands of Alg can be observed at 3449 cm\(^{-1}\), 1592 cm\(^{-1}\), and 1404 cm\(^{-1}\) representing the OH stretching, asymmetric –COO–, and symmetric –COO– stretching, respectively. Mazuki et. al [16] and Fuzlin et. al [20] also reported that the similar characteristics peaks of Alg occurred at 3391 cm\(^{-1}\), 1652 cm\(^{-1}\), and 1440 cm\(^{-1}\). On the other hand, the characteristic bands for PVA can be observed at 3220 cm\(^{-1}\), 2939 cm\(^{-1}\), 1418 cm\(^{-1}\), 1085 cm\(^{-1}\), and 831 cm\(^{-1}\) for OH stretching, -CH group stretching, -CH wagging, -CO stretching, and C-C stretching, respectively [15, 21].

For Alg-PVA polymer blends, the intensity of the hydroxyl bands increases compared to the pure Alg (Figure 2a). The band also slightly narrower with the addition of PVA content which could be the results of intermolecular interaction of hydrogen bonding from PVA occurs between Alg and PVA. According to Xing et. al [22], it is said that the intermolecular interaction of hydrogen bonding allows the mixing of polymers containing hydroxyl groups with other polyester which can results in completely or partially miscible system. On the other hand, it can be observed that the intensity of the bands at 2939 cm\(^{-1}\) becomes higher with increasing content of PVA in the blends which corresponding to the –CH group stretching of PVA.

It is also noticed from Figure 2b that there is an appearance of new peak at 1716 cm\(^{-1}\) which is assigned for C=O group stretching of PVA [23]. A study conducted by Saadiah et. al [24] also reported similar appearance of new peak (1740 cm\(^{-1}\)) which is assigned to the stretching of C=O groups of PVA. In addition, Figure 2b reveals the band of carboxylate group is slightly shifted to higher wave number.
which is from 1592 cm$^{-1}$ to 1600 cm$^{-1}$ also illustrated the hydrogen bonding interaction occurs between the hydroxyl groups of PVA with –COO- of Alg [24]. An appearance of peak at 1250 cm$^{-1}$ also was observed corresponding to C-O-C asymmetric stretching of ester group present in PVA. Based on the FTIR observation, it shows a positive correlation between the present system and other research works where the occurrence of intermolecular forces of H–bonding leads to the creation of more vacant site between the Alg and PVA during the complexation when it serves as polymer host in polymer electrolytes. It is apparent that the complexation has successfully occurred between Alg and PVA, which lead to the changes of their conductivity.

![Figure 1. FTIR spectra of (a) raw Alg, (b) raw PVA, and (c) Alg-PVA polymer blends (wavelength ranges of 700-4000 cm$^{-1}$).](image-url)
Figure 2. FTIR spectra of Alg-PVA blends in wavelength ranges of (a) 2700-3900 cm\(^{-1}\), (b) 1200-2000 cm\(^{-1}\), and (c) 700-1400 cm\(^{-1}\).

3.2. EIS

Figure 3 shows conductivity study for Alg-PVA polymer blends at various ratio compositions. Previous work done by Mazuki et. al [16] and Fuzlin et. al [20] revealed that the single polymer of alginate conductivity at room temperature is \(\sim 3 \times 10^{-8}\) S/cm and found to be similar as reported in the present system. It can be seen that with the addition of PVA, the conductivity starts to increase up to 30 % of PVA in Alg with 7.52 \(\times 10^{-8}\) S/cm. Due to the chain flexibility present in PVA, it allows attraction forces of inter- or intra- molecular between both the polymers to fasten the chain mobility as it develop a segmental motion in the PVA chain and thus conductivity increases [25]. It might also be due to the enhancement of amorphousness of sample at this ratio which made easier hydrogen bonding from PVA to Alg to occur thus increased the conductivity to optimum value [26]. Moreover, the increase in the PVA ratio in Alg attributed to the increase in the segmental motion of polymer-blended backbone consequently, creating more vacant site for the ions if introducing with suitable ionic dopant.

In contrast, the conductivity of the polymer blends starts to decrease to lower value with the addition of PVA content above 30%. The decreased in conductivity may due to the crowding and saturation of the Alg biopolymer molecular interaction that decreases the degree of complexation when PVA was added above 30 % this would, in turn, lead to the pathway interaction obstruction between Alg and PVA. As a result, this obstruction decreases the conductivity when added above 30 % of PVA [17, 25]. It can be observed that Alg-PVA blends with 70:30 weight ratios show a relatively higher conductivity when compared to their pristine polymer and other Alg-PVA blends. Therefore, it delivers that Alg-PVA polymer blends with ratio of 70:30 can be favorable to be use as a host polymer as an application in polymer electrolytes system.
Figure 3. Plot of conductivity as a function of percentage of PVA added into Alg.

4. Conclusion
Polymer blend based on alginate (Alg) incorporated by polyvinyl alcohol (PVA) was successfully prepared via solution casting method. The complexation between Alg and PVA based on FTIR analysis were found at 1250 cm\(^{-1}\), 1592 cm\(^{-1}\), 1716 cm\(^{-1}\), 2939 cm\(^{-1}\), and 3449 cm\(^{-1}\) corresponding to –OH bending, –COO- stretching, C=O stretching, -CH group, and –OH stretching, respectively. This confirms that there is interaction of hydrogen bonding in the blends and provides more complexation sites for ion to conduct compared to electrolyte employing only one polymer host. Alg-PVA blend of 70:30 compositions were found to be the optimum ratio with the highest conductivity among the polymer blends which is \((7.52 \pm 0.04) \times 10^{-8}\) S/cm. The decrease in conductivity exhibited by AP4, AP5, and AP6 electrolytes can be attributed to the lower number density of mobile ions in the bulk electrolytes. Based on the observations made, it is believed that the Alg-PVA blend is a promising candidate for polymer host materials for application in polymer electrolyte system.

5. References

[1] Arya, A. and A. Sharma, Polymer electrolytes for lithium ion batteries: a critical study. Ionics, 2017. 23(3): p. 497-540.
[2] Khiar, A.S.A., R. Puteh, and A.K. Arof, Conductivity studies of a chitosan-based polymer electrolyte. Physica B: Condensed Matter, 2006. 373(1): p. 23-27.
[3] Wang, W., X. Guo, and Y. Yang, Lithium iodide effect on the electrochemical behavior of agarose based polymer electrolyte for dye-sensitized solar cell. Electrochimica Acta, 2011. 56(21): p. 7347-7351.
[4] Noor, N.A.M. and M.I.N. Isa, Investigation on transport and thermal studies of solid polymer electrolyte based on carboxymethyl cellulose doped ammonium thiocyanate for potential application in electrochemical devices. International Journal of Hydrogen Energy, 2019. 44(16): p. 8298-8306.
[5] Moniha, V., et al., Conductive bio-polymer electrolyte iota-carrageenan with ammonium nitrate for application in electrochemical devices. Journal of Non-Crystalline Solids, 2018. 481: p. 424-434.
[6] Pasini Cabello, S.D., et al., New bio-polymeric membranes composed of alginate-carrageenan to be applied as polymer electrolyte membranes for DMFC. Journal of Power Sources, 2014. 265: p. 345-355.
[7] Rasali, N., Y. Nagao, and A. Samsudin, Enhancement on amorphous phase in solid biopolymer electrolyte based alginate doped NH 4 NO 3. Ionics, 2019. 25(2): p. 641-654.

[8] Xie, M., et al., Surface modification of graphene oxide nanosheets by protamine sulfate/sodium alginate for anti-cancer drug delivery application. Applied Surface Science, 2018. 440: p. 853-860.

[9] Ratner, M., J. MacCallum, and C. Vincent, Polymer electrolyte reviews. Elsevier, London, 1987: p. 173-236.

[10] Chen, Z., et al., Intermolecular interactions in electrospun collagen–chitosan complex nanofibers. Carbohydrate Polymers, 2008. 72(3): p. 410-418.

[11] Lu, J.-W., et al., Electrospinning of sodium alginate with poly(ethylene oxide). Polymer, 2006. 47(23): p. 8026-8031.

[12] Aziz, S.B., et al., Protonic EDLC cell based on chitosan (CS): methylcellulose (MC) solid polymer blend electrolytes. Ionics, 2020. 26(4): p. 1829-1840.

[13] Felfel, R.M., et al., Structural, mechanical and swelling characteristics of 3D scaffolds from chitosan-agarose blends. Carbohydr Polym, 2019. 204: p. 59-67.

[14] Rajendran, S., M. Sivakumar, and R. Subadevi, Investigations on the effect of various plasticizers in PVA–PMMA solid polymer blend electrolytes. Materials Letters, 2004. 58(5): p. 641-649.

[15] Saadiah, M. and A. Samsudin. Electrical study on Carboxymethyl Cellulose-Polyvinyl alcohol based bio-polymer blend electrolyte in IOP Conference Series: Materials Science and Engineering. 2018. IOP publishing.

[16] Mazuki, N., et al., An investigation on the abnormal trend of the conductivity properties of CMC/PVA-doped NH 4 Cl-based solid biopolymer electrolyte system. Ionics, 2019. 25(6): p. 2657-2667.

[17] Buraidah, M.H. and A.K. Arof, Characterization of chitosan/PVA blended electrolyte doped with NH4I. Journal of Non-Crystalline Solids, 2011. 357(16-17): p. 3261-3266.

[18] Bhargav, P.B., et al., Structural and electrical properties of pure and NaBr doped poly (vinyl alcohol) (PVA) polymer electrolyte films for solid state battery applications. Ionics, 2007. 13(6): p. 441-446.

[19] Mazuki, N., et al., Studies on ionics conduction properties of modification CMC-PVA based polymer blend electrolytes via impedance approach. Polymer Testing, 2020. 81: p. 106234.

[20] Fuzlin, A. and A. Samsudin, Studies on favorable ionic conduction and structural properties of biopolymer electrolytes system-based alginate. POLYMER BULLETIN, 2020.

[21] Khalid, I., et al., Preparation and characterization of alginate-PVA-based semi-IPN: controlled release pH-responsive composites. Polymer Bulletin, 2017. 75(3): p. 1075-1099.

[22] Xing, P., et al., Miscibility and specific interactions in poly (β-hydroxybutyrate-co-β-hydroxyvalerate) and poly (p-vinylphenol) blends. European polymer journal, 1998. 34(8): p. 1207-1211.

[23] Mansur, H.S., et al., FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. Materials Science and Engineering: C, 2008. 28(4): p. 539-548.

[24] Saadiah, M., et al., Reducing crystallinity on thin film based CMC/PVA hybrid polymer for application as a host in polymer electrolytes. Journal of Non-Crystalline Solids, 2019. 511: p. 201-211.

[25] Prajapati, G.K., R. Roshan, and P.N. Gupta, Effect of plasticizer on ionic transport and dielectric properties of PVA–H3PO4 proton conducting polymeric electrolytes. Journal of Physics and Chemistry of Solids, 2010. 71(12): p. 1717-1723.

[26] Zainuddin, N., et al., Investigation on favourable ionic conduction based on CMC-K carrageenan proton conducting hybrid solid bio-polymer electrolytes for applications in EDLC. International Journal of Hydrogen Energy, 2020.
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