

4-1-2019

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Recommended Citation

Mohd Ali, Noor Saadiah; Zhang, Dishen; Nagao, Yuki; and Samsudin, Ahmad Salihin (2019) "Molecularly Conductive Behavior of Blended Polymer Electrolyte-based CMC/PVA," *Makara Journal of Technology*. Vol. 23: Iss. 1, Article 4.

DOI: 10.7454/mst.v23i1.3639

Available at: <https://scholarhub.ui.ac.id/mjt/vol23/iss1/4>

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Molecularly Conductive Behavior of Blended Polymer Electrolyte-based CMC/PVA

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Abstract

This study investigated the electrical conduction and structural behavior of blended polymer electrolyte (BPE)-based carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA) in the development of solid-state electrochemical devices. Based on impedance spectroscopy and correlating Fourier transform infrared (FTIR) with thermogravimetric analysis, a framework was proposed to explain the structural enhancement of the BPE system. As revealed by FTIR, the optimum conductivity of CMC/PVA BPEs was $9.21 \times 10^{-6} \text{ Scm}^{-1}$ for 80:20 composition attributed to the intermolecular attraction between the polymers. Thermal stability of the CMC/PVA was influenced by the formation of a hydrogen bond between the hydroxyl (-OH), carboxylate (-COO-), and ether linkage (-COC-) functional groups. The finding provides insights into blended polymer electrolyte-based CMC/PVA, which is beneficial in designing safe, thin, and lightweight energy storage devices.

Abstract

Penilaian Kekonduksian dan CMC/PVA Filem Nipis Polimer Campuran. Karya ini menyelidiki penemuan pengaliran elektrik dan tingkah laku struktur elektrolit polimer campuran (BPEs) berasaskan carboxymethyl cellulose (CMC) dan polivinil alkohol (PVA) ke arah pembangunan peranti elektrokimia keadaan pepejal. Berdasarkan spektroskopi impedans (EIS) dan mengaitkan fourier transform inframerah (FTIR) dengan analisis thermogravimetric (TGA), kami telah menca-dangkan satu rangka kerja untuk menjelaskan peningkatan struktur sistem BPE. Kekonduksian optima CMC/PVA BPEs dicapai ialah $9.21 \times 10^{-6} \text{ Scm}^{-1}$ untuk komposisi 80:20 yang dikaitkan dengan tarikan dengan molekul antara polimer yang telah didedahkan oleh FTIR. Kestabilan haba CMC/PVA didapati dipengaruhi oleh pembentukan ikatan hidrogen antara kumpulan berfungsi hidroksil (-OH), karboksilat (-COO⁻) dan rantaian ether (-COC-). Penemuan ini memberi beberapa pandangan tentang polimer campuran yang diadaptasi berasaskan CMC/PVA yang bermanfaat dalam mereka bentuk pe-ranti simpanan yang selamat, nipis dan ringan.

Keywords: blended polymer electrolytes, carboxyl methylcellulose, ionic conductivity, structural studies

1. Introduction

Understanding the fundamentals of conductivity and structural behavior of polymers is crucial in developing a novel polymer electrolyte (PE) system. PEs have proven to be promising materials for advanced electrochemical devices. Polyethylene oxide (PEO) has always been the subject of intense research for the PE system [1]. Although this non-biodegradable synthetic polymer offers appealing advantages, it triggers severe environmental issues. Thus, considerable efforts have been devoted to

discover new eco-materials that contribute to a reduction of environmental problems.

At present, a trend in studying biodegradable natural and synthetic polymers has been established. Most studies on conducting polymers have focused on using a single polymer type as a host, which includes seaweed, agarose, chitosan, sago, and cellulose polymer; these materials have limited conductance ability because their conductivity value ranges from approximately 10^{-9} to approximately 10^{-8} S/cm [2]-[6]. The single polymer has limited

application because it has poor mechanical strength and thermal stability [7]. This condition motivates the researcher to adopt various methods such as copolymerization [8], crosslinking [9], and blending [10], which are effective to enhance the electrical and chemical properties of the PEs.

This study focuses on CMC and PVA as host polymer. CMC is one of the most attractive polymers due to its low cost, excellent hydrophilicity, and biocompatibility. However, attaining good conductivity is difficult because CMC shows intrinsic drawbacks such as low mechanical strength, thereby limiting the conductance ability. Thus, one of the approaches to improve the electrical properties is via blending the CMC with PVA, which is able to enhance the conductive mechanical properties.

In this study, we investigated the effect of blending CMC and PVA at different ratios (100/0, 90/10, 80/20, and 50/50) and compared them with the pure polymers. Here we report the optimum conductivity and occurrence of intermolecular attraction between the CMC and PVA, which increase the conductivity and thermal stability of the BPE system. To the best of our knowledge, this study is the first to reveal the simplest approach to enhance the interaction between the CMC and PVA, which affect the polymer chain flexibility and stability. To date, no systematic study has been conducted to determine the molecular conductive behavior enhancement for the blended polymer electrolyte-based CMC/PVA.

2. Methods

Materials. Carboxymethyl cellulose (CMC) with 90,000 molecular weight was commercially obtained from ACROS Organic Co. Polyvinyl alcohol (PVA) was supplied by Merck Schuchardt. The PVA used in this study was 85% hydrolyzed with molecular weight of 70,000.

Sample preparation. An appropriate amount of CMC and PVA was dissolved in 98 mL of distilled water based on the ratios 100/0, 90/10, 80/20, and 50/50 and designated as CP0, CP1, CP2, and CP3, respectively. The mixture was stirred until homogenous and the resulting solution was cast into petri dishes. The homogenous solution was oven dried at 60 °C and 300 min [11]. To ensure complete drying of the solvent, the semi-dried BPEs were placed in a desiccator.

Scanning electron microscopy (SEM). A section of thin film was analyzed via Tabletop Miniscope TM3030Plus (Hitachi High Technologies, Japan) for surface morphology and mapping. Charge-up reduction mode was used at accelerating voltage of 10 kV.

Fourier transform infrared (FTIR). The attenuated total reflectance (ATR) method was adopted using diamond crystals in a PerkinElmer FTIR spectrophotometer. A total

of 10 co-added scans covering 4,000 cm^{-1} to 700 cm^{-1} wavenumber range at spectral resolution of 2 cm^{-1} . Prior to the characterization of BPE samples, a background spectrum was obtained in the same ambient condition.

Thermogravimetric analysis (TGA). The thermal properties of the BPE system were analyzed using Mettler Toledo TGA coupled with DSC. Approximately 5 mg of BPE sample was considered and heated at an elevated temperature range of 30–800 °C under 10 °C min^{-1} nitrogen atmosphere.

Electrical impedance spectroscopy. The conductivity of BPE samples was characterized using 3532–50 LCR Hi-Tester (Hioki, Japan) at ambient room temperature. The samples were sandwiched between two stainless steel blocking electrodes and frequency ranges from 50 Hz to 1 MHz were applied. The conductivity can be calculated using Equation 1, where l is the thickness of the BPEs, A is the cross-sectional area, and R_b is the bulk resistance extracted from the Cole–Cole plot.

$$\sigma = l/R_s A \quad (1)$$

3. Results and Discussion

Molecular behavior in CMC/PVA

SEM analysis. Electron microscopy is advantageous because it allows scanning through various elemental mapping techniques [12]. Figure 1 shows the electron images of the surface morphology for various BPEs system. Figures 1(a) represent sample CP0 (pure CMC), which showed a homogenous surface. On the other

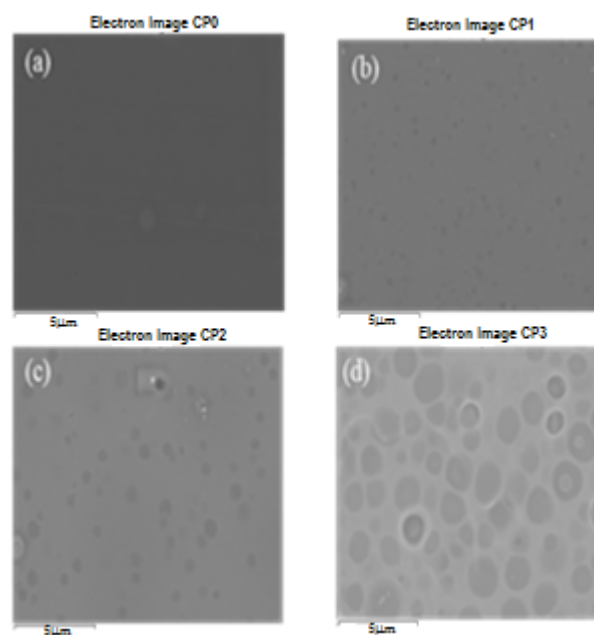


Figure 1. ATR–FTIR Spectra for Various Ratios of BPE System

hand, CP1 until CP3 showed no phase segregation, which suggests that the BPEs have an amorphous nature [13]. However, the addition of PVA seems to create some regular globs with various sizes caused by different ratios of PVA [14]. This results may be attributed to the non-adhesive property of PVA, which restricts the adhesion and spread of the CMC [15].

ATR-FTIR analysis. The complexation between CMC and PVA was investigated via ATR-FTIR and is shown in Figure 2. All BPE systems show five fingerprint peaks of CMCs located at 1060, 1329, 1423, 1592, and 3356 cm^{-1} , which correspond to bending C-O-C, bending-OH, scissoring- CH_2 , asymmetric- COO^- , and stretching-OH, respectively; this finding is similar to a previous report [16]. The incorporation of PVA causes the appearance and disappearance of some peaks, suggesting that the complexation between CMC and PVA has occurred. The most common complexation is the intermolecular hydrogen (H-) bonding due to the presence of highly electronegative elements such as N, O, or F [17]. Complexation could change the molecular chain which affect the physical properties, thereby improving the thermal and electrical properties [18]. Obvious complexation can be observed at C-O-C, COO^- , and -OH peaks, where their intensity and wavenumber have reduced or shifted. This condition is explained by the existence of an active site, which is able to interact with the CMC to PVA through intermolecular H-bonding, thereby progressively reducing the peak intensity [17]. Peaks corresponding to COC- shifted from 1060 cm^{-1} to 1098 cm^{-1} . On the other hand, peaks observed at 1592 cm^{-1} assigned to COO^- shifted from 1592 cm^{-1} (CP0)

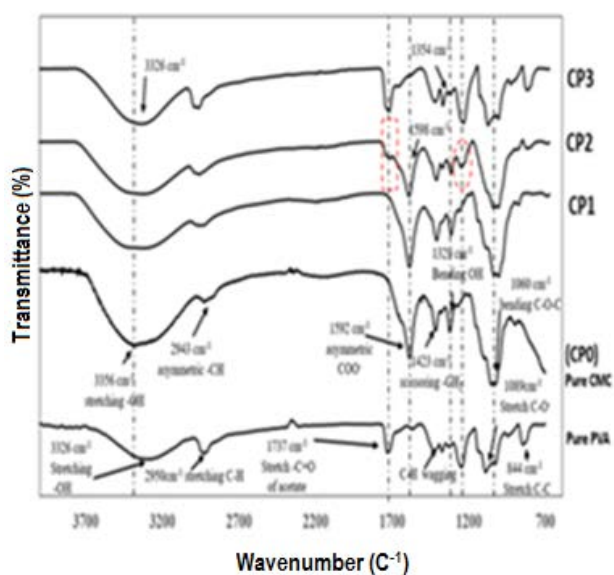


Figure 2. ATR-FTIR Spectra for Various Ratios of BPE System

to 1598 cm^{-1} (CP2). The appearance of new peaks in the CP2 sample at 1737 cm^{-1} (C=O of acetate) confirm the substitution of PVA into CMC. These new peaks are attributable to the PVA, which is partially hydrolyzed; thus, the carbonyl group was expected in that region [19]. In addition, the H-bonding caused the -OH band at 3356 cm^{-1} to narrow and shift to a lower wavenumber 3326 cm^{-1} . Apparently, all changes elucidated by ATR-FTIR confirmed the complexation during the blending of CMC and PVA.

TGA analysis. The thermal stability of CMC/PVA BPEs has been studied because it is a critical issue in potential application and the spectra is represented in Figure 3. The spectra revealed three stages of decomposition. All BPE samples were thermally stable up to 300 °C, which was relatively higher than the level of other polymer electrolytes. The first stage is always associated with water loss in the range of 25–200 °C. The weight lost involved in this area is small at less than 20% [20]. CMC is known to be hygroscopic (i.e., have high moisture sensitivity) with a polar functional group that retains moisture from the environment. However, upon blending with PVA, the stability of the resulting BPE system improves.

This condition is elucidated by the analysis of maximum decomposition temperature summarized in Figure 3. Thermal decomposition temperature increased from 311.16 °C to 318.33 °C when PVA was incorporated into the CMC. At this temperature, maximum weight loss occurred due to the decomposition of carboxylate group, which was the characteristic structure of CMC [21]. This result was in agreement with the findings of

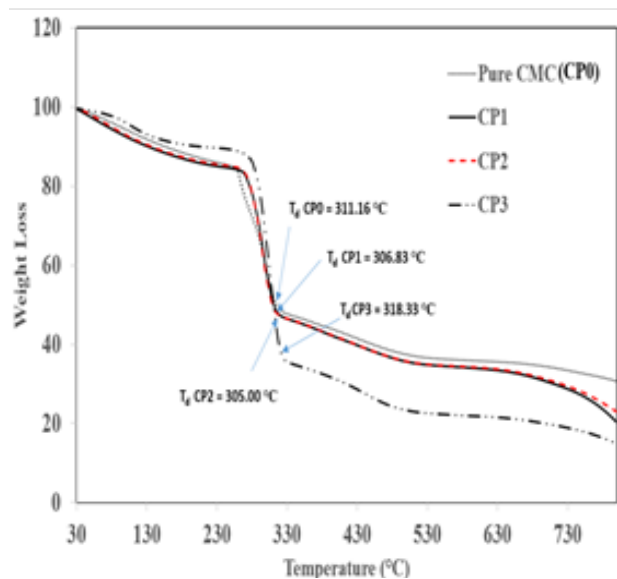


Figure 3. TGA Spectra for Various Ratios of BPE System

Mahdavinia et al. [22] that temperature of approximately 300 °C is susceptible to the decomposition of bond scission in the PVA backbone. However, CP1 and CP2 showed a slower slope, which demonstrated high thermal stability, whereas CP3 underwent rapid weight loss, making it less thermally stable. This behavior may be due to the complexation between the CMC and PVA, which was previously mentioned in FTIR analysis. Notably, the third decomposition occurred in the plateau region from 330 °C to 800 °C due to ash formation [23].

Impedance analysis. Variations in the conductivity of different ratios of CMC/PVA BPEs are shown in Figure 4. The conductivity was optimized at CP2 with value of $9.12 \times 10^{-6} \text{ Scm}^{-1}$ compared with single-polymer CMC with value of $\sim 10^{-7} \text{ Scm}^{-1}$. This increment can be influenced by intermolecular attraction forces between the CMC and PVA. Rudzhiah [24] claims that introducing CMC into carrageenan can enhance the conductivity due to molecular interaction. According to Sundaramahalingam [25], blending the polyethylene oxide (PEO) and polyvinyl pyrrolidone (PVP) with ratio of 30/70 increases the conductivity to $1.01 \times 10^{-9} \text{ Scm}^{-1}$. Satyendara [26] achieved conductivity of $8.79 \times 10^{-7} \text{ Scm}^{-1}$ upon blending the PVA and PVP. Collectively, these studies provide important insights into the blending method that governs the molecular conductance behavior. The molecular interaction was observed thoroughly via SEM, FTIR, and TGA, which were the main factors to promote faster internal modes where bond rotation facilitated segmental motion of the polymer chain. Consequently, chain flexibility and mobility improved and caused the conductivity to increase by one order of magnitude.

However, upon further addition of PVA (CP3), the conductivity dropped due to a large amount of PVA, which hindered the intermolecular attraction with CMC [27], thereby decreasing the conductivity.

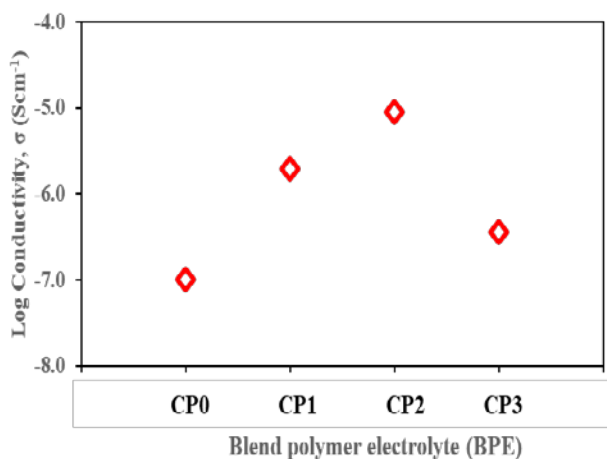


Figure 4. Conductivity for Various Ratios of BPE System

4. Conclusions

The study aimed to investigate the effect given by different ratios of CMC and PVA to enhance the molecular conductivity. The SEM showed that PVA has non-adhesive behavior, which is responsible for the formation of globules. Despite the appearance of the globules, the EDX image revealed that all BPE systems are homogenous and have no phase segregation. The observed complexation revealed by FTIR is explained by the appearance, shift in wavenumber, and reduced peak intensity, which has focused on the $-\text{COC}-$, $-\text{COO}-$, and $-\text{OH}$ group found at wavenumbers 1060, 1592, and 3356 cm^{-1} , respectively. This highly polar region is susceptible to H-bonding, which eventually affects the thermal stability of the blend polymer electrolyte-based CMC/PVA. All BPE systems are thermally at temperature beyond 300 °C due to strong intermolecular attraction. During this interaction, the flexibility and mobility of the polymer chain improved, thereby resulting in higher conductivity. The optimum ratio of CMC/PVA is 80/20, where the conductivity increased by one order of magnitude from approximately 10^{-7} Scm^{-1} to approximately 10^{-6} Scm^{-1} . This finding can be regarded as a preliminary study to design more advanced conducting polymer electrolytes involving the addition of dopant or plasticizer.

Acknowledgments

This work was financially supported by the Ministry of Higher Education for Fundamental Research Grant Scheme (RDU 170115), Faculty of Industrial Science and Technology, Universiti Malaysia Pahang, and the Japan Advanced Institute of Science and Technology.

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