Effect of polar aprotic solvents on hydroxyethyl cellulose-based gel polymer electrolyte

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Received: 5 November 2017 / Revised: 3 January 2018 / Accepted: 15 January 2018
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Abstract
Quasi-solid bioelectrolytes based on hydroxyethyl cellulose (HEC) and sodium iodide (NaI) in three different polar aprotic solvent systems, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and dimethylacetamide (DMA), were fabricated and characterized. FTIR studies revealed active solvent-ion interactions in DMF-based electrolytes in comparison to DMA and DMSO. The effect of the solvent system on the crystallinity of HEC gel electrolytes was more significant at low NaI concentration. In each solvent system, the highest ionic conductivity was achieved at 70 wt% NaI and generally DMF-based electrolytes showed higher conductivity than the other solvents. The availability of multiple complexation sites present in DMF is ascribed to improvement in ion mobility and hence conductivity. Rheological analysis was carried out to elucidate the mechanical properties of the gels. Generally, the mechanical strength of the polymer gels was unaffected by the type of solvent.

Keywords Hydroxyethyl cellulose · Solvents · Dimethylformamide · Dimethylacetamide · Dimethyl sulfoxide

Introduction

Ever since its introduction in 1970s, polymer electrolyte has been an active field of research. The implementation of solid polymer electrolytes has provided the solutions to pragmatic problems encountered in traditional liquid electrolyte such as leakage and solvent volatility [1]. However, this is often achieved at the expense of ionic conductivity which in turn affects the electrolyte performance in electrochemical devices [2]. This contradiction gave rise to the inception of gel polymer electrolyte (GPE), a unique category of electrolyte which inherits both the conductive properties of liquid and mechanical properties of solid.

Typically, the preparation of GPE involves the dissolution of inorganic salt and polymer in a non-volatile solvent system.

The primary function of the polymer is to serve as the matrix of the gel in order to bestow mechanical stability. Addition of inorganic salts introduces charge carriers into the matrix which elevates the ionic conductivity of the electrolyte. Most often, the major composition of the electrolyte is made of the solvent component which is regarded as packets of liquid trapped within the polymer chains. The solvent in fact is a crucial part of the system as it affords the space for charge carrier migration, diminishes crystallinity of the gel, decreases polymer-polymer interaction, and increases the free volume and segmental mobility of the system [3]. Therefore, the choice of solvent employed in a GPE is very salient as it impacts the overall physical, chemical, and electrical properties of the material. In recent literature, much emphasis has been given to explore the effect of polymers and salts on the properties of the electrolyte [1, 4–6]. However, studies dedicated to comprehend the effect of solvents on the electrolyte properties have been scarce. Therefore, in this study, we explored the effects of three different polar aprotic solvents on fabrication of GPE based on hydroxyethyl cellulose (HEC).

In accordance to the current pursuit for sustainable materials, polymer electrolytes fabricated from natural polymers, in particular, cellulose derivatives, have obtained special focus recently. Cellulose derivatives are often incorporated into a synthetic polymer system with the purpose of improving the...
is governed by non-covalent interactions such as van der Waals, charge transfer, and hydrogen bonding. Beyond the critical strain value, these interactions are disrupted leading to a collapse in the gel structure [41].

Besides the critical strain values, the physical properties of the gel microstructure can be explained in terms of the loss factor, $\tan \delta$, which is equal to the ratio of $G''$ to $G'$, i.e., the imaginary part to the real part of the deformation energy. When $\tan \delta < 1$, $G'$ dominates over $G''$, and the gel exhibits a quasi-elastic behavior in which the gel experiences full or partial microstructural regeneration upon deformation. When $\tan \delta = 1$, the flow point (“cross-over”) is attained. Beyond the flow point, $G''$ exceeds $G'$ ($\tan \delta > 1$) and the viscous property of the gel prevails leading to an irreversible microstructural collapse [42]. In all three samples studied, $\tan \delta > 1$ when the strain applied was close to 250%. Therefore, it can be concluded that HEC-based gels have similar mechanical strength regardless of the solvent system. This can be also due to the fact that the polymer to solvent weight ratio was similar in all three samples.

**Conclusions**

FTIR studies confirmed the enhanced interaction between ions and solvents in DMF-based electrolytes compared to DMA- and DMSO-based electrolytes. The crystallinity of HEC gel electrolytes was found to be influenced by the solvent system. At low salt concentration, DMSO-based electrolytes exhibited lower crystallinity compared to DMF and DMA. But, at higher salt concentration, this effect was renounced. The highest ionic conductivity was recorded upon 70 wt% of NaI in each solvent system, with overall maximum value of $2.16 \times 10^{-2}$ S cm$^{-1}$ in DMF. The pronounced ionic conductivity in DMF-based system can be attributed to the presence of additional ion complexion sites in this solvent compared to DMA and DMSO. From rheological analysis, it was found that the highest conducting HEC electrolytes in each solvent system showed prominent solid character and the mechanical stabilities of these gels were not affected by the solvent systems.

**Funding information** This work is supported by the University of Malaya through FG031-17AFR grant. V. Selvanathan is grateful to the Ministry of Higher Education (MOHE), Malaysia, for the MyBrainSc scholarship.
Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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