Effect of $NaClO_4$ Dopant on Chemical Bond and Ionic Conductivity of Benzoyl Kappa-carrageenan Gel Biopolymer Electrolyte

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Abstract: Gel biopolymer electrolytes based on benzoyl kappa-carrageenan (Bz-κcar) as polymer host and sodium perchlorate ($NaClO_4$) as dopant was successfully produced. The concentration of $NaClO_4$ was varied from 0.5 to 3.0 wt.% in order to investigate its effects on the chemical bonds and the ionic conductivities (σ) of the electrolytes. Characterizations were performed by Fourier-transform infrared spectroscopy (FTIR) and electrochemical impedance analysis (EIS). Significant changes in the FTIR spectra were detected indicated chemical interactions between Bz-ƙcar and $NaClO_4$. The ionic conductivity of the gel electrolytes increased with higher concentration of $NaClO_4$, suggesting that $NaClO_4$ was an effective charge carrier in the system. The highest σ of the gel electrolyte attained at ambient temperature (298 K) was 1.29×10^{-3} S cm^{-1}. The temperature dependence of conductivity is Arrhenian in the studied temperature range and achieved elevated σ of 7.90×10^{-3} S cm^{-1} at 100 °C with small values in the activation energy (E_a) were observed in all the electrolytes prepared.

Keywords: kappa-carrageenan, gel electrolyte, conductivity, chemical interaction, sodium perchlorate, biopolymer.

1.0 Introduction

Derived from red seaweed, kappa-carrageenan (κcar) is an anionic sulfated linear polysaccharide with a linear backbone built of an alternating (1 → 3)-linked β-D-galactopyranose and (1 → 4)-linked α-D-galactopyranose [1]. κcar is a great choice as polymer host in an electrolyte system due to its particular interest such as biodegradable, renewable, abundant, cost-effective, non-hazardous and availability of its active sites (OH- and $-OSO_3^-$ groups) to accommodate coordination interaction with guest cations [2]. Published reports on the application of ƙcar as biopolymer electrolytes were actively progressing over the recent years. The κcar-based electrolytes were reported to have high ionic conductivity, excellent thermal stability, high ions mobility and good electrochemical stability [3,4].

Nevertheless, the ionic conductivity (σ) of pure κcar in solid or thin films are considerably low, around 10^{-7} S cm^{-1} [5]. The introduction of charge carrier or conducting salt into the ƙcar matrix are essential in order to increase the σ to sufficient practicality. Recent studies on the thin film of ƙcar/dopant systems were published [6-8]. Generally, salt aids to enhance the σ of an electrolyte system due to its ions mobility in the polymer matrices. The mobility of the ions is highly dependent on the structural phase of the polymer host. Amorphous phases are preferable compared to crystalline phases due to the less ordered structure that enables better movement of ions in the polymeric chain. In that case, gel polymer electrolytes offer a preferable alternative to solid polymer electrolytes due to the less rigidity and diminished crystallinity in the polymeric chains that enables higher ions mobility in the system [9,10]. Earlier studies on carrageenan-based gel polymer electrolytes were published and presented promising application in metal-air electrochemical cell [11,12].

Sodium-based electrolytes are becoming more popular as they have a lower cost and a greater natural abundance than lithium-based electrolytes. Additionally, it was demonstrated that they have excellent ionic conductivity, broad electrochemical stability windows, and high decomposition temperatures [13,14]. Sodium perchlorate ($NaClO_4$) is a great choice of dopant with these excellent qualities. Recently, the incorporation of $NaClO_4$ as a dopant in sodium-based gel polymer electrolytes for ultrastable microsupercapacitors were reported to successfully improved ionic conductivity [15]. The microsupercapacitors based on sodium are thought to hold a proactive approach as a solid-state energy source for high-performance energy solutions. The ionic conduction properties of $NaClO_4$ salt in a new crystalline phase of carboxymethyl cellulose were studied [16]. The study concluded that higher $NaClO_4$ concentration in the biopolymer electrolyte films has not depreciated the ionic conductivity due to the presence of free ions that are available for conduction. Other research work published on the construction of high voltage supercapacitors based on hybrid $NaClO_4$-water/acetonitrile electrolyte [17]. Wide electrochemical stability window of ~3.16 V was achieved as a result of coordination between Na^+ cations and water molecules. The hybrid electrolyte was also reported to exhibit low viscosity, high conductivity, moisture-tolerant and flame-retardant properties.

Our recent work reported on the chemical modification of ƙcar, produced benzoyl kappa-carrageenan [18]. Benzoyl kappa-carrageenan (Bz-κcar) is a derivative of κcar that was synthesized by Friedel-Craft acylation method. The substitution of benzoyl molecules into the polymer matrix had resulted in reduced hydrophilicity and enhanced ionic conductivity. The chemical structure of Bz- κcar is shown in **Figure 1**. Hence, based on the high potential of $NaClO_4$ in electrolytes as reported in the previous studies, the investigation on the inclusion of $NaClO_4$ as dopant in Bz- κcar gel system is of our interest. In this study, the effects of $NaClO_4$ concentrations in Bz- κcar in terms of the chemical bond and ionic conductivity will be of our main focus.

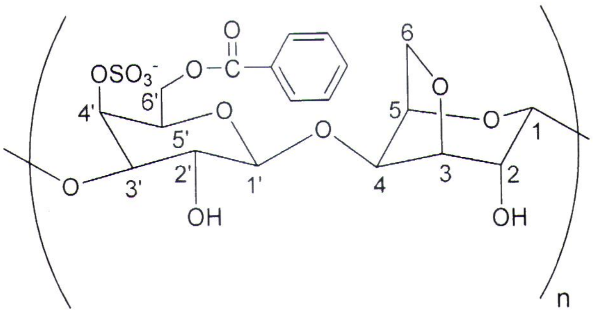


Figure 1 Chemical structure of Bz- κcar.

2. Materials and methods

2.1 Materials

kappa-carrageenan (κcar) powder (molecular weight: 788.7 g/mol) was purchased from Sigma Aldrich, Malaysia. Ethylene glycol (purity: ≥99.5%) was purchased from Merck, Malaysia. All chemicals were of analytical grade and used without further purification.

2.2 Preparation of Bz- κcar gels electrolyte

ƙcar was used as a precursor to prepare Bz-κcar powder according to a published method [18]. Bz- κcar gel was prepared by dissolving 1.0 g of sample powder in ethylene glycol at the concentration of 3.3% w/v at ambient temperature. The thick gel was stirred overnight in order to obtain complete dissolution. Different concentrations in weight percentages (wt. %) of sodium perchlorate ($NaClO_4$) was added into the gel. The mixture was stirred for 24 hr for complete dissolution. The gel was kept in an airtight container to prevent any moisture contact. The variation of $NaClO_4$ wt.% in Bz- κcar systems and the designations are tabulated in **Table 1**.

Table 1 Bz-ƙcar/ $NaClO_4$ systems and the designations.

Biopolymer	$NaClO_4$ wt. %	Sample designation
Bz- κcar	0	BN0
	5	BN1
	10	BN2
	15	BN3
	20	BN4
	25	BN5
	30	BN6

3. Characterization

3.1 Fourier Transform Infra-Red Analysis (FTIR)

The analysis was performed by using Perkin- Elmer Spectrum 2000, USA in the range of 4000-650 cm^{-1} with scanning resolution 4 cm^{-1}. The analyses were carried out to investigate any peak shifts and changes on the spectra.

3.2 Impedance spectroscopy

Impedance spectra was measured using a high-frequency response analyser (HFRA: Solartron 1296) with frequency ranging from 100 Hz to 1MHz with 10 mV amplitude. A dip-cell probe for gel sample was used to measure the conductivity of ƙcar and Bz-κcar gel samples. The cell constant was determined with a solution of 0.01 M KCl at ambient temperature (298 K). The effect of temperature on the conductivity was measured within temperature range 298 to 373 K

The ion transport mechanism can be expressed after Eq. (1):

$$\sigma = \sigma_o \exp\left(-E_a/kT\right) \tag{1}$$

where σ_o is a pre-exponential factor, E_a is the activation energy, k is the Boltzmann constant and T is the absolute temperature.

4. Results and Discussion

The FTIR spectra of Bz-κcar gel electrolytes systems (BN0 – BN6) is shown in **Figure 2**. The main characteristic peak of Bz-κcar gel (BN0) is observed at 1658 cm^{-1} attributed to the carbonyl C=O stretching. A pair of C=C stretching signals in the aromatic ring at 1410 and 1456 cm^{-1} is also detected [18]. Peak at 880 cm^{-1} is attributed to C-O-C vibration of the 3,6-anhydro-D-galactose residue, while the intense peak at 1034 cm^{-1} represents the C-O stretching mode. Signals at 1204 cm^{-1} and 864 cm^{-1} were assigned to O=S=O symmetric vibration and to $-O-SO_3$ stretching vibration at the C-4 position of galactose [19].

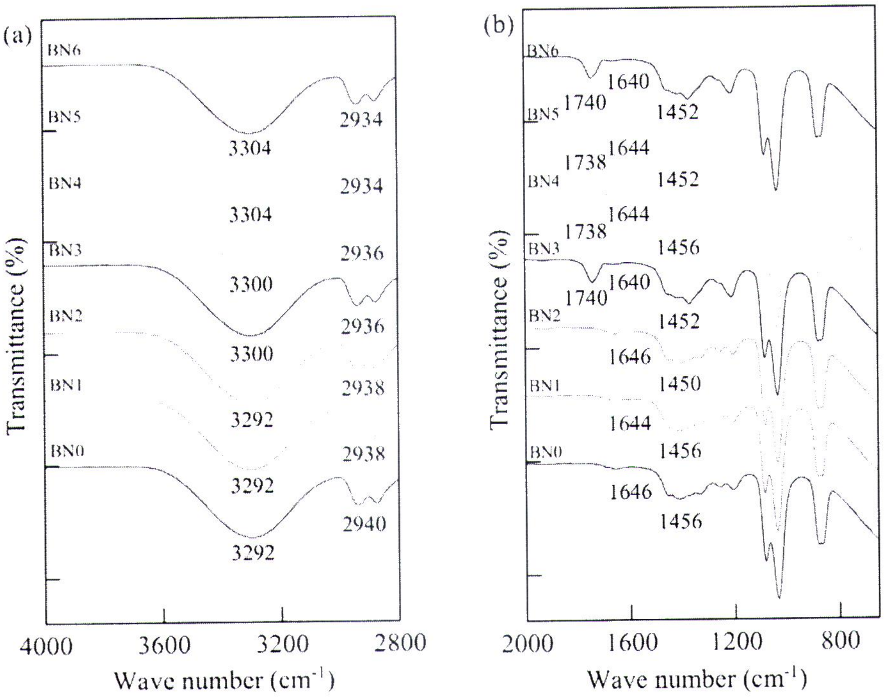


Figure 2 FTIR spectra of BN0 – BN6 at (a) 2800 to 4000 cm^{-1} and (b) 650 to 2000 cm^{-1}.

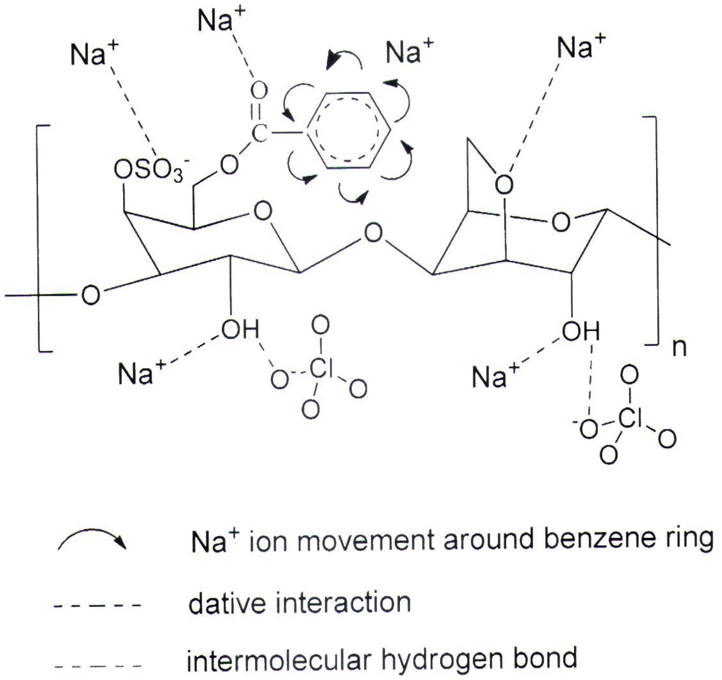
Bz-κcar/ $NaClO_4$ gel electrolytes systems were developed in BN1-BN6 samples. The effects of $NaClO_4$ salt inclusion on the chemical bond in Bz-κcar gel polymeric chain is observed based on the signal shifts in the wavenumber and changes in the intensity of the peaks. Based on **Figure**

2, broad hydroxyl (-OH bond) stretching vibration bands at around 3200 – 3600 cm^{-1} in the BN0 - BN6 systems were detected. The broad bands were caused by the presence of diol group in the polymer solvent, ethylene glycol ($HOCH_2CH_2OH$) [20]. Meanwhile, the –OH stretching vibration in BN0 – BN2 showed no shift in the peak signals indicating that low addition of $NaClO_4$ salt has no significant impact on the chemical bonds in the polymeric gel. On the other hand, significant shifts in the wavenumbers were observed in the higher inclusion of $NaClO_4$ as observed in the BN3 - BN6 systems. The -OH band signals have shifted to higher wavenumbers up to 12 cm^{-1} compared to the free-salt polymer system, BN0. As the OH bond is highly polar, the possible dative interaction occurred is proposed between the electronegative oxygen atom and the sodium ion, (Na^+) that is dissociated from the dopant in the gel matrix. Additionally, potential interaction might had occurred between the perchlorate ion, ClO_4^- and the hydrogen in the –OH bond thus created intermolecular hydrogen bond [12]. This explained the high shifts in the wavenumbers and implied that $NaClO_4$ was well dissociated in the biopolymer network.

Other spectra changes were observed in the signals of benzoyl molecule ($-C(O)-C_6H_5$) in Bz-κcar. Clear formation of carbonyl, C=O bonds were observed in the BN3 – BN6 spectra indicating that higher inclusion of $NaClO_4$ created more chemical interaction between the free ions and the C=O bond. This is supported by the obvious wavenumber shifts in the C=O bands appeared in the BN1 – BN6 signals (1664 – 1740 cm^{-1}) compared to the pristine gel (BN0) system at 1658 cm^{-1}. Detectably, the C=C aromatic ring stretching in BN0 at both 1456 and 1646 cm^{-1} signals were shifted to lower wavenumbers upon the addition of $NaClO_4$. Clear changes were seen in the BN6 signals as the peaks have shifted to 1452 and 1640 cm^{-1} suggesting that there were also dative interactions occurred in the region. Other significant shifts observed are in the O=S=O signals in BN2 - BN6 systems as the band wavenumbers have shifted to higher wavenumbers compared to BN0. Little changes were noticed in the C-O band signals as there were only 2 cm^{-1} shifts were detected in all the Bz-κcar/ $NaClO_4$ gel systems (BN1 – BN6) in comparison with the BN0 signal indicating that there was no chemical interaction occurred within the C-O bond. Similarly, no significant changes were observed in the C-O-C and $-O-SO_3$ bands signifying that there was no chemical interaction occurred between Bz-κcar gel matrix and Na^+ ion within the bonds. **Table 2** shows the summarized assignments of the characteristic bands in BN0 - BN6 while **Scheme 1** displayed the proposed interactions of Bz-κcar with Na^+ and ClO_4^- ions.

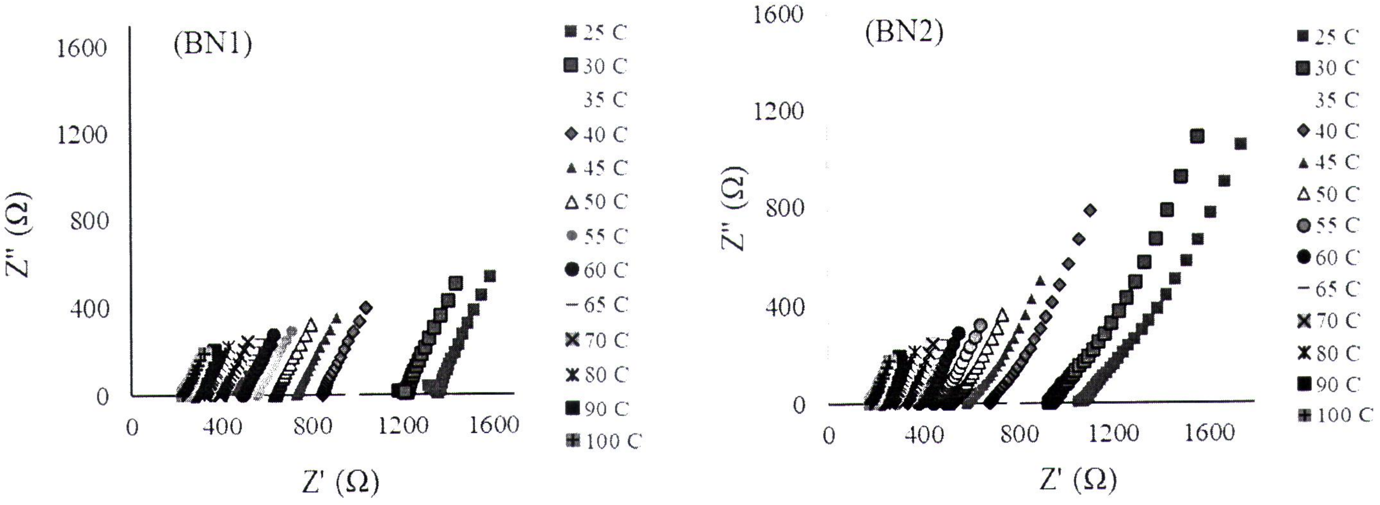
Table 2 Assignments of the characteristic bands in BN0 - BN6.

Assignments of bands	Wavelength (cm^{-1})						
	BN0	BN1	BN2	BN3	BN4	BN5	BN6
O-H	3292	3292	3292	3300	3300	3304	3304
CH_2 asymmetric stretching	2940	2938	2938	2936	2936	2934	2934
C=O	1658	1668	1664	1740	1738	1738	1740
C=C	1456, 1646	1456, 1644	1450, 1646	1452, 1640	1456, 1644	1452, 1644	1452, 1640
O=S=O	1204	1204	1206	1208	1208	1208	1210
C-O	1034	1036	1036	1036	1036	1036	1036
C-O-C	880	880	880	880	878	880	878
$-O-SO_3$	864	866	864	866	864	864	864



Scheme 1 The proposed interactions of Bz-κcar with Na^+ and ClO_4^- ions

In order to investigate whether $NaClO_4$ capable to function as a charge carrier and enhance the ionic conductivity of Bz-κcar, electrochemical impedance spectroscopy (EIS) analysis was performed on the biopolymer gels. The impedance plots of the gel electrolytes, BN1 – BN6 at various temperatures are shown in **Figure 3** (BN1 – BN6). The bulk resistance (R_b) was determined from the interception of the tilted spike at the real impedance axis (Z′). Noticeably, smaller R_b values were observed with increasing temperatures in all the gel electrolytes indicating a higher value of conductivity [21].



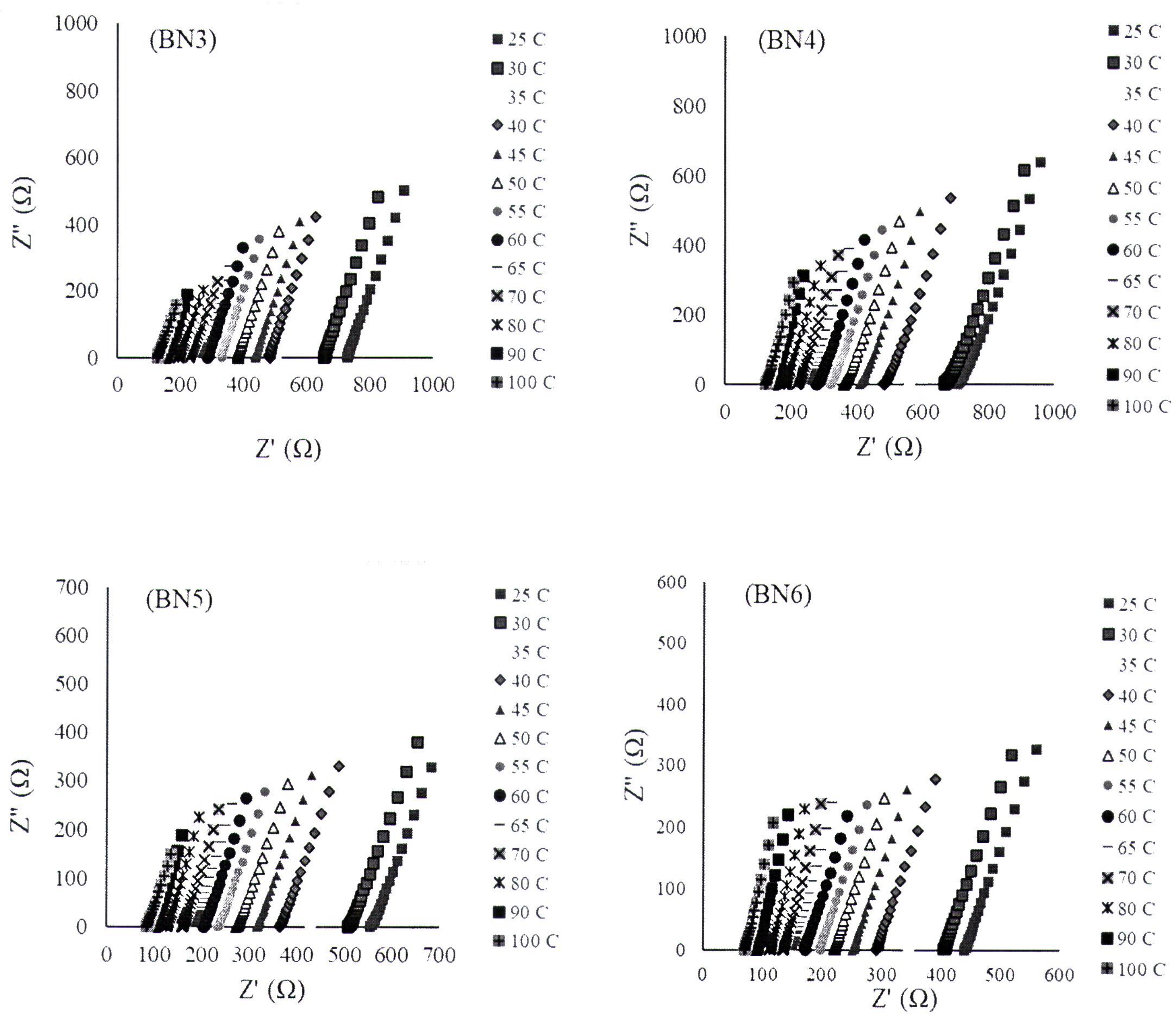


Figure 3 Nyquist plot of BN1- BN6 gel electrolytes at various temperatures.

Table 3 portrayed the summarized conductivity values of the gel electrolytes. The ionic conductivity in pure Bz-κcar gel published in our previous report was 3.10 × 10^{-4} S cm^{-1} at ambient temperature [18]. At similar temperature, the conductivity of Bz-κcar was found to increase to 4.16 × 10^{-4} S cm^{-1} at the lowest inclusion of $NaClO_4$ salt (BN1). The highest ionic conductivity, 7.90 × 10^{-3} S cm^{-1} was achieved in the BN6 system at 373 K. The high ionic conductivity was found to be better than in previous studies on carrageenan-based gel electrolytes [22]. Nonetheless, it was also discovered to be slightly lower than some of the earlier work [23-25]. This could be due to the low $NaClO_4$ loading in the Bz-car gel. Higher

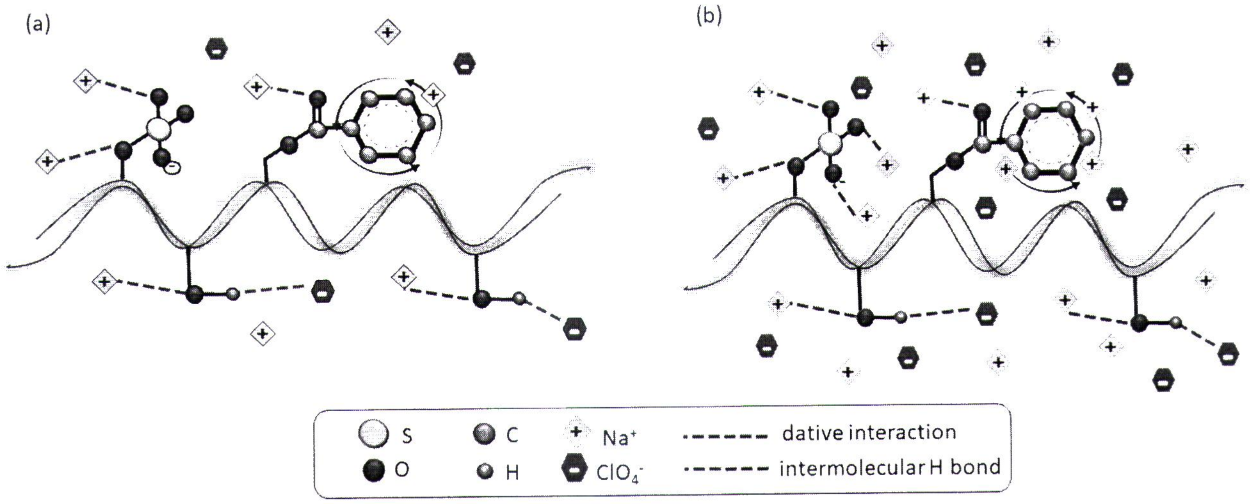
$NaClO_4$ concentrations than 30 wt. % are anticipated to further increase ionic conductivity as an increasing trend is observed upon the salt inclusion and the saturation point has not yet been reached.

Table 3 Summarized σ of BN1 – BN6 gel electrolytes at various temperatures.

Temperature (°C)	Conductivity (σ)					
	BN1	BN2	BN3	BN4	BN5	BN6
25	4.16×10^{-4}	4.85×10^{-4}	7.78×10^{-4}	7.75×10^{-4}	1.01×10^{-3}	1.29×10^{-3}
30	4.66×10^{-4}	5.27×10^{-4}	8.66×10^{-4}	8.25×10^{-4}	1.10×10^{-3}	1.40×10^{-3}
35	5.99×10^{-4}	6.58×10^{-4}	1.12×10^{-3}	9.81×10^{-4}	1.31×10^{-3}	1.65×10^{-3}
40	6.71×10^{-4}	7.60×10^{-4}	1.18×10^{-3}	1.14×10^{-3}	1.54×10^{-3}	1.95×10^{-3}
45	7.82×10^{-4}	9.05×10^{-4}	1.30×10^{-3}	1.35×10^{-3}	1.78×10^{-3}	2.25×10^{-3}
50	9.00×10^{-4}	1.03×10^{-3}	1.49×10^{-3}	1.52×10^{-3}	2.05×10^{-3}	2.58×10^{-3}
55	1.03×10^{-3}	1.18×10^{-3}	1.71×10^{-3}	1.73×10^{-3}	2.39×10^{-3}	2.89×10^{-3}
60	1.17×10^{-3}	1.39×10^{-3}	1.97×10^{-3}	1.97×10^{-3}	2.72×10^{-3}	3.31×10^{-3}
65	1.31×10^{-3}	1.58×10^{-3}	2.22×10^{-3}	2.25×10^{-3}	3.09×10^{-3}	3.75×10^{-3}
70	1.46×10^{-3}	1.73×10^{-3}	2.47×10^{-3}	2.50×10^{-3}	3.50×10^{-3}	4.18×10^{-3}
80	1.78×10^{-3}	2.10×10^{-3}	2.90×10^{-3}	3.04×10^{-3}	4.40×10^{-3}	4.98×10^{-3}
90	2.13×10^{-3}	2.57×10^{-3}	3.70×10^{-3}	3.84×10^{-3}	5.55×10^{-3}	6.22×10^{-3}
100	2.28×10^{-3}	3.06×10^{-3}	4.40×10^{-3}	4.45×10^{-3}	6.56×10^{-3}	7.90×10^{-3}

Noticeably, in this work, the inclusion of $NaClO_4$ has increased the conductivity of the pure Bz-κcar gel. The ionic conductivity trend was found to increase from BN1 to BN6 at each temperature, suggesting that the addition of $NaClO_4$ has effectively increased the ionic conductivity of Bz-κcar gel. The improved conductivity with higher amount of $NaClO_4$ is related to the increase number of mobile charge carriers (Na^+ and ClO_4^-) in the systems that created more dative interactions and intermolecular hydrogen bonds with polar groups in Bz-κcar as discussed in the FTIR spectra. The proportional trend in ionic conductivity with temperature indicates that elevated temperatures favor greater Na^+ and ClO_4^- mobility in Bz-κcar segments.

The chemical structure of Bz-κcar that has additional benzoyl molecule in its polymer chain is most likely contributed to the positive trend. Benzene molecule is a nucleophile because of its delocalized electrons [26]. Thus, the molecule has electron rich areas which allow it to donate them to electrophiles. In this case, the electrons were donated to the electrophile in the system, Na^+. It is proposed that, as the electrons were delocalized, the electrons tend to move around the six carbons in the benzene molecule. As the electrons were moving, it is suggested that the Na^+ ions in the electrolyte system is attracted to move or mobile as well, due to the dative interaction attraction with the electrons. Thus, this has enhanced the mobility of the Na^+ ions in the biopolymer gel system. In addition, the polar carbonyl group (C=O) in the benzoyl molecule also contributed to the electron rich sites. Hence, this has created more available dative interactions between the Na^+ ion and Bz-κcar chain. **Scheme 2** presented the illustration of the chemical interactions between the ions and the polar groups in Bz-κcar matrix at low and high concentration of $NaClO_4$. Noticeably, high $NaClO_4$ concentration generated more chemical interactions thus made the biopolymer to be more conductive.



Scheme 2. Illustration of chemical interactions in Bz-κcar at (a) low concentration and (b) high concentration of $NaClO_4$ dopant.

Hence, to summarize, concentration of $NaClO_4$ and temperature has proportionally increased ionic conductivity in the system. The mobility of both cation (Na^+) and anion (ClO_4^-) in the biopolymer gel matrix was caused by the dative interaction and intermolecular hydrogen bond attractions towards Bz-κcar chain. The attractions had increased the mobility of the ions and thus generated motion of the polymer chain segments, resulted in enhanced ionic conductivity [27].

Figure 4 depicts the temperature dependence of conductivity for BN1 to BN6 gel electrolytes. The log conductivity graph of the gel electrolytes systems was plotted as a function of reciprocal temperature. The close to unity regression values ($R^2 \approx 1$) revealed that the biopolymer electrolytes exhibit Arrhenius behavior within the studied temperature range. This implied that the hopping of ionic species (Na^+ and ClO_4^- ions) during the segmental motion of the polymer has helped with ionic transport while the conduction mechanism is thermally assisted. [28]. The slope of the Arrhenius plot can be used to calculate the activation energy, E_a. E_a is the most important factor in determining ionic mobility. The lower the E_a value, the greater the ion mobility because the energy barrier required for a reaction to occur is reduced [29]. High ion mobility will then favor the ionic transport and thus increase the ionic conductivity. The calculated E_a values are shown in **Table 4**.

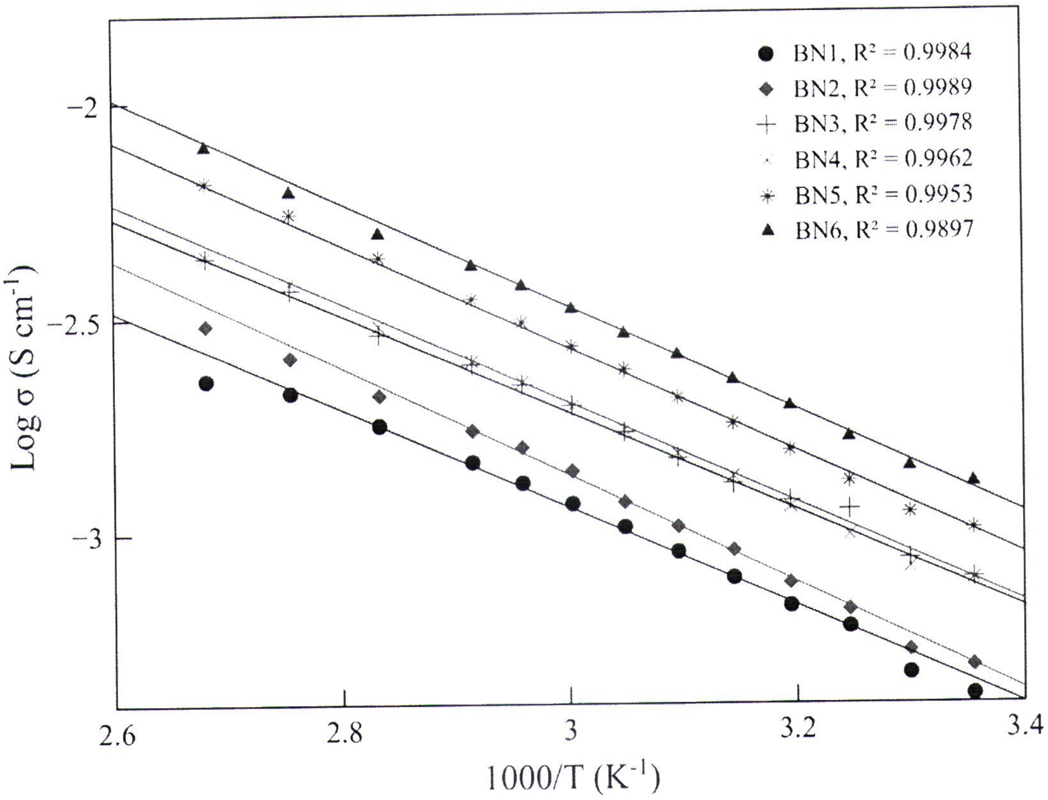


Figure 4 The temperature dependence of conductivity for BN1 to BN6 gel electrolytes.

Table 4 Activation energy (E_a) for gel electrolytes BN1 to BN6

Sample	Activation energy, E_a (eV)
BN1	0.2266
BN2	0.2422
BN3	0.2214
BN4	0.2326
BN5	0.2473
BN6	0.2326

Apparently, the E_a values in BN1 to BN6 systems were small values (range 0.22 – 0.24 eV) suggesting the high mobility of Na^+ ions in the Bz-κcar/$NaClO_4$ gel electrolyte systems due to the decrease in the energy barrier for the ion transport. This explained the high ionic conductivity values attained. The high mobility is most possibly due to the gel form of the polymer matrix that enables easy movements of the ions in the system. Moreover, the highly amorphous phase of Bz-κcar backbone as previously reported [18] might had further contributed to the situation. However, fluctuating trend was observed in the E_a values with BN3 system recorded the lowest E_a, 0.2214 eV. Nonetheless, the relatively similar E_a values in all the systems indicates that concentration of $NaClO_4$ salt did not significantly influence the E_a and mobility of Na^+ and ClO_4^- ions.

5. Conclusion

Highly conductive gel polymer electrolytes based on Bz-κcar and $NaClO_4$ were developed. The changes in the chemical bonds displayed in the FTIR spectra indicated that there were chemical attractions occurred between Bz-κcar and $NaClO_4$ dopant, identified as dative interaction and intermolecular hydrogen bond. The continuous attractions had favored the Na^+ and ClO_4^- ions mobility in the gel electrolyte system, thus generated motion of the Bz-κcar chain segments and increase ionic conductivity. The increasing ionic conductivity values upon higher inclusion of $NaClO_4$ dopant indicated that $NaClO_4$ had effectually act as charge carrier in the system. Utmost ionic conductivity achieved was in the BN6 system, 7.90×10^{-3} S cm^{-1} at 373 K. Nonetheless, the concentration of $NaClO_4$ was found to not significantly influence the E_a and mobility of the charge carriers. Small E_a values was found in all the electrolyte systems (BN1 - BN6). The temperature dependence of conductivity follows Arrhenius behavior within the measured temperature range. These results suggest that the Bz-κcar/$NaClO_4$ gel electrolyte shows potential to be applied in electrochemical devices.

Acknowledgments

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