Green Polymer Electrolyte Host Based on Newly Synthesized Benzoyl ƙ-Carrageenan: Less Hydrophilic and Improved Conductivity

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Abstract: Newly synthesized benzoyl kappa carrageenan (Bz-ƙcar) has been successfully produced by Friedel Craft acylation method. The successful substitution of benzoyl molecule into kappa carrageenan (ƙcar) polymeric chain was confirmed by FTIR analysis based on the formation of new carbonyl (C=O) and C=C bonds in Bz-ƙcar. ^{1}H-NMR analysis has further proven the benzoylation by the appearance of new multiple resonances peaks at δ =6.6-9.50 ppm belongs to the characteristic signals of protons in aromatic benzoate group. XRD analysis showed reduced crystallinity of the synthesized carrageenan while elemental analyser analysis revealed the increase percentages of carbon in Bz-ƙcar upon the substitution. Highest degree of substitution obtained is 0.27. TGA showed lower degradation temperature in the synthesized carrageenan while water contact angle analysis demonstrated that Bz-ƙcar is less hydrophilic compared to the pristine ƙcar. Solubility tests showed that Bz-ƙcar is best dissolved in ethylene glycol. The benzoylation has also improved ionic conductivity of Bz-ƙcar to 3.10 x 10^{-4} Scm^{-1} at ambient temperature.

Keywords: carrageenan, electrolyte, benzoyl, hydrophilic, conductivity, acylation.

1.0 Introduction

Kappa-carrageenan (ƙcar) is an anionic sulfated linear polysaccharide extracted from red seaweed with a linear backbone built of an alternating (1 → 3)-linked β-D-galactopyranose and (1 → 4)-linked α-D-galactopyranose [1]. Eucheuma cottonii is known as the important species that yields ƙcar [2]. Major applications of ƙcar include its uses as an additive in the foods industry [3], cosmetic and personal care products [4], and pharmaceutical industry [5]. Special characteristics of ƙcar involve biocompatibility, biodegradability, high capacity of water retention and mechanical strength of its gel. Over the past decade, the usage of ƙcar in electrochemistry field has been actively developed and progressing [6, 7]. Recent utilizations of ƙcar as propitious electrolytes in electrochemical devices were also reported [8].

However, similar to other polysaccharide, the main concern is the high polarity and hydrophilicity of ƙcar due to the large numbers of hydroxyl group (OH) in its chemical structure [9]. In this case, ƙcar has strong interactions with water molecules, as the hydroxyl groups are capable to form hydrogen bonds with polar water molecules. Unfortunately, the presence of water/moisture in most of electrochemical devices such as battery and dye-sensitized solar cell is not favorable. The interaction of moisture with air/moisture sensitive metal/parts in the devices might have caused explosion and risking the surrounding. Additionally, the exposure to moisture will lead to corrosion issue in the devices, thus deteriorates and affecting the devices' performance. Chemical modifications on ƙcar to alter the hydrophilic properties of ƙcar were previously reported. Recently, in food industry application, hydrophobic modification of ƙcar microgel particles was performed for the stabilisation of foams [10]. Previously, Tye and co-workers (2018)

performed alkali modification on ƙcar [11]. The results showed that the alkali-modified ƙcar exhibited better thermal stability, water vapour barrier property and less hydrophilic as compared to the unmodified carrageenan film. Besides that, study on the synthesis of acylated ƙcar was reported. Long alkyl chain, decanoyl chloride was used as acylating agent in the synthesis [12]. The hygroscopic nature of the acylated carrageenan was reduced compared to pure carrageenan. However, although all the investigations reported reduced hydrophilicity, no study on the potential of the modified ƙcar as electrolyte were reported.

Another concern on ƙcar as polymer host in electrolyte system is its thin film conductivity (σ) is rather low, (10^{-7} S cm^{-1}). Increment in σ is important to be applicable as electrolyte in electrochemical devices. Therefore, studies of synthesized ƙcar in order to enhance the σ were previously reported. In recent past, succinyl ƙcar was synthesized by mixing ƙcar with succinic anhydride $(CH_2CO)_2O$ via one-step modification reaction [13]. The substitution of the succinic group into ƙcar backbone has improved the σ and its interaction with ions compared to its pristine form. In other study, O-methylene phosphonic κ-carrageenan (OMPC) was chemically synthesized via phosphorylation reaction [14]. Methylene phosphonic acid was introduced into carrageenan as a phosphoryl functional group to produce phosphorylated carrageenan. The σ of OMPC film were 1.54×10^{-5} S cm^{-1}, one order of magnitude higher than the pure carrageenan. The authors concluded that the improvement in the σ is due to the oxygen-rich ionogenic group ($-CH_2PO_3H_2$) substituted into the side chain of ƙcar. Synthesis of carboxymethyl carrageenan was formerly reported [15]. The substitution of polar group (CH_3COOH), brought more oxygens in the polymeric matrix, thus provided vacancy for cations to coordinate with the polymer. As a result, the σ was reported to enhance by three orders of magnitude to 2.0×10^{-4} S cm^{-1}, compared to the pure ƙcar film. Nonetheless, although all the synthesis had successfully increased the σ, with the increase number in the polar groups, the hydrophilic properties were also increased, thus affecting the electrolytes' performance in electrochemical devices.

Therefore, our aim is to modify hydrophilic and low σ ƙcar into less hydrophilic and conductive benzoyl ƙcar (Bz-ƙcar). Here, ƙcar is synthesized to undergo acylation reaction and benzoyl chloride (BC) acts as the acylating agent. To the best of our knowledge, the investigation on the synthesis of Bz-ƙcar and its application as polymer host in an electrolyte system has never been reported elsewhere. Thus, this study is expected to give new idea to improve the properties of ƙcar-based electrolyte specifically, and polysaccharide based electrolyte generally.

2. Materials and methods

2.1 Materials

ƙappa-carrageenan (ƙcar) powder (molecular weight: 788.7 g/mol) and benzoyl chloride (BC) (purity: 99%) liquid were purchased from Sigma Aldrich, Malaysia. Pyridine (purity: ≥99%) was purchased from Merck, Malaysia while ethanol used was from HmbG Chemicals (purity: >95%). All chemicals were of analytical grade and used without further purification.

2.2 Synthesis of benzoyl ƙ-carrageenan

Bz-ƙcar was prepared with new synthesis route. Series of ƙcar: BC mass ratios were prepared (1:0, 1:1, 1:3, 1:5, 1:7 and 1:9). Some modification parts are similar to a previously reported acylated chitosan method [16]. ƙcar powder was soaked and stirred in pyridine for 24 hours at 50°C for good dispersion. Then, liquid BC was soaked and stirred in pyridine until dissolved at 60°C. The mixture of pyridine and BC was added dropwise into the ƙcar mixture in 2 hours while being stirred continuously at 60°C. Then, the mixed solution was heated to 60°C under reflux and a heterogeneous product aggregation was observed in the final solution. Pale yellow solution was filtered by a vacuum pump and washed thoroughly with ethanol to

remove excess pyridine. Light yellow powder sample was obtained and dried overnight in the oven. To finish, the powder sample was stored in air tight container until further use.

The synthetic procedure of benzoyl carrageenan synthesis is shown in Figure 1. Herein, the hydrogen atom in the hydrophilic hydroxyl group (-OH) is suggested to be substituted with benzoyl molecule (C_6H_5CO-), through electrophilic substitution (acylation) reaction.

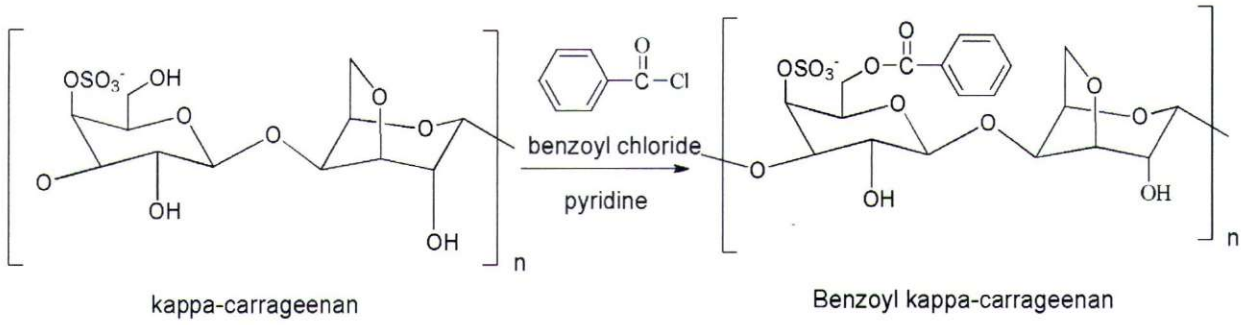
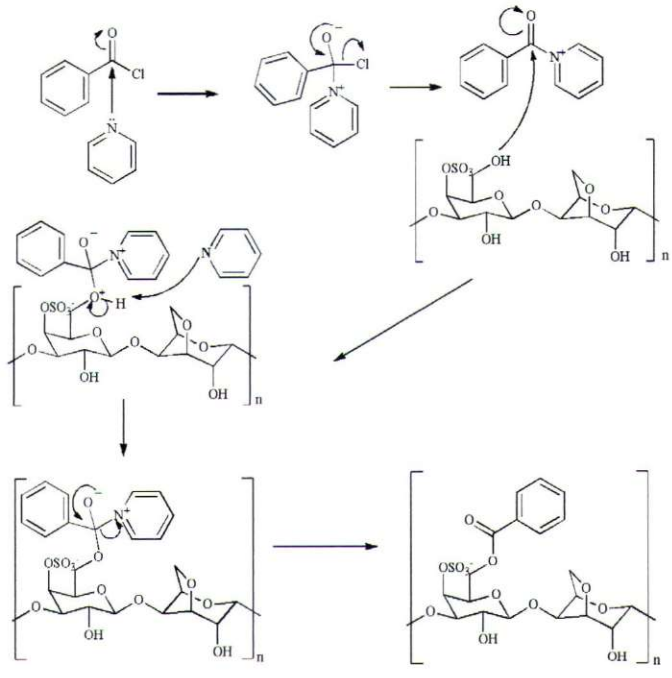


Figure 1: Synthetic procedure of Bz-ƙcar.

In this synthesis, benzoyl chloride acts as an electrophile and acylating agent that delivers benzoyl molecule into ƙcar polymeric chain. Pyridine served as nucleophile for carbonyl groups and catalyst in this acylation reaction. The nitrogen atom in pyridine is nucleophilic as the lone pair of electrons on nitrogen cannot be delocalized around the ring. The reaction initiated with pyridine performed nucleophilic attack on the carbonyl group to form benzoyl pyridinium salt. The carbonyl groups are then activated towards nucleophilic attack by the hydroxyl group in ƙcar. Next step is the deprotonation by pyridine and removal of pyridine as good leaving group. Thus, Bz-ƙcar is produced as the final product. The complete proposed mechanism is shown in Scheme 1.



Scheme 1. Proposed reaction mechanism for the benzoylation of ƙcar.

2.3 Preparation of ƙcar and Bz-ƙcar gels

Both ƙcar and Bz-ƙcar soft gel samples were prepared by dissolving each sample powder in ethylene glycol at the concentration of 3.3% w/v at ambient temperature. The thick gels were stirred overnight in order to obtain complete dissolution. The dissolved gel then kept in air tight container to prevent any moisture contact.

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 due to the chemical interaction between polymer ƙcar and BC salt.

3.2. Elemental analyzer

The percentage of carbon (C), and sulphur (S) for ƙcar and Bz-ƙcar powders were analyzed by using Vario el III, ELEMTAR, Hanau, Germany. The degree of substitution was calculated based on equation (1) [13]:

$$\text{Degree of substitution} = \frac{\text{ratio carbon: sulphur}_{\text{Bz-ƙcar}} - \text{ratio carbon: sulphur}_{\text{ƙcar}}}{\text{number of new added carbon}} \quad (1)$$

3.3 ^{1}H-NMR spectroscopy

^{1}H-NMR spectra were recorded on a Bruker Advance III HD 400 MHz spectrophotometer. Intact samples of ƙcar powder was dissolved in D_2O and Bz-ƙcar was dissolved in deuterated dimethylsulfoxide (DMSO-d_6). Samples were transferred into a static magnetic field to excite the nuclei and measure the emitted frequencies.

3.4 X-Ray Diffraction (XRD)

A Bruker D8 Advance X-ray diffractometer was used to analyze the degree of crystallinity of ƙcar and Bz-ƙcar powders. The data were collected from a range of diffraction angle 2θ from 3° to 60° at the rate 0.05° s^{-1}. The crystallinity index (X_{CI}) has been calculated using peak separation software EVA. Amorphous subtraction method has been used in calculating the X_{CI} of the biopolymer electrolytes [17]. The amorphous contribution of ƙcar has been subtracted from the diffraction spectra. Then, X_{CI} was calculated from the ratio of the remaining diffractogram area due to crystalline ƙcar and the total area of the original diffractogram. The determination of X_{CI} is shown in equation (2):

$$X_{CI} = \frac{A_c}{A_t} \quad (2)$$

where X_{CI} referring to the crystallinity index of the biopolymer, A_c represents the crystalline area and A_t represents the total area of the diffractogram.

3.5 Thermogravimetric analysis (TGA)

A Simultaneous Thermal Analyser (STA) brand NETZSCH model STA 449 F3 Jupiter was used to investigate the thermal behavior of the polymers. Both ƙcar and Bz-ƙcar powder samples with a mass of (3- 5 mg) were tested under nitrogen gas atmosphere at a heating rate of 10°C/ min at a temperature range from 30°C - 600°C.

3.6 Solubility test

The solubilities of ƙcar and Bz-ƙcar powders were evaluated in multiple solvents: pure water, acetonitrile, tetrahydrofuran, pyridine, dimethyl sulfoxide and acetic acid (99.9% purity). All samples were prepared at the concentration of 1.0% w/v and stirred overnight at 25 °C. The solution was filtered and dried to determine the amount of undissolved sample left. Solubility percentage was calculated based on equation (2).

$$\text{Solubility (\%)} = \frac{\text{mass of sample after dissolution (g)}}{\text{mass of sample before dissolution (g)}} \times 100\% \quad (2)$$

3.7 Water contact angle

The water contact angle of the ƙcar and Bz-ƙcar gel samples were measured using The Ossila Contact Angle Geniometer (model L2004A1) with angle range of 5° to 180°. A thin layer of gels was spread on a slide glass (75 mm x 25 mm) and fixed on the horizontal movable stage (50 mm x 50 mm). The WCA was measured soon after dropping an ultra-pure water drop (10 µL) using Eppendorf micropipette.

3.8 Impedance spectroscop

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

4. Results and Discussion

The FTIR spectra of ƙcar and synthesized ƙcar powders with different ratios of BC (ƙcar:BC - 1:0, 1:1, 1:3, 1:5, 1:7 and 1:9) are shown in Figure 2. The characteristic peaks at 922 cm^{-1} is attributed to C-O-C vibration of the 3,6-anhydro-D-galactose residue, while the intense peak at 1037 cm^{-1} represents the C-O stretching mode in ƙcar. Peaks at 1231 cm^{-1} and 844 cm^{-1} were assigned to O=S=O symmetric vibration and to $-O-SO_3$ stretching vibration at the C-4 position of galactose in the ƙcar polymer chain respectively [18].

In order to confirm the benzoyl molecule (C_6H_5CO-) substitution into ƙcar chains, changes on the FTIR signals were observed. Based on Fig. 2(a), a broad stretching vibration of hydroxyl group (OH band) in ƙcar powder (ratio 1:0) is detected at around 3200 – 3600 cm^{-1}. As the ratio of benzoyl chloride increases (ratio 1:1-1:9), the intensity of the broad OH band is noticed to be reduced, thus indicating the decrement of hydroxyl bond in the ƙcar structure. This observation might be related to the electrophilic substitution of hydrogen atom in the -OH group with C_6H_5CO-molecule leading to disruption of hydrogen bonds in the polymer matrix thus signifying the reduction of hydrophilic nature in the synthesized ƙcar.

The further confirmation of benzoyl substitution is shown in Figure 2(b) by the appearance of several new bands in the synthesized ratio 1:3, 1:5, 1:7 and 1:9. New carbonyl (C=O) stretch peak appeared at 1716 cm^{-1} [13]. The intensity of the C=O signal is enhanced with higher ratio of BC salt indicating successful substitution of C_6H_5CO- occurred. A pair of new peak is also detected at 1451 and 1605 cm^{-1} bands belongs to the aromatic C=C stretch [19], thus confirming the successful substitution of C_6H_5CO- into the ƙcar matrix. Noticeably, a new C-Cl peak is formed at 710 cm^{-1} in higher ratios; (1:5, 1:7 and 1:9), which might be due to the excess of BC salt in the synthesized ƙcar.

Significant shifts in the wavenumbers in pure ƙcar (ratio 1:0) and ƙcar with increasing ratios of BC salt (ratio 1:1 – 1:9) were observed. Stretching modes in C-O-C and C-O in the synthesized ƙcar were shifted slightly to higher and lower wavenumbers respectively. The O=S=O symmetric vibration band also showed significant changes as the band shifted to higher wavenumbers. The shifts of the characteristic

bands might be caused by the coordination interaction of oxygen atoms as electron rich species in the polymer matrix with the hydrogen ion (H^+) that is detached from the hydroxyl bond as a result of the acylation reaction. Hence, these changes suggest the successful substitution of benzoyl molecule in the ƙcar matrix. The summarized shifts and assignments of the individual characteristic bands are shown in Table 1. Based on all these IR peak changes, we conclude that Bz-ƙcar has been produced.

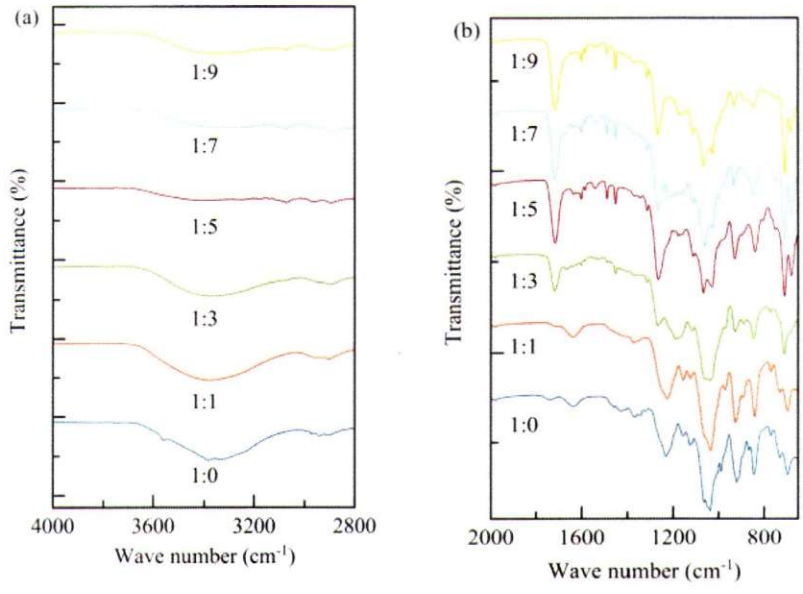


Figure 2: FTIR spectra of different ratios ƙcar: BC (1:0, 1:1, 1:3, 1:5, 1:7 and 1:9) at (a) 4000- 2800 cm^{-1} and (b) 2000- 650 cm^{-1}.

Table 1: The assigned bands and wavelength of the synthesized ƙcar powders.

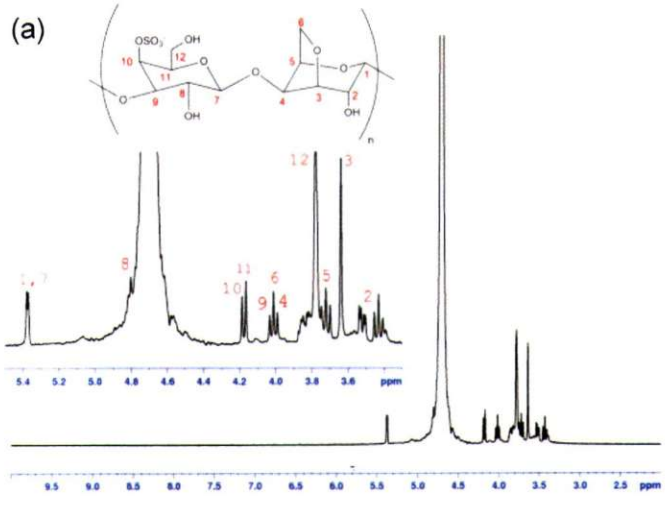
Assignments of bands	ƙcar: BC ratio Wavelength (cm^{-1})					
	1:0	1:1	1:3	1:5	1:7	1:9
O-H	3384	3381	3374	3368	3327	3378
C-O-C	921	926	927	929	933	933
C-O	1037	1036	1036	1028	1027	1027
O=S=O	1231	1224	1267	1267	1267	1268
C=O	None	None	1718	1716	1716	1716
C=C	None	None	1452,1602	1451,1602	1451,1602	1451,1602
C-Cl	None	None	711	710	710	708

The elemental analysis of C and S for series of ƙcar: BC ratios are tabulated in Table 2. The analysis displayed higher percentage of C as the ratios of BC salt increase. This suggests that the synthesized ƙcar has reacted with BC salt and benzoylation has taken place in ƙcar matrix. The upmost percentage of C is observed in the ratio 1:5 of ƙcar: BC, an increase of 35% compared to the pristine ƙcar (ratio 1:0). The degree of substitution (DS) were calculated based on equation (1) by comparing the C and S ratio obtained from element analysis in each ratio. Notably, ratio 1:5 showed the highest degree of substitution (DS) at 0.27, suggesting ratio 1:5 of ƙcar: BC contains the highest benzoyl substitution in ƙcar matrix and implies as the most ideal ratio for the synthesis. The DS started to decrease as higher amount of BC salt was included (ratio 1:7 and 1:9) which could be caused by the saturation or agglomeration of BC salt in the polymer matrix thus hinder the substitution to occur.

Table 2: Elemental analysis and DS of synthesized ƙcar.

ƙcar: BC sample	C (%)	S (%)	C/S	DS
1:0	28.00	4.70	5.96	-
1:1	28.30	4.60	6.15	0.03
1:3	32.50	5.00	6.50	0.08
1:5	37.90	4.75	7.98	0.27
1:7	37.20	4.90	7.59	0.23
1:9	37.80	5.20	7.27	0.19

Further evidence of benzoyl substitution into ƙcar matrix is supported by ^{1}H-NMR spectroscopy. ^{1}H-NMR spectroscopy has the advantage of high selectivity and suitable for quantitative approximation for different types of carrageenan [20]. The ^{1}H-NMR spectra of ƙcar and Bz-ƙcar (ratio 1:5) samples are shown in Fig. 3 (a and b) respectively (chemical shift ranging between δ = 2.0 and 10.0 ppm). Proton signals of ƙcar backbone (Fig. 3a) appear at range 3.45-5.38 ppm and the chemical shifts could be assigned as follows: ^{1}H-NMR (D_2O): δ = 5.37(H1), δ = 3.52 (H2), δ = 3.63–3.69(H3), δ = 3.98 (H4), δ = 3.50-3.53 (H5), δ = 4.01 (H6), δ = 5.36 (H7), δ = 4.81 (H8) δ = 4.03 (H9), δ = 4.18 (H10) δ = 4.16 (H11) and δ = 3.77 (H12), comparable with previous studies [13, 14] .Chemical shifts spectrum of Bz-ƙcar (Fig. 3b) showed similar characteristic to ƙcar proton signals with appearance of new multiple resonances peaks (δ =6.6-9.50 ppm) belongs to the characteristic signals of protons in aromatic benzoate group (C_6H_5CO-). Similar proton signals of benzoylated derivatives were published [17, 21]. These findings proved the electrophilic substitution of benzoyl group into ƙcar matrix and supported the FTIR analysis. Thus, this has also confirmed that the synthesis was successfully accomplished.



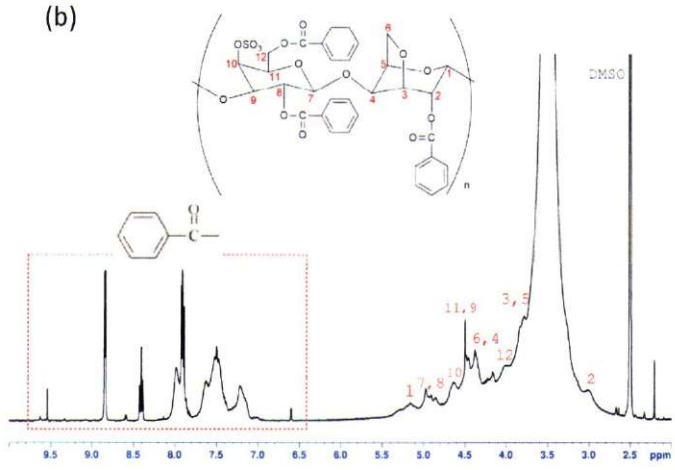


Figure 3: 1H-NMR spectra of (a) ƙcar and (b) Bz-ƙcar.

Fig. 4 shows the X-ray diffraction pattern of pure ƙcar powder and Bz-ƙcar powder (ratio 1:5). Observably, the nature of pure ƙcar film is semicrystalline, with a small hump at 2θ = 2.0 -10.0° and a broad hump at around 2θ = 12.0 - 41.0°. Sharp peaks were shown at 2θ = 29.0° and 41.0° similar to the conventional characteristic diffraction peaks of ƙcar reported [22, 23].

Modification of ƙcar has exhibited significant changes in the structural phase of the biopolymer as displayed in the diffractogram of Bz-ƙcar (Fig. 5(b)). Noticeably, there were multiple formation of new peaks ranging at 2θ = 9.0 - 37.0° with accentuated peaks at 2θ = 12°, 14°, 19°, 25°, 32° and 37°. The appearance of these new peaks is probably due to the engagement of crystalline benzoyl molecule in the biopolymer backbone, that leads to the formation of polymer–benzoyl complexes as the optimum amount of benzoyl chloride was included. Residue of unreacted benzoyl chloride might have also been the cause. Comparable trend was observed in the synthetization of acylated chitosan derivatives [24] .

Observably, upon modification, the small hump at 2θ = 6.0 -12.0° has not been significantly changed. However, reduced intensity with disordered structure of the synthesized Bz-ƙcar (Fig. 5(b)) as compared to the pristine ƙcar (Fig. 5(a)) is observed at 2θ = 10.0 - 40.0°. This observation might be related to the electrophilic substitution of the hydroxyl (OH) group with aromatic benzoyl (C_6H_5-CO-) molecule in the ƙcar matrix (Scheme 1). Consequently, there were disruption of inter and intramolecular hydrogen bonding in the biopolymer matrix thus resulted in the disordered arrangement in the synthesized benzoyl ƙcar chain. The disordered structural arrangement has then affected the crystallinity of the biopolymer as the crystallinity index (X_{CI}) of benzoyl ƙcar was found to lessened at 24.3% as opposed to the pure ƙcar, 26.7%. Thus, this has also shown that the modification of ƙcar has arranged the polymer chain structure whereby the new arrangement has enhanced the formation of amorphous phase. Table 3 shows the percentages of X_{CI} and amorphous in ƙcar and Bz-ƙcar.

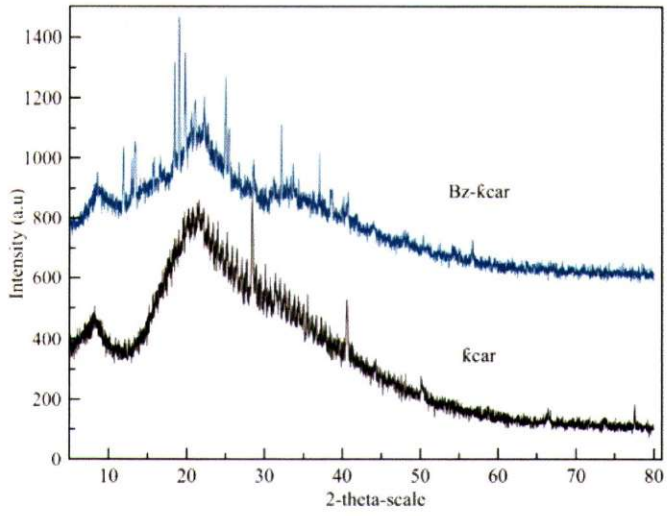


Figure 4: XRD pattern of ƙcar and Bz-ƙcar powders.

Table 3: Crystallinity index and amorphous percentages of ƙcar and Bz-ƙcar.

Sample	Crystallinity index, X_{CI} (%)	Amorphous (%)
ƙcar	26.7	73.3
Bz-ƙcar	24.3	75.7

The TGA and DTG curves of ƙcar and Bz-ƙcar are shown in Fig. 5. Based on the figure, three distinct stages of weight losses were observed in ƙcar, while Bz-ƙcar showed two stages of weight losses. The first weight loss stage in ƙcar is about 5.2% at temperature range of 40 and 140 °C. Bz-ƙcar showed lower weight loss approximately 4.8% at similar temperature range. These initial weight losses are due to the presence of moisture in the samples and related to the characteristic of polysaccharides that have strong affinity for water [9]. Reduced moisture weight loss in Bz-ƙcar is related to its less hydrophilicity characteristic due to the acylation of benzoyl molecule and disruption hydrogen bonding in the polymer chain thus reduce polar interactions with water molecules.

Second degradation peak of ƙcar was found at temperature peak 222.9 °C with small weight loss about 6.1%, followed by the third degradation stage started at 231.0 °C and reached a maximum at 251.8 °C. The synthesized polymer, Bz-ƙcar exhibited lower degradation temperature which maximum degradation peak appeared at 205.9 °C with 58% weight loss. This degradation step was identified as devolatilization step where the main pyrolytic process occurred and various volatile components may release gradually. According to previous study, this degradation step was attributed to the loss of $-SO_3$ - group from the pendant chains attached to the polymeric backbone and also may be due to the polysaccharide backbone fragmentation [25, 26]. Noticeably, the second degradation temperature of the acylated ƙcar were lower compared to the original biopolymer. This might be due to the effect of disruption of hydrogen bonding in the molecule chains, thus leading to disordered structure and the reduced crystallinity of Bz-ƙcar as discussed in the structural analysis part. Therefore, less energy was needed for

Bz-ƙcar to degrade. Nevertheless, the degradation temperature of the Bz-ƙcar is still favorable and suitable to be applied for industrial application.

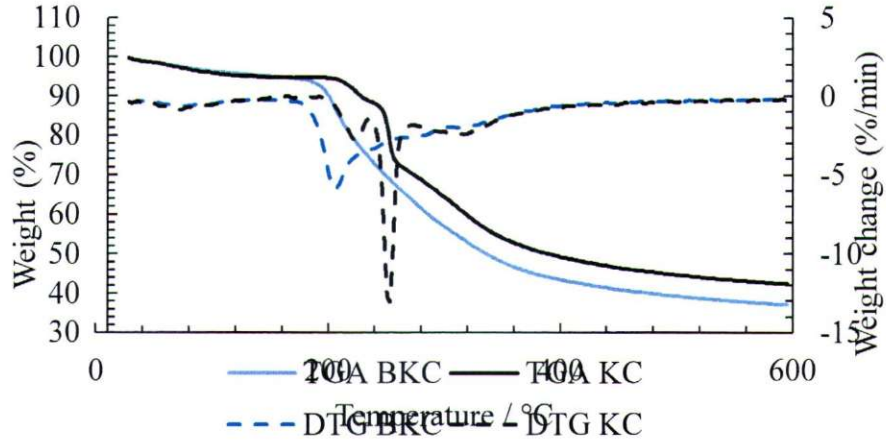


Figure 5: TGA and DTG curves of ƙcar and Bz-ƙcar.

To examine the effects of the benzoyl substitution on ƙcar's hydrophilicity, solubility test on ƙcar and Bz-ƙcar powders in several solvents with vary range polarity indices were performed. Solubility is regarded as the ability of solute to form solution with solvent. Table 4 displays solubility percentages of ƙcar and Bz-ƙcar in seven different solvents. Generally, the higher the polarity index, the more polar the solvent is, as a result of the strong hydrogen bonds in the molecule [27].

Noticeably, the original polymer, ƙcar, showed complete dissolution in both highly polar solvents; water and dimethyl sulfoxide (DMSO). On the other hand, Bz-ƙcar showed reduced solubility percentage in both water and DMSO. A decrease of ~38% solubility is observed in water, while ~85% Bz-ƙcar dissolution is observed in DMSO, signifying the reduced polarity of Bz-ƙcar compared to the original ƙcar. These findings might be due to the interrupted hydrogen bonds in Bz-ƙcar resulted in reduced polar groups in the polymer chain, thus limit the interactions with the polar solvents. Complete dissolution of Bz-ƙcar is observed in ethylene glycol (EG), suggesting EG as the most ideal solvent for Bz-ƙcar. The high solubility of Bz-ƙcar in EG is most likely related to the semi-polar characteristic of Bz-ƙcar, as the strong inter and intramolecular hydrogen bonds in the polymer chains are not entirely destroyed. This explains the relatively low degree of substitution (DS) in Bz-ƙcar as discussed in the elemental analysis part.

Low percentages in solubility are detected in the less polar solvents for both ƙcar and Bz-ƙcar. Better dissolution in acetic acid is observed in ƙcar, as opposed to Bz-ƙcar. Whereas, the synthesized Bz-ƙcar portrayed improved solubility percentage trend in solvents with low polarity values (acetonitrile, pyridine and THF), indicating its less polar behavior compared to ƙcar. These findings have proven that the acylation of benzoyl molecule into the polymer chains has altered its physical characteristic. Reduced solubility in highly polar solvents and better dissolutions in less polar solvents were achieved as a result of the reduced polarity and hydrophilicity in Bz-ƙcar. Hence, accomplish our aim in this study.

Table 4: Solubility percentages of ƙcar and Bz-ƙcar in different solvents.

Solvent	Polarity index [28, 29]	Solubility (%)	
		ƙcar	Bz-ƙcar
H_2O	10.2	100	62
DMSO	7.2	100	85
Ethylene glycol	6.9	75	100
Acetic acid	6.0	24	18
Acetonitrile	5.8	5	20
Pyridine	5.3	23	27
THF	4.0	6	13

The WCA of ƙcar and Bz-ƙcar gels are shown in Figure 5(a) and 5(b) respectively while the WCA data analysis are shown in Table 5. The polynomial fit of the unmodified gel, ƙcar, showed a very low average angle of 15.31°, signifying its highly hydrophilic properties as WCA smaller than 90° generally signifies a surface having the affinity toward the liquid [30]. However, the average WCA of synthesized Bz-ƙcar gel increased to 26.52° indicating reduced hydrophilicity of Bz-ƙcar gel. The reduced hydrophilicity of Bz-ƙcar was mainly due to its reduced interaction with water molecules as a result of the interrupted inter and intramolecular hydrogen bonds in its polymer matrix. The substitution of hydrophobic benzoyl group in Bz-ƙcar matrix might had also hindered the polymer interaction with water molecules. The low WCA value in both ƙcar and Bz-ƙcar is most likely related to the gelled form of the polymers, as ethylene glycol was applied as the solvent and has strong affinity towards water molecules. The left and right root mean square error (RMSE) values for both polymer gels are below than 1.0 indicating the simulated angle values are in good fits.

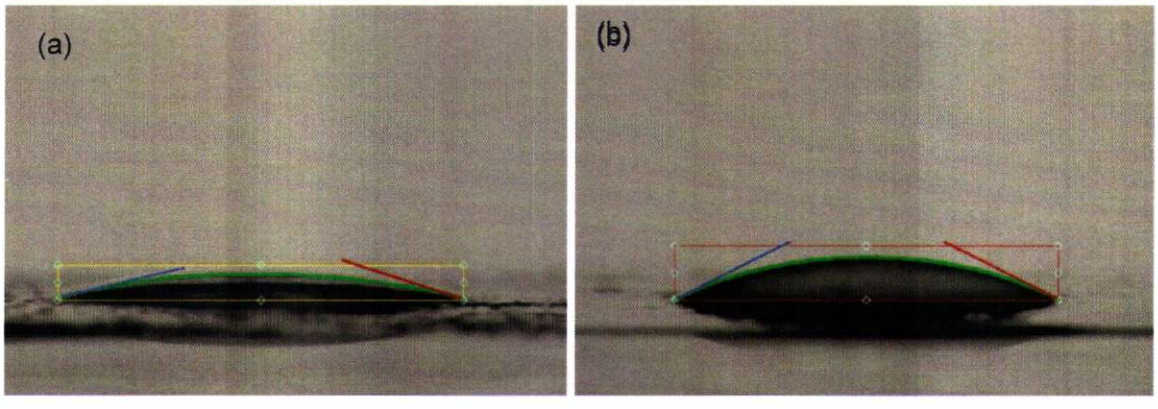


Figure 6: Water contact angles of (a) ƙcar and (b) Bz-ƙcar.

Table 5: WCA analysis of ƙcar and Bz-ƙcar.

Gel	Left Angle (°)	Right Angle (°)	Average Angle (°)	Left RMSE	Right RMSE
ƙcar	13.06	17.57	15.31	0.47	0.58
Bz-ƙcar	26.55	26.48	26.52	0.38	0.38

Electrochemical impedance spectroscopy is an analysis to determine the ionic conductivity (σ). The Nyquist plots of ƙcar and Bz-ƙcar gels are shown in Figure 7. The bulk resistance (R_b) was determined from the interception of the tilted spike at the real impedance axis (Z'). Bz-ƙcar gel displayed smaller R_b value as compared to ƙcar gel indicating higher value of σ. Figure 8 illustrated the conductivity of both pristine and synthesized polymers at ambient temperature (298 K). It is observed that the σ of synthesized Bz-ƙcar is higher than its pristine ƙcar. The σ of ƙcar achieved was 8.20 x 10^{-5} Scm^{-1}, while the σ of Bz-ƙcar showed an increment close to 1 magnitude to 3.10 x 10^{-4} Scm^{-1}. This has proven that the acylation of benzoyl molecule into ƙcar matrix has improved its σ. This might be related to the disruption of strong hydrogen bonding and reduced crystallinity of Bz-ƙcar as shown in the FTIR and structural analyses. As the crystallinity decreased, the increase in the amorphous phase has softened the polymer backbone and enhanced the flexibility and segmental motion of the polymer chains [31] . The gel form of Bz-ƙcar had also contributed to the flexibility of the polymer chain. As a result, the enhancement in the ionic conductivity is perceived. The high σ of Bz-ƙcar achieved, without inclusion of any charge carrier or cation salt indicates the highly potential of Bz-ƙcar as a gel polymer host in electrolyte system.

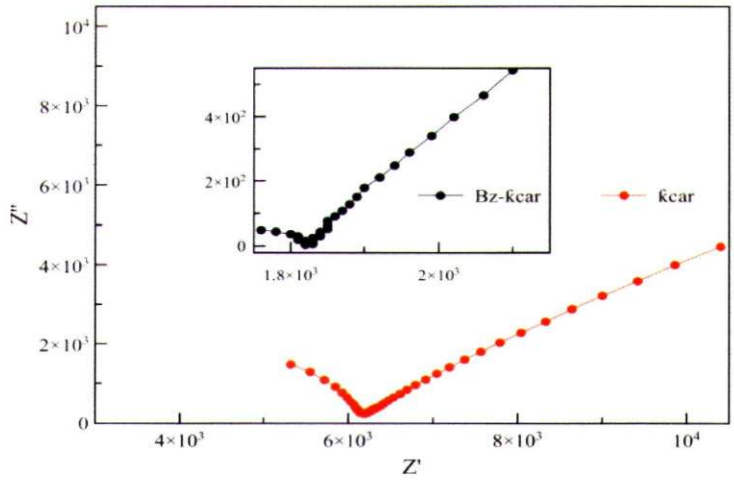


Figure 7: Nyquist plots of ƙcar and Bz-ƙcar gels

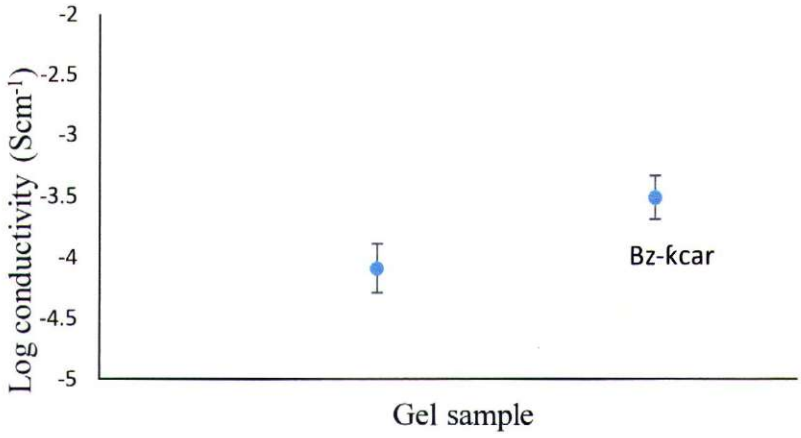


Figure 8: Ionic conductivity,σ of ƙcar and Bz-ƙcar gels

5. Conclusions

Benzoyl kappa carrageenan (Bz-ƙcar), a new ƙcar derivative with less hydrophilic and improved conductivity has been successfully produced via electrophilic substitution in acylation reaction. Benzoyl chloride was employed as the acylating agent. Pyridine was used as the catalyst and nucleophile source in the reaction. The substitution of aromatic benzoyl molecule into the polymer chain has led to less hydrogen bonding and polar interactions with water molecules, thus reduce the hydrophilicity of Bz-ƙcar. The chain flexibility of Bz-ƙcar gel is improved thus increase the ionic conductivity. Bz-ƙcar has high potential to be applied as a green electrolyte in electrochemical devices. Better performance of Bz-ƙcar with incorporation of charge carrier such as lithium or sodium salts is anticipated in our next study.

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