Preparation, Characterization and Swelling Studies of Carboxymethyl Sago Starch Hydrogel

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Abstract

Carboxymethyl sago starch (CMSS) hydrogel was prepared by dissolving CMSS in HCl solution under vigorous stirring to form gel. The parameters studied were the effect of the percentage of CMSS, concentration of the acid solution, reaction time and reaction temperature to identify the optimum condition of preparation of CMSS hydrogel. 60% of CMSS in 2.0M acid solution for 12 hours reaction time at room temperature were the optimum conditions for CMSS hydrogel. The hydrogel was characterized by using Fourier Transform Infrared (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). FTIR spectrum of CMSS shows an additional absorption band at 1597 cm^{-1} indicating the substitution of $\text{CH}_2\text{COO-Na}^+$ group on the starch molecular chain during carboxymethylation, while the spectrum of CMSS hydrogel shows an additional sharp absorption band at 1723 cm^{-1} indicating that the Na in CMSS is being exchanged to H from hydrochloric acid solution. SEM image of CMSS hydrogel shows pores in structure and connected to each other to form networks. TGA curve shows that the maximum rate of thermal decomposition of CMSS hydrogel is higher than CMSS at 330.22 $^{\circ}\text{C}$ with 60.22% major weight loss. This could be due to the presence of the cross-linkages in the CMSS hydrogel. CMSS hydrogel gives high swelling degree in PBS solution at pH 7 and low swelling degree in acidic medium.

Introduction

Polysaccharides are polymeric carbohydrate molecules that can be subjected to a wide range of chemical and enzymatic reactions. They have biocompatible and biodegradable properties with low immunogenicity. Polysaccharides can be easily obtained and found in living organisms [1]. Some of the examples of polysaccharides are starch, alginate, cellulose, hemicellulose including chitin which originated from animals. Sago starch is isolated from sago palm called Metroxylon Sago which can be found abundantly grows well in marshy areas mostly in Sarawak State in Malaysia [2]. It has outstanding biological properties such as biocompatibility, biodegradable, and nontoxicity. However, in some applications, the usage of starch was confined due to a deficiency on its solubility and has a tendency to retrograde. Retrogradation is a non-reversible process that occurs when a cooked starch solution is cooled, molecular interaction between amylose and other glucose units abound to form double helix, resulting in the formation of colloidal crystallites [3]. Chemical modification is introduced to overcome the inherent defects and gain innovation in the utilization of starch. It involves the introduction of various functional groups into starch structure including cationic and anionic groups [4]. Sago starch undergoes carboxymethylation process to produce carboxymethyl sago starch that has a variety of promising properties like high solubility, thermal stability, ion activity, and higher reaction efficiency [5].

Hydrogels are polymer networks that are able to absorb and retain a huge amount of water due to the presence of their hydrophilic groups. The term "network" is implied indicating that cross-links must be present for the prevention of the dissolution of the polymer chain before use [6]. Hydrogel has gained considerable attention in recent years due to its unique properties as a biocompatible smart material, which can be designed to achieve desirable properties [7]. It is widely used in various applications such

as agriculture, waste water treatment, food packaging, cosmetic, biotechnology, pharmaceutical, biomedical including drug delivery applications [8, 9]. Carboxymethyl sago starch hydrogel can be prepared via cross-linking technique. Crosslinking is a process of forming a network, where the polymers are linked together either by ionic and covalent bonds, van der Waals interaction, hydrogen bonding or physical entanglements [10]. Crosslinking can involve the exchange of sodium with hydrogen ion, namely hydrogen bond formation. It is a rapid process but proceeds gradually with time [11].

The aim of this paper is to prepare and characterize carboxymethyl sago starch hydrogel and study its swelling behavior. The finding may lead to potential drug and vaccine carrier in future studies as currently, the use of biopolymers in drug delivery and vaccination has gained huge attention since these polymers can provide better materials due to its compatibility, degradation behavior and non-toxic administration [12].

Materials And Methods

Materials

Carboxymethyl Sago Starch (D.S 0.75) was prepared at Nuclear Malaysia Laboratory. Sago starch was supplied by Song Ngeng Sago Ind. Sibu Sarawak. The CMSS had been synthesized, and purified as described in Zainuddin [13]. The degree of substitution was determined as mentioned in Zainon et. al., [14]. Sodium monochloroacetate (SMCA), acetic acid and nitric acid were purchased from Sigma-Aldrich. Phenolphthalein, diphenylamine reagent, sodium chloride, sodium hydroxide, solvents such as isopropanol, methanol (99%) and absolute ethanol were purchased from R & M Chemicals. Hydrochloric acid (Fuming 37%) was purchased from Fisher Chemicals (Loughborough, UK). All chemical reagents were of analytical grade. Deionized and distilled water were used throughout the experiment.

Preparation of CMSS hydrogel

CMSS hydrogel was prepared by dissolving the CMSS in hydrochloric acid solution under vigorous stirring and left in petri dish to allow crosslinking process to complete. CMSS hydrogel was put into tea bag and immersed in deionized water at room temperature to remove uncross-linked hydrogels that dissolved and extracted into the water. The successful cross-linked hydrogel remained inside the tea bag then collected out from the deionized water and oven dried at 60°C constant weight was achieved. The effect of percentage of CMSS (40-80% w/v), HCl concentration (0.5-2.5M), reaction time (12-72 Hours) and reaction temperature (RT-70°C) were studied to obtain the optimum condition. The optimum condition of the CMSS hydrogel was determined based on its gel content.

Gel Content and Swelling of CMSS Hydrogel

The measurement of gel content was carried out in deionized water at room temperature. The insoluble part of the CMSS hydrogel after immersion were measured to estimate the content of the hydrogel. The swollen sample after immersion indicates the degree of the swelling ability. Samples were removed from

water after immersion and weighed, then dried at 60°C until constant weight was achieved. Percentage of gel content was calculated by the following equation:(See Equation 1 in the Supplementary Files)

Where W1 is the initial weight of the xerogel before immersion and W2 is the weight of dried insoluble part of hydrogel after immersion. Xerogel is a solid formed with unhindered shrinkage obtained when the liquid phase of a gel is removed by evaporation.

Swelling Studies in Different Media

A completely dried CMSS hydrogel was weighed and immersed in 150 ml deionized water at room temperature for 48 hours, the CMSS hydrogel was removed and weighed and dried. The degree of swelling was calculated by the following equation: (See Equation 2 in the Supplementary Files)

Where Ws is the weight of swollen hydrogel and Wd is the initial weight of xerogel. The swelling studies were investigated by using different immersion media such as buffer solution at different pH levels, pH (4, 7, and 10), salt solution (NaCl), 1.0M of HCl and NaOH solution. Data presented in this study was the mean values of triplicate measurements.

Characterization of CMSS hydrogel

The structure of sago, CMSS, and CMSS hydrogel were identified by FTIR analysis using spectrometer (100 Series Perkin Elmer) with universal Attenuated Total Reflectance (UTAR) technique. All samples were analyzed in powder form, irradiated with infrared in the range of 4000-280 cm^{-1} . Thermal stability of sago, CMSS, and CMSS hydrogel were examined using TGA (Perkin Elmer TGA7). The samples were heated from 35.00 to 600.00°C with the rate of 5°C/min in the flow of inert nitrogen gas. The morphology of hydrogel was studied using scanning electron microscopy (FEI, Quanta 400). The hydrogel sample was soaked in deionized water and then was freeze-dried to remove the water molecule and all samples were mounted on metal stubs and sputter-coated with gold.

Results And Discussion

Preparation of CMSS hydrogel

The Effect of Percentage of CMSS

Fig. 1 shows the percentage of gel content and degree of swelling of various percentage of CMSS from 40 to 80% (w/v) in 1.0M HCl solution. The percentage of gel content increased gradually with the amount of CMSS until the optimum amount 60% indicating that the increasing amount of CMSS provide more crosslinking area thus increasing the gel content. However, higher than 60% w/v, the gel content started to decrease slightly. The formation of the crosslinked CMSS hydrogel with acid solution may be reaching its optimum at 60% (w/v) CMSS. When the percentage of CMSS was higher than 60% w/v, there was limited amount of H^+ available in the mixture to promote crosslinking process as the same volume of HCl was used. Thus, resulting in less number of cross linkages between the CMSS chain although the percentage

of CMSS increased. Meanwhile, the degree of swelling is inversely proportional to the percentage of gel content. Increased in gel content caused decreased in swelling capability. It may due to the degree of crosslinking which affected the water uptake [15]. Higher CMSS concentration produces more crosslinked point in polymeric chains thus increase crosslinking network which results in less swelling when it is brought in water. Increased crosslinking network, lead to formation of a tighter network. This caused difficulty for water to permeate and reduced the amount of water being trapped inside hydrogel network thus resulted in low degree of swelling [13, 15]. 60% (w/v) of CMSS gives highest gel content (62.05%), thus was chosen throughout the experiment to prepare hydrogel as a sorbent.

The Effect of HCl Concentration

The effect of different concentration (0.5 to 2.5 M) of HCl solution on gel content and degree of swelling of CMSS hydrogel is shown in Fig. 2. The percentage of gel content increased as the concentration of HCl increased. Similar result have been reported by Takigami et al., [11] stated that the number of crosslinks increases with the increase of acid concentration. However, the graph plotted shows a slight decrease of gel content at 2.5 M that might be due to acid hydrolysis of the linkage at high concentration of acid solution. From the data obtained, 2.0 M of HCl gave the highest gel content and has been chosen as a suitable concentration of HCl in preparing the hydrogel in the next parameter. The swelling capability of CMSS hydrogel as expected, decreased as the concentration of the HCl increased. With the increase of the gel fraction, water absorption decreased significantly depending on the acid concentration [11]. High swelling degree of hydrogel with 0.5M HCl indicates that it has high ability to absorb water. Pushpamalar et al., [16] reported in her study, hydrogels that are relatively weak and consist of a low number of intermolecular bonds are able to expand by absorbing water and holding it in their void. As the intermolecular bonds and the crosslink density increased, hydrogel becomes tightly packed, lessening the ability of the hydrogel to absorb water. This lead to the decrease of swelling degree of hydrogel with high concentration of HCl. Similar finding was reported by Sadeghi et al., [17] stated that higher crosslinker concentration diminished the free space between the polymer chain and subsequently resulting in highly crosslinked rigid structure that cannot be extended and hold a vast amount of water.

The Effect of Reaction Time

The third parameter investigated was the effect of reaction time (12 to 72 hours) for the crosslinking process to completely occur. Fig. 3 shows that there is no significant difference in gel content of CMSS hydrogel at 12, 24 and 36 hours, and it decreased slightly at 48 and 72 hours reaction time. A possible explanation may be the fact that the prolongation of the reaction time does not affect the gel content as the crosslinking process already achieved the maximum value in a short period of time. Although 36 hours reaction time gave 71.89% of gel content, 12 hours reaction time is preferable to avoid waste of time. Usually, swelling capability decreases as the gel content of the hydrogel increases. However, in this parameter, the swelling capability decreased with the increased of reaction time although the gel content did not show significant increment. As the reaction time increased, the structure of the hydrogel became stronger and denser. This could be due to a longer period of time increased the crosslink density and

caused the decreasing the swelling capability of the hydrogel [18]. Kabiri et al., [19, 20] mentioned in their studies that there is a possibility of the additional linkage that increased the crosslink density, which resulted in reducing swelling capacity.

The Effect of Reaction Temperature

The effect of the reaction temperature of 60% CMSS in 2.0M HCl at 12 hours of reaction time was examined from room temperature (24°C) to 70°C. Fig. 4 shows slightly change in gel content as the temperature increase. This could be due to the degree of crosslinking of hydrogel decreased due to acid hydrolysis of CMSS at high temperature, thus reduced the number of long chain polymer that available for crosslinking resulting in decreased of gel content of the hydrogel. Similar result reported by Takigami et al., indicated that reaction at high temperature will cause starch hydrolysis and gives low gel formation [11]. The swelling capability in this study was different than the expected trend as it decreased with the decrease of the gel content. When hydrogel comes in contact with any solvent molecules, the solvent tries to attack the hydrogel surface and penetrate within the polymeric network structure [21]. However, in this experiment, it was observed that the appearance of the gel prepared at high reaction temperature was hard and rigid. This could prevent the hydrogel to swell as the water found difficulty to pass through the surface of the hydrogel thus decreased the swelling capability.

Swelling Properties

Hydrogel is known with its ability to absorb and hold huge amount of solvent in its network structure. This swelling property is a very crucial factor for its further application. The swelling studies would suggest a good prediction on the ability of the hydrogel to interact with the surrounding media, its smart behavior could be used in many application especially in control release of drug delivery [7]. Fig. 5 shows the swelling degree for the CMSS hydrogel at different immersion media. PBS 7 gave high swelling degree indicating that this CMSS hydrogel swells well in PBS 7 solution. In acidic media (PBS 4), more –COOH groups are formed, which induce the formation of the hydrogen bond of –COOH with CMSS hydrogel, leading to a more compact network in CMSS hydrogel and caused a decreased in the swelling degree [7, 22]. Similarly, when CMSS hydrogel was immersed in HCl solution, the presence of H^+ ions in the surrounding induced the hydrogen bond formation and resulting in low swelling degree. In salt solution (NaCl), the swelling ability of CMSS hydrogel significantly decreased compared to the swelling in deionized water. Gupta et al., [23] stated that the phenomenon can be explained on the basis of osmotic pressure developed due to the unequal distribution of ions in the medium and the polymer network. When the polymer immersed in NaCl solution, the development of osmotic pressure is much lower since the external solution contains Na^+ and Cl^- , the presence of Na^+ ions in the outer solution causes a decrease in the osmotic swelling pressure which operates due to the difference of counter ions in a gel phase and solution phase, therefore, reducing the swelling ability. Sadeghi et al., [17] also reported that this behavior was often attributed to the charge screening effect and ionic crosslinking of monovalent cations. In alkaline solution (NaOH and PBS 10), it was observed that there was no swelling degree recorded as the CMSS hydrogel completely dissolved in the alkaline solution after 48 hours immersion time. This might

due to the degradation of the CMSS hydrogel crosslinked network at high concentration of alkaline solution present in the surrounding resulting in reformation of -COONa thus dissolved in the media. These results indicated that CMSS hydrogel prepared in this study exhibited pH-sensitive characteristic and affected by its surrounding environment

Characterization of CMSS hydrogel

Fourier Transform Infrared analysis

FTIR spectroscopy is an effective technique to analyze the functional group of the materials. Fig. 6 shows the FTIR spectra of sago starch, CMSS, and CMSS hydrogel. The spectrum of sago starch shows the absorption band at 3273 cm^{-1} , which is due to O-H stretching vibration, as well as intramolecular and intermolecular hydrogen bonds in glycosidic bond in the sago starch molecule [7]. The absorption band at 2910 cm^{-1} shows C-H stretching and 1643 cm^{-1} shows tightly bound water presence in the starch molecule. The appearance of the absorption band at 1350 cm^{-1} belongs to -CH_2 symmetrical band, while the broad band at the range of $1100\text{-}990\text{ cm}^{-1}$ indicates the C-O stretching from C-O-C and C-O-H in glycosidic ring of starch molecule.

The FTIR spectrum of CMSS shows the shifting of O-H stretching band to lower wavenumber at 3175 cm^{-1} . This probably due to the low intermolecular hydrogen bonds between O-H group left in the glycosidic rings of CMSS prior to the substitution reaction take place during carboxymethylation process [13]. Additional absorption band at 1597 cm^{-1} indicates substitution of $\text{CH}_2\text{COO}^-\text{Na}^+$ group on the starch molecular chain during carboxymethylation.

CMSS hydrogel spectrum shows a new absorption band at 1723 cm^{-1} indicating that the Na in CMSS being exchanged to H from hydrochloric acid solution. The concentration of hydrochloric acid solution used was 2.0 M, thus a sharp absorption band can be observed indicating that most of the -COONa converted to COOH . The intensity of the absorption band depends on the concentration of the acid used, low concentration of acid shows a weak absorption band of conversion of -COONa to COOH [24]. A similar result was reported previously where the replacement of Na in carboxymethyl group with hydrogen from acid occurred depending on the type of acid and concentration [11]. The absorption band at 1421 cm^{-1} and 1238 cm^{-1} are respectively due to -CH_2 scissoring and -OH bending vibration, while OCH-O-CH_2 stretching represented by the absorption band at 1000 cm^{-1} .

Thermogravimetric analysis

TGA analysis is a convenient analysis to study the thermal decomposition and thermal stability of polymer. It is a quantitative measurement of the weight change of a sample against the temperature applied. TGA thermograms of native sago starch, CMSS, and CMSS hydrogel are shown in Fig. 7. Native sago starch, CMSS, and CMSS hydrogel have two steps of decomposition. The first step below $150\text{ }^\circ\text{C}$ correspond to the removal of moisture from the surface and entrapped water in the sample. The second

step occurred around 200 °C to 500 °C is due to the decomposition of starch backbone and leaving a residue. Zhang et al., [25] stated that water was the main product decomposition at temperature below 300 °C and further heating up above 500 °C resulted in carbonization and ash formation.

For CMSS, the maximum weight loss occurred at 295.33 °C which is lower than native sago starch before carboxymethylation (309.57 °C) with 49.71% of total CMSS decomposed and 42.37% residue due to the presence of ash and sodium salt in CMSS. It had been found that the carboxymethylation process decreased the thermal stability of starch materials [25]. The maximum thermal decomposition of CMSS hydrogel was 330.22 °C with 60.22% major weight loss, slightly increased compared to native sago starch and CMSS. Increase in the maximum thermal decomposition of CMSS hydrogel could be due to the presence of cross-linkages in CMSS hydrogel [24]. High cross-linked structure and compact network improve the degree of stability of hydrogel resulted in higher temperature needed to decomposed them [7].

SEM analysis

Scanning Electron Microscopy (SEM) is an excellent technique in examining the surface morphology of a sample. Fig. 8(a) shows a smooth surface and oval-shaped granules sago starch with a diameter in the range of 20-40 µm similar to the previous study reported by Ahmad et al., [26]. Fig. 8(b) shows massive distorted and irregular shape of carboxymethyl sago starch. In comparison with native starch, the surface of CMSS is rough and groove indicates that the breakage of chemical bond by a strong alkaline environment during carboxymethylation process. Thus, the carboxymethylation is not only the reaction on surface of starch granules but also from within [24]. The micrograph also shows that the CMSS remain intact and agglomerate after preparation with aqueous-alcoholic medium studied. Fig. 8(c), shows CMSS hydrogel has spongy surface with empty space called pores in structure and connected to each other to form networks as a consequence of the crosslinking process [27].

Conclusion

Carboxymethyl sago starch hydrogel was successfully prepared in hydrochloric acid solution. Carboxymethylation decreased the thermal stability of sago starch, but cross-linking increased the thermal stability of CMSS hydrogel. FTIR spectrum of CMSS hydrogel showed that the Na in CMSS successfully exchanged to H from hydrochloric acid solution. SEM image of CMSS hydrogel shows pores in the structure and connected to each other to form networks. Swelling studies of CMSS hydrogel prepared exhibited a smart behavior as it reacts depending on its surrounding environment and displays pH-sensitive characteristic. Finding of this study suggests the potential of CMSS hydrogel in broad application, especially in drug delivery.

Declarations

Authors' Contributions

Normastura Sulta designed the study, elucidate the results and wrote the manuscript. Norhazlin Zainuddin developed the methodology in producing the hydrogels as well as supervised the whole concept. Mansor Ahmad improved the methodology and concept of hydrogels fabrication. Mas Jaffri Masarudin contributed to the discussion of results. All authors commented on the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests

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Figures

Figure 1

Effect of percentage amount of CMSS in 1.0M HCl on gel content and swelling of CMSS hydrogel at room temperature for 24 hours of reaction time.

Figure 2

Effect of HCl concentration on gel content and swelling of 60 % CMSS hydrogel at room temperature for 24 hours of reaction time

Figure 3

Effect of reaction time on gel content and swelling of 60% CMSS hydrogel in 2.0M HCl at room temperature

Figure 4

Effect of reaction temperature on gel content and swelling of 60% CMSS hydrogel in 2.0M HCl at 12 hours of reaction time

Figure 5

Swelling of CMSS hydrogel at different media at room temperature

Figure 6

FTIR spectra for Sago Starch, CMSS and CMSS Hydrogel

Figure 7

(a) TGA and (b) DTG thermograms of Sago Starch, CMSS and CMSS hydrogel

Figure 8

SEM images of (a) sago starch, (b) CMSS and (c) CMSS hydrogel

Supplementary Files

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