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EFFECT OF MONO- AND DIVALENT SALTS ON THE PROPERTIES OF CARBOXYMETHYL CELLULOSE HYDROGEL UNDER IRRADIATION TECHNIQUE

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ABSTRACT

Swelling properties and gel fraction of CMC hydrogels prepared by gamma radiation in presence of mono-and divalent salts (NaCl and $CaCl_2$) were studied. Two parameters such as effect of radiation dose and ionic strength of salts on the properties of hydrogel were observed. Swelling ratio and gel fraction of hydrogels depend on radiation dose and ionic strength of salts. Results also indicate that CMC with divalent salt, the gelation capacity is higher than that of mono-valent salt and swelling capacity of CMC hydrogel with mono-valent salt is higher than that of CMC hydrogel with di-valent salt. In addition, gel fraction increases and swelling ratio decreases with increased ionic strength of salt but at higher ionic strength > 0.41 M, an unexpected inversion of the trend is observed and gives low cross-linking value.

Key words: Gel fraction, Swelling ratio, Gelation, Cross-linking, Ionic strength, Sodium chloride, Calcium chloride.

INTRODUCTION

In recent years, increasing interest in natural-based superabsorbent hydrogel has developed mainly due to high hydrophilicity, biocompatibility, non-toxicity, and biodegradability of biopolymers. Natural-based polymer, cellulose and its derivatives are environmentally friendly, as they are degradable by the action of several bacteria and fungi present in air, water and soil[1]. Cellulose is the most abundant naturally occurring polymer, found as main constituent of plants and natural fibres such as cotton and linen. The large

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availability of cellulose in nature and the mentioned properties make cellulose based hydrogels particularly attractive. Carboxymethyl cellulose (CMC) is a polyelectrolyte cellulose derivative which is used in various fields such as detergent, food, paper and textile industries[2-6]. These materials are defined as cross-linked macromolecular networks that can absorb water or physical fluids up to many times of their own weight in a short time, but are not dissolved when brought into contact with water[7]. Because of excellent characteristics superabsorbent hydrogels are widely used in many fields, such as agricultural and horticultural, disposable diapers, feminine napkins, pharmaceuticals and medical applications[8-9]. Hence, synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency and initial absorption rate, has been goal of several research groups in the past decades[10-13].

Hydrogels can be synthesized using either chemical or by the application of ionizing radiation. Radiation method is a very convenient tool for the preparation of hydrogel because the product is free from chemical initiator and simultaneous sterilized final product is obtained. It was established that cellulose and its derivatives are radiation-degrading type polymers[14-16]. The molecular weight of CMC molecules reduced when exposed to gamma rays or electron beam radiation. Random cleavage of glycoside bonds in the main chain, initialized by radicals placed on macromolecules is the leading reaction of natural polymers. Under irradiation, carboxymethyl cellulose degrades faster when processed in dilute solution[17]. Recently, some researcher established that hydrogels of CMC in high concentrated aqueous solution (paste-like) can be prepared by radiation induced cross-linking[18]. But in presence of alkaline earth metal, dilute solution of CMC molecules can form gel under irradiation[19]. CMC with alkaline earth metals, ions of salts may be interacted with the charges on polymer chain and CMC tends to form coils. Formation of radicals on such coiled polymer chains can make possible formation of inter- and intra-molecular cross-linking by the action of radiation. The main objective of this study is to develop hydrogels from dilute solution of CMC in presence of mono- and divalent salts and compare the properties of hydrogel with monovalent salt and that of hydrogel with divalent salt.

EXPERIMENTAL

Raw materials

Carboxymethyl cellulose (CMC) with 2.34, degree of substitution, was purchased from Daicel Chemical Industry Co., Ltd. Japan. Sodium chloride (NaCl) and Calcium chloride dihydrate ($CaCl_2.2H_2O$ of analytical grade were purchased from Wako Pure Chemical Industries Co., Japan.

Preparation of CMC solution and hydrogel

Homogeneous solutions containing 5% of CMC were prepared in deionized water with and without addition of salts (sodium chloride, calcium chloride). The ionic strength of salts was adjusted at 0.05, 0.10, 0.21, 0.41 and 0.83M in different samples. Then the solutions were irradiated with gamma-rays from Co-60 source by varying radiation dose from 5 to 50 kGy at room temperature. The irradiated samples were freeze-dried to constant weight using freeze dryer FD-550 (Tokyo Rikakikai Co., Ltd.). The dried samples were used for the measurement of properties.

Measurement of gel fraction

The gel sample dried to constant weight was immersed in deionized water for 48 h at room temperature for removing sol parts. Then the undissolved part of sample was taken out and dried in a vacuum oven at 50ºC to constant weight. The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (W_d/W_i) \times 100$$

where W_i is the initial weight of dried gel sample and W_d is the weight of dried gel sample after extraction with deionized water.

Measurement of swelling ratio

The swelling ratio of cross-linked sample was estimated by Japan Industrial Standard (JIS) K8150. The gel sample dried to constant weight was immersed in deionized water for 48 h at room temperature; the hydrogel was filtered using a stainless steel net of 30 meshes and weighed after removing the surface water by tissue paper. The swelling ratio was calculated as follows:

$$\text{Swelling ratio} = [W_s - W_d)/W_d],$$

where W_s is the weight of gel in swollen state and W_d is the initial weight of dry gel.

RESULTS AND DISCUSSION

Effect of radiation dose on gel fraction of CMC hydrogel

5% CMC solution with 2.04% monovalent salt and 5% CMC solution with 2.04% divalent salt were irradiated with different radiation dose at room temperature. Fig. 1 shows the effect of radiation dose on gel fraction of CMC hydrogel. The gel fraction increases with increased radiation dose and reaches a maximum values at the radiation dose of 50 kGy. For

5% CMC with NaCl, the gel fraction increases from 0 to 54.2%, when the radiation dose increases from 5 to 50 kGy. On the other hand for 5% CMC solution with $CaCl_2$, the gel fraction increases from 50.2 to 71.2% at the same dose range applied on CMC with NaCl. The increasing trend of gel content with increased radiation dose may be due to the increased number of free radicals on the CMC chain and can easily form more cross-linking between CMC chains.

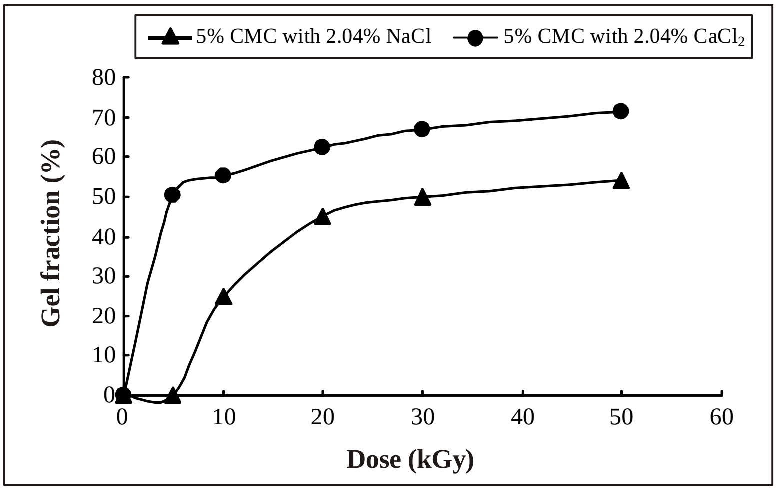

Fig. 1: Effect of radiation dose on gel fraction of CMC hydrogel

Effect of concentration of salt on gel fraction of CMC hydrogel

Figure 2 shows the effect of concentration of salts on gel fraction of CMC hydrogel. It is found that gel fraction increases with increased concentration of salts and attained maximum values at 0.21M $CaCl_2$ and 0.4 M NaCl. It is also observed that the amount of gel fraction of CMC hydrogel with NaCl is lower than that of CMC hydrogel with $CaCl_2$. At 5 kGy dose, the gel fraction value of CMC hydrogels with 0.21M $CaCl_2$ is ~39.1% whereas the gel fraction of CMC hydrogel with 0.21M and 0.4 M NaCl is not found. At 10 kGy radiation dose the gel fraction value of CMC hydrogel with 0.21M $CaCl_2$ is ~ 58% but the gel value of CMC hydrogel with 0.21M NaCl is ~21.7% and with 0.4 M NaCl is ~25%.

It is well-known that CMC is a polyelectrolyte cellulose derivative which shows sensitivity to ionic strength of salt. It may be mentioned here that the sensitivity of CMC depends on the nature of metal ion[20]. The sensitivity of polyelectrolyte for the mono-valent cations such as Li, Na, K are relatively lower than that of polyelectrolyte for divalent cations like Ca, Mg etc. This suggests that the affinity between the CMC molecule and Ca^{+2} is stronger than that of CMC and Na^+ [21-22]. Increasing electrostatic attraction between anionic charges of polymer chains and multivalent cations (Ca^{2+}) leads to increase ionic cross-linking of polymer. The interaction of carboxylic groups of CMC with multivalent metal ions forms ionoprotic gels, which are predominantly stabilized by the electrostatic interaction. In addition, interaction between the –OH groups of the polymer (CMC) and the metal ions contribute to the stability and the water insolubility of these polymeric aggregates[23]. As a result, increasing the charge of cation, degree of cross-linking (gel fraction) of CMC hydrogel is increased.

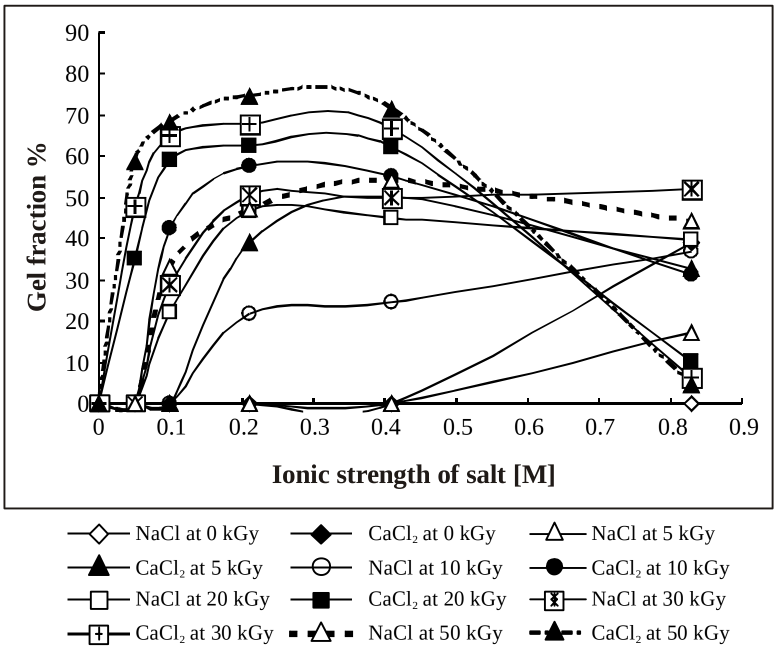

Fig. 2: 5% CMC with mono-and divalent salt

In this study it is also observed that ionic strength of salt had a remarkable effect on the cross-linking of CMC but at high ionic strength showed a reversible result. It is found that CMC gave a physical gel with 0.83 M $CaCl_2$ and obtained gel fraction is ~39%. It is also found that gel fraction of CMC hydrogel with > 0.4 M $CaCl_2$ has a decreasing trend with radiation. The gel fraction of CMC hydrogel with 0.21M $CaCl_2$ is ~ 58% at 10 kGy radiation dose but that of CMC hydrogel with 0.83 M $CaCl_2$ is ~31% at the same radiation dose. It can be explained that the polymer solution becomes more viscous with > 0.41M $CaCl_2$ and free radical on polymer chain obtained by the action of radiation may not move easily to form cross-link, may degrade the polymer chains and reduces the gel fraction of hydrogel.

Effect of salts (NaCl and $CaCl_2$) on swelling ratio of CMC hydrogel

Figure 3 depicts the swelling curves of the 5% CMC hydrogels in deionized water as a function of dose and concentration of salt. The swelling capacity of hydrogels decreases with increased radiation dose as well as with increased ionic strength of salts. This result indicates that increased radiation dose and ionic strength increase cross-linked density of hydrogel. Swelling ratio reflects the cross-linking of a polymer. Increased cross-linked density of a polymer reduces the swelling behaviors of a polymer because a limited scope is available for free water to enter into the vacant spaces of cross-linking network.

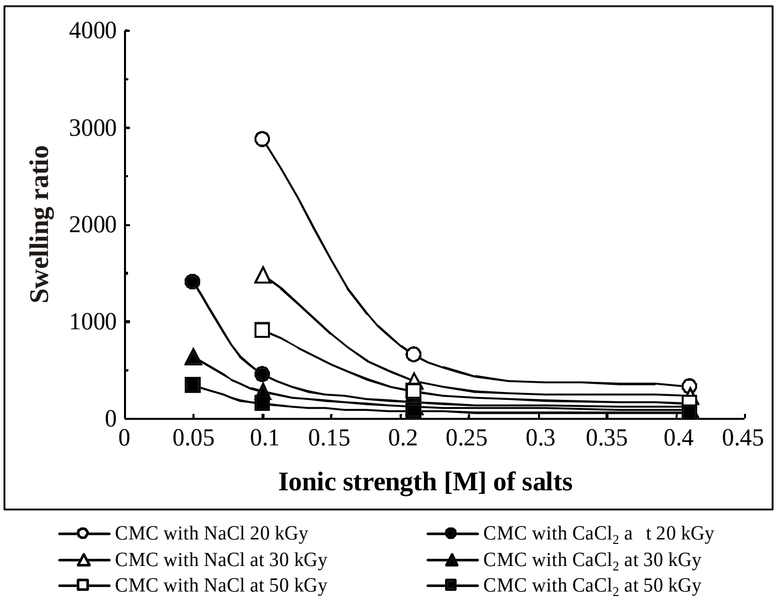

Fig. 3: Effect of mono- and divalent salts on swelling behavior of CMC hydrogel with various radiation doses

Swelling ratio of CMC hydrogel with $CaCl_2$ is lower than that of CMC hydrogel with NaCl. This result reveals that cross-linking (gel content) of CMC hydrogel with $CaCl_2$ is higher than that of CMC hydrogel with NaCl.

CONCLUSION

Addition of salt has a significant effect on cross-linking of CMC solution under irradiation. From the results it is observed that CMC with $CaCl_2$ gives a good gel fraction value than that of CMC with NaCl. It is also observed that maximum gel value of CMC

(5%) hydrogel is achieved at 0.2M ionic strength of $CaCl_2$ and 0.4M ionic strength of NaCl. From this observation it can be concluded that cross-linking of CMC depends on nature of metal ion, ionic strength of salts and radiation dose.

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