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HYDROGELS OF CARBOXYMETHYL CELLULOSE CROSSLINKED WITH IRRADIATION AT DILUTE AND PASTE-LIKE CONDITION

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ABSTRACT

Polysaccharides such as cellulose, starch and their water-soluble polymer derivatives have been known as degradable type polymers under action of ionizing radiation. Recently, we found that water-soluble polysaccharides derivatives such as carboxymethyl cellulose (CMC) lead to radiation cross-linking at high concentrated aqueous solution (more than 10%, paste-like state). It was proved that the crosslinking was remarkably affected by their concentration. It was assumed that radiation formation of hydrogels of these polysaccharides derivatives were mainly due to the mobility of side chains. Side chains radicals were formed mostly via indirect effects, by the abstraction of H atoms by the intermediate products of water radiolysis. Some important characteristics of these prepared hydrogels were investigated.

Key words: Carboxymethyl cellulose, Irradiation, Hydrogel, Cross-linking, Radicals, Paste-like.

INTRODUCTION

Hydrogels of natural polymers, especially polysaccharides have been used because of their unique abilities to improve properties. In recent years, increasing interest in natural-based superabsorbent hydrogel has developed mainly due to high hydrphilicity, biocompatibility, non-toxicity, and biodegradability of biopolymers. Because of their exceptional properties, polysachharides are the main part of the natural based superabsorbent hydrogels[1-3]. Carboxymethyl cellulose (CMC), an anionic water-soluble polysaccharide, is important modified cellulose derivatives in which original H atoms of cellulose hydroxyl groups are separated by carboxymethyl substituent, $-CH_2COO^-$ by its

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reaction with alkali and chloro acetic acid. Hydrogels can be synthesised using either by chemical or irradiation technique. Ionization radiation has been well known as a very convenient tool for modification of polymer materials through cross-linking, grafting and degradation techniques. Polysaccharides, such as cellulose and its derivatives, when exposed to ionizing radiation, has long been recognized as degradable type of polymer[4,5]. The ethers of celloluse suffer reduction of molecular weight when exposed to gamma rays or electron beam irradiation. Random cleavage of glycoside bonds in the main chain, initialized by radicals placed on macromolecules, is the leading reaction of natural polymers. Furthermore, irradiation of polymers of this type, e.g., carboxymethyl cellulose resulted in their faster degradation when processed in dilute aqueous solution[6]. In a previous study, it was found that biodegradable ethers of cellulose, namely, carboxymethyl cellulose (CMC), of a high degree of substitution (DS) and at a high concentration can be effectively cross-linked to the form of a hydrogel[7]. In this investigation, the effects of the concentration and radiation dose on the cross-linking of CMC with a DS of 1.36 (CMC 1.36) in aqueous solutions under ionizing radiation were examined. The radiation yield, swelling behavior of CMC hydrogel were evaluted.

EXPERIMENTAL

Materials

The sodium CMC (DS 1.36) used in our experiments was a commercial product obtained from Daicel Co., ltd. Japan.

Sample preparation and irradiation

Deionized water was mixed homogeneously with an appropriate amount of polymer with blending machine. The prepared sample was kept for a few days at room temperature to ensure complete dissolution and uniform distribution of polymer chains. Higher concentration solutions were very thick and semisolid gum like gels. The mixture was sealed in polyethylene bags for air-free irradiation, after degassing by a vacuum machine.

Irradiation was carried out with a γ ^{60}Co source by varying radiation dose from 5 to 50 kGy at a dose rate of 10 or 1 kGy/h 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 content in the dried cross-linked sample was estimated by measuring its

insoluble part after extraction in distilled water for 48 h at room temperature. The gel fraction was calculated according to the following equation:

$$\text{Gel Fraction (\%)} = (G_d / G_i) \times 100 \quad \ldots(1)$$

Where G_i is the initial weight of dried sample and G_d is the weight of dried gel sample after the 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:

$$\text{Swelling ratio} = (G_s - G_i) / G_i \quad \ldots(2)$$

Where G_s is the weight of gel in swollen state and G_i is the initial weight of dried sample.

RESULTS AND DISCUSSION

Synthesis of hydrogel

Crosslinking successfully competes with glycoside bone cleavage as the concentration of polymer in a solution oversteps some critical values. Polysaccharides derivatives undergo degradation at diluted solution (below 5%). Because chains of CMC at low concentrated aqueous solutions are separated by water and placed at a distance from each other, which prevents intermolecular reaction from occurring. At low concentrations, polymer chains in solution are hydrated and simply entangled with one another. Then the yield of cross-linking is trivial, and the leading radiation-induced reaction is scission of glycosides bonds. Cross-linking is observed only for irradiation at paste-like state of high concentration. CMC at concentrations of 10% to 30% have a paste–like texture. Cross-linking is observed only for irradiation at paste-like state of high concentration. The effect of the concentration of CMC with a DS of 1.36 against delivered dose is illustrated in Fig. 1. Gel fraction rises sharply just after exceeding the gelation point and levels off later. Maximum gel fraction was achieved at concentrations from 10% to 30%, while a high concentration, such as 50% and above (60%), gives a low gel fraction. It is known that the presence of water enhances the mobility of the rigid molecules of polymer allowing macro

radicals to recombine each other, and moreover the products of water radiolysis can induce more macro radicals. Hence the presence of water enhances the yields of macro radicals. So from practical point of view, the polymer should be homogeneously mixed with water to prepare homogeneous sample. However, for a higher concentration (i.e., 50% and above), it is difficult to obtain homogenously dispersed polymer in the whole volume of sample. In a high concentration, low gel fraction was obtained due to the heterogonous state with water.

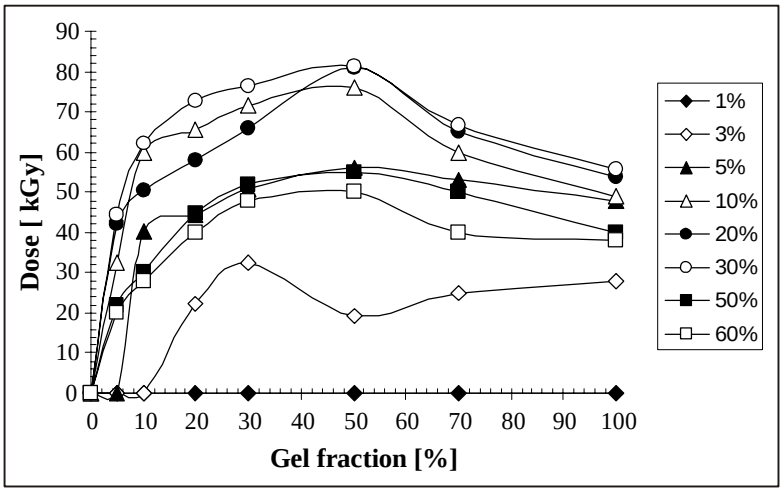

Fig. 1: Gel fraction of CMC hydrogel formed by irradiation of the polymer by gamma rays in aqueous solutions

Swelling of hydrogel

The main feature of hydrogel is its ability to absorb and hold in its structure an amount of solvent. Swelling is usually defined as the mass of solvent absorbed per g of dried gel and is dependent on the hydrophilicity of the polymer, the density of intermolecular links. Fig. 2 shows the swelling of the hydrogels CMC. Swelling is the highest at the beginning stages of irradiation, just after the dose oversteps gelation point. Statistically, one cross-link per chain is necessary to form an insoluble macroscopic gel[8]. In the case of 3% CMC hydrogel the network is weak and susceptible to breakage, but because of a relatively low number of intermolecular bonds, more water molecules can easily penetrate. The swelling of decreases with increasing dose as well as with increasing the concentration of CMC (20 & 30% CMC). This is because of the increase in cross-linking density the hydrogel becomes more tightly packed and firm. Hence, the water sorption ability lessens.

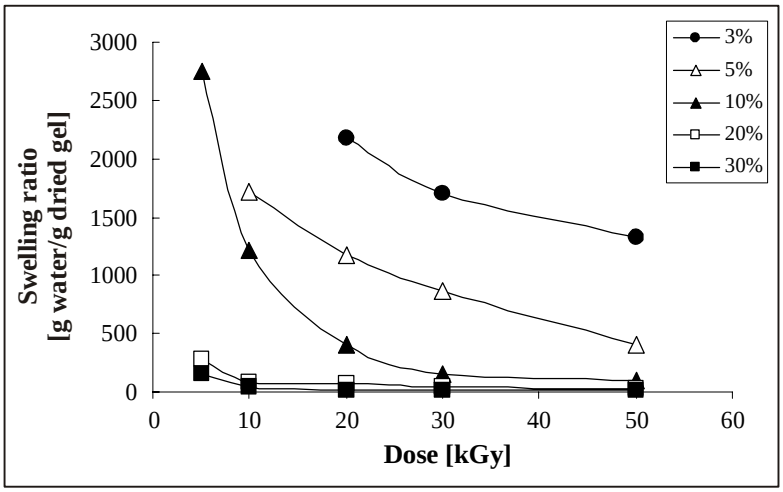

Fig. 2: Swelling of CMC hydrogels in deionized water at room temperature

CONCLUSION

A series novel hydrogels based on polysaccharides derivatives were synthesized by irradiation without any additives. It was found that low concentrated polysaccharides derivatives of radiation degradation type cross-linked by simple technique. High concentrated paste-like condition was favorable for crosslinking. These hydrogels exhibited good swelling in water and these type of hydrogel (natutal based hydrogel) possess satisfying biodegradability. Thus, the hydrogels based on polysaccharide derivatives are expected to be useful as biomedical, agricultural, and cosmetic materials components.

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