RADIATION-INDUCED CROSSLINKING
OF CELLULOSE ETHERS

Radosław A. Wach[1], Hiroshi Mitomo[1], Fumio Yoshii[2], Tamikazu Kume[2]

[1] *Department of Biological and Chemical Engineering, Gunma University, Japonia*

[2] *Takasaki Radiation Chemistry Research Establishment, JAERI, Japonia*

Abstract

The effects of high-energy radiation on four ethers of cellulose: carboxymethyl (CMC), hydroxypropyl (HPC), hydroxyethyl (HEC) and methylcellulose (MC) were investigated. Polymers were irradiated in solid state and in aqueous solutions at various concentrations. Degree of substitution (DS) of the derivatives, the concentration of their aqueous solutions and irradiation conditions had a significant impact on the obtained products. Irradiation of polymers in solid state or in diluted aqueous solutions resulted in their degradation. However, it was found that for concentrated solutions gel formation occurred. Paste-like form of the initial material, when water plasticizes the bulk of polymer as well as the high dose rate, what prevents oxygen penetration to the polymer during irradiation, have been found favorable for hydrogel formation. Up to 95% of gel fraction was obtained from solutions of CMC with concentration over 50% irradiated by γ-rays or electron beam. It was pointed out that the ability to the formation of the three-dimensional network is related to the DS of anhydroglucose units and a type of chemical group introduced to main chain of cellulose. Produced hydrogels swelled markedly in water. Despite of the crosslinked structure they underwent degradation by the action of cellulase enzyme or microorganisms from compost, and can be included into the group of biodegradable materials.

1. INTRODUCTION

Cellulose is a main component of plant mass of the most widely encountered natural biological material. The reactivity of the three hydroxyl groups at positions 2, 3 and 6 of the glucosyl unit offers a variety of possibilities for making useful derivatives of this raw material. Among them cellulose ethers are used extensively. In these derivatives the hydrogen atoms of the hydroxyl groups of cellulose are partially replaced by alkyl or substituted-alkyl groups [1].

It is well known that water-soluble synthetic polymers at a certain range of concentration in solution can be crosslinked by high-energy radiation to the form of hydrogels [2]. The polymeric network which exhibits the ability to absorb and retain a significant amount of water within its structure, but which does not dissolve is defined as hydrogel. One can regard hydrogels as material possessing both liquid like and solid like properties. The former one results from the fact that the main

component of hydrogels is water. The later one is due to some elastic strength of the network, which maintains the shape of the gel but allows for increasing its dimensions. Thus, penetration of another solvent or low molecular weight solutes throughout the bulk of gel is possible. An important impact on the results of irradiation of polymers in aqueous solution has such factors as: concentration of polymer in solution, dose and dose rate, presence of oxygen, chemically active additives and others. Hydrogels formed by irradiation techniques found applications in many fields of our daily life for example in biomedical devices [3, 4].

Polysaccharides including cellulose derivatives, are biodegradable and harmless to the environment. However, they were generally found to degrade under ionizing radiation [5, 6]. Only few evidences of their radiation-initiated crosslinking at special conditions have been reported [7, 8]. In our preliminary study, it was found that one of the ether of cellulose – carboxymethylcellulose (CMC) of high degree of substitution (DS) and at high concentration in water solution can be effectively crosslinked to the form of hydrogel [9, 10]. The aim of this study was to examine the effect of some factors on crosslinking of cellulose ethers in aqueous solutions under ionizing radiation. Radiation yield, swelling behavior and biodegradability of hydrogels were evaluated.

2. EXPERIMENTAL

Four ethers of cellulose were used in our investigations: carboxymethyl-cellulose (CMC) obtained from Daicel, Japan, hydroxypropylcellulose (HPC) from Nippon Soda Japan, methylcellulose (MC) from Shin Etsu Japan and hydroxyethylcellulose (HEC) from Sumitomo Seika Japan. Some properties of these polymers are summarized in Table. Cellulase C-0901 enzyme (*penicillium funiculosum*) was obtained from Sigma Chemical Co., USA. All chemicals were analytical grade.

In order to prepare samples, distilled water was mixed homogeneously with an appropriate amount of polymer. Material was kept for 7 days at room temperature to ensure completely dissolution and to form homogeneous mixture. Higher concentrated solutions had paste-like consistancy. Mixtures were sealed in polyethylene bags or, those intended for irradiation without access oxygen, in poly(vinylidene chloride) packages. Solid samples were sealed prior to irradiation into glass vials after elimination of air. Concentrations were calculated as polymer/water [wt/wt] x 100% ratio.

Irradiation was carried out using gamma ^{60}Co source at a dose rate of 10 or 1 kGy/h at ambient temperature. Alternatively, EB accelerator was applied with current 1 mA, voltage 1 MeV.

Table. Cellulose ethers; [η] – intrinsic viscosity, M_w – weight average molecular weight.

Sample	(DS)[a]	[η] / [dL./g]	M_w / x 10^{-5} [Da]
CMC 2.2	2.2	5.59	5.22
CMC 1.29	1.29	7.38	5.39
CMC 0.86	0.86	6.79	4.22
HPC1	3.0	4.49	6.60
HPC2	3.0	7.98	12.5
MC5	1.8	1.96	1.20
MC6	1.8	7.58	14.0
HEC7	2.0	3.72	2.02
HEC8	2.0	5.39	3.09
HEC9	2.0	9.35	5.82

[a] molecular substitution (MS) for HPC and HEC.

Initial weight-average molecular weights of the polymers were determined from intrinsic viscosity on the basis of the Mark-Houwink equation [η] = K x DP[a] (for CMC, HPC and HEC) and [η] = K x M_w[a] (for MC), where K and a are constants, DP is the weight-average degree of polymerization. To calculate molecular weight, the obtained DP was multiplied by the mass of the substituted anhydroglucose unit. The viscosity was measured by an Ubbelohde viscometer in water or in 0.1 M NaCl aqueous solution, in the case of CMC, at 25°C. For these polymers constant K and a are equal to 1.8 x 10^{-2}, 0.97 for CMC [11], respectively; 7.2 x 10^{-3}, 0.915 for HPC [12]; 1.1 x 10^{-2}, 0.87 for HEC [13] and 3.16 x 10^{-3}, 0.55 for MC [14]. Viscosity of degraded samples was examined with a rotary viscometer made by Tokyo Keiki Co. Ltd., Japan, after dilution to the concentration of 1%.

Amount of gel fraction and swelling properties of CMC hydrogel were determined gravimetrically. Gel content in the dried hydrogels was estimated by measuring insoluble part after extraction in deionised water for 7 days at room temperature. Gel fraction was calculated as follows:

$$\text{Gel fraction [\%]} = (Gd / Gi) \times 100 \qquad (1)$$

where: Gi is the initial weight of polymer, Gd is the weight of the dried insoluble part after extraction.

Degree of swelling was estimated after the gel placed in deionised water reached equilibrium. When Gs is the weight of hydrogel in swollen state, swelling was calculated as follows:

$$\text{Swelling [grams of water / 1 g of dried gel]} = (Gs - Gd) / Gd \qquad (2)$$

Radiation yields of crosslinking and scission were calculated on the basis of Charlesby-Rosiak equation by sol-gel analysis [15].[1]

Enzymatic degradation was carried out in an acetic acid – NaOH Buffer, at pH 5.0, by cellulase enzyme. About 10 mg of dried film of gel

132

part, with a thickness about 0.3 mm, were immersed in the enzyme solution of volume of 2.5 ml at 35°C, for given time. The concentration of the enzyme was 0.1 mg ml^{-1}. After incubation, the samples were kept in distilled water to wash away the degraded polymer then, dried at 35°C under vacuum. Result of degradation is expressed as remained sample weight:

$$\text{Sample weight } [\%] = Ge / Gd \times 100\% \tag{3}$$

where Ge and Gd are the weights of film after and before enzymatic tests, respectively.

The microbial degradability of polymer in composted soil was evaluated on the base of the production of CO_2. Microbial Oxidative Degradation Analyzer [16], comprised of 4 independent measurement lines, was used. Sample mixed with sand and compost was placed in heated reaction columns. Produced CO_2 was collected quantitatively. Pure compost as well as contained cellulose was used as reference.

3. RESULTS AND DISCUSSION

All examined polymers exposed to γ-rays in solid state and in diluted aqueous solution undergo mainly degradation. In Fig. 1 there is presented a degradation of HPC2. The viscosity of solutions was measured after their dilution to the concentration of 1%. The most significant decrease of viscosity has been observed at the early stages of irradiation, at low doses. The rate of viscosity reduction is lower for solid than for solution. It proves that the presence of water accelerates radiation-induced reactions by indirect effect, through intermediate products of water radiolysis. It seems
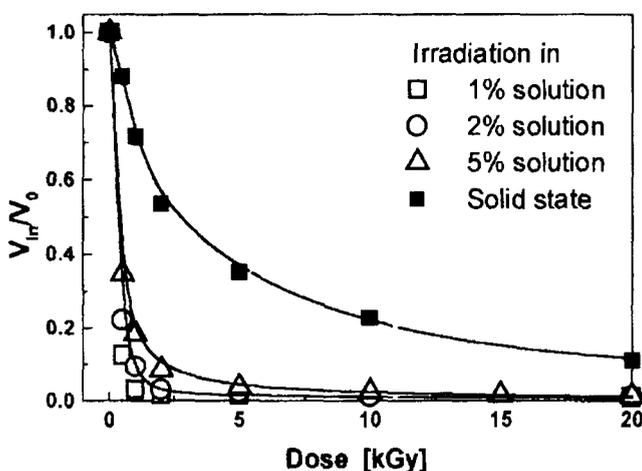

Fig. 1. Degradation of HPC2 irradiated in solid and diluted aqueous solution. Viscosity of solutions after dilution to 1% concentration: V_{irr} – the viscosity of polymer solution after irradiation, V_0 – initial viscosity of the polymer.
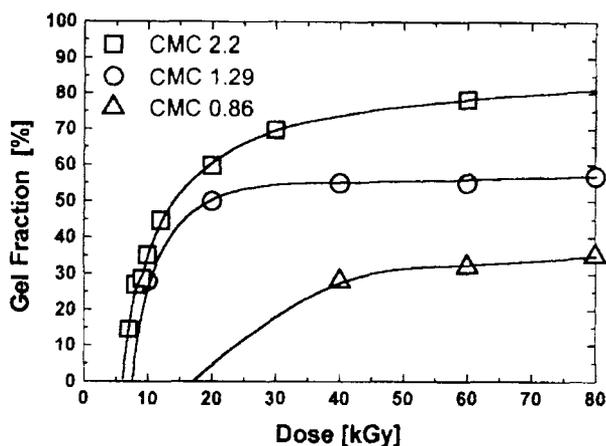
Fig. 2. Crosslinking of CMC of different degree of substitution in aqueous solutions.

that in this case the reduction of the solution viscosity is directly related to the diminishing of molecular weight of the HPC. The cleavage of main chain bonds occurs randomly, thus the longest chains undergo the most frequent breaks. It was postulated that cellulose and its derivatives degrade by the rupture of glycosidic bonds, which are the weakest in the main chain of such macromolecules [17, 18]. HPC1, the lower molecular fraction of the same polymer, CMC, HEC and MC, when irradiated in solid state or in diluted aqueous solution, degrade at the same manner under the ionizing radiation.
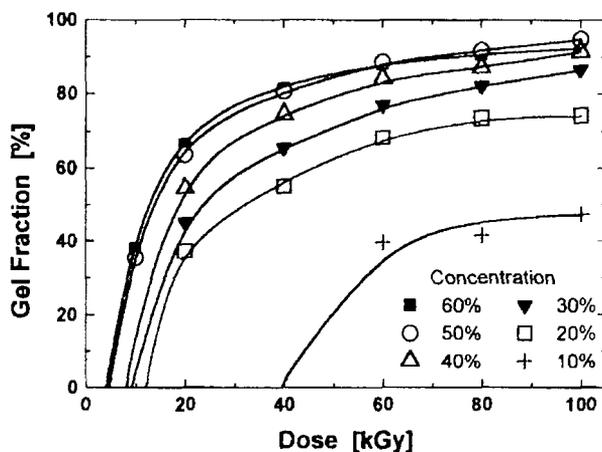

Fig. 3. Crosslinking of CMC 2.2 irradiated by EB in deoxygenated aqueous solution.

Crosslinking successfully competes with the glycoside bone cleavage as the concentration of cellulose derivatives in solution oversteps some critical value. Gelation occurrence depends on the molecular weight, the degree of substitution of cellulose and irradiation conditions. CMC with

higher DS form gel easier and more efficiently than that with lower DS as presented in Fig. 2 for 20% solutions. CMC with a DS of 2.2 gives the highest gel content among the three samples. Hence, it can be concluded that intermolecular linkages are a result of ionizing of side groups. In Fig. 3 the formation of gel is showed for CMC 2.2 irradiated by EB at high concentrations. These results do not differ much from those got for γ-rays irradiation. For this polymer irradiated with a dose of 100 kGy at concentrations 50 and 60% the amount of gel fraction equals to about 95%. The maximum of gel fraction obtained for the same dose in 10% aqueous solution is less than 50%.

The summary of results obtained for radiation processing of CMC is presented in Fig. 4. The two areas are distinguished. Crosslinking of CMC with a high DS occurs even at a relatively low concentration, whereas for CMC with a low DS a high concentration of solution is required to achieve insoluble gel. Thus, crucial for gel production is application of cellulose derivative with a high DS and irradiation of the derivative on aqueous solution at high concentration.
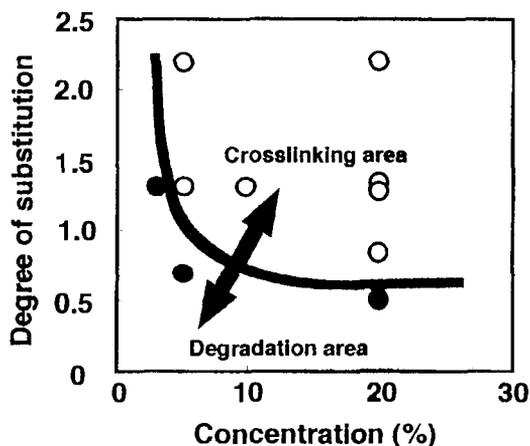

Fig. 4. Influence of degree of substitution and concentration of CMC in aqueous solution on formation of gel under action of ionizing radiation.

Estimation of radiation yield of crosslinking and scission delivers the information, which characterize behavior of polymers under the influence of high-energy radiation. The absolute values of the radiation yields of crosslinking and scission for solutions of CMC with a DS of 2.2 treated by EB are presented in Fig. 5. The radiation yield of scission, G(s) remains at the same level, on the other hand the radiation yield of crosslinking grows progressively throughout all examined concentrations. This is the reason of increasing ability to formation of gel for more concentrated solutions (compare Fig. 2).
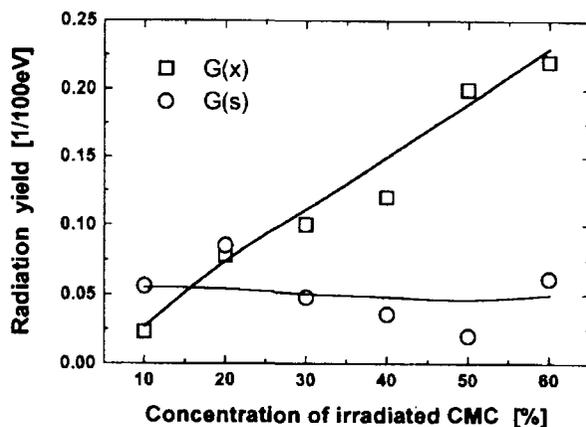
135

Fig. 5. Values of radiation yield of crosslinking, G(x) and degradation, G(s) of CMC with a DS of 2.2 irradiated by an EB in aqueous solutions.

Opposite to CMC, the formation of gel at solutions of HEC and HPC differs considerably due to the type of irradiation. The gel fraction is significantly higher for irradiation with higher dose rate as presented in Fig. 6. EB irradiation results in the formation of gel fraction as high as 85%.
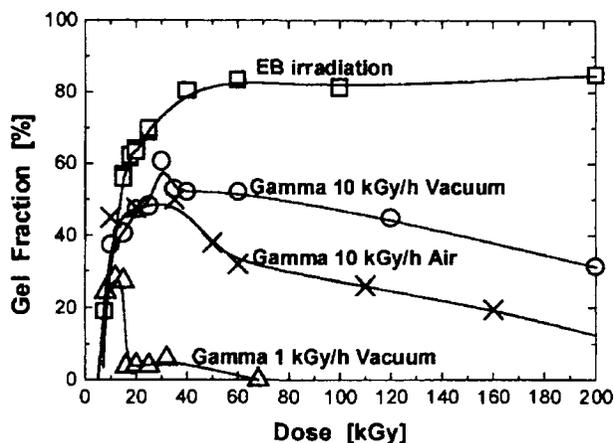

Fig. 6. Crosslinking of HPC2 irradiated with different conditions at 20% aqueous solution.

Gamma processing with the dose rate 10 and 1 kGy/h gives maximum of gel fraction less than 60 and 30%, respectively. It seems that the temporal concentration of free radicals in the system, determined by the dose rate, is the important factor influencing the formation of gel. To the intermolecular recombination it is required the existence of two active species on neighboring chains at the same time. The probability of such situation is higher as higher is the dose rate. Under the chosen conditions of irradiation the concentration of radicals in the system varied ca. 500 (or 5000 for 1 kGy/h) times. It is due to the fact that EB irradiation gives more than

136

several hundreds times higher dose rate comparing to γ-irradiation. In the HPC solution irradiated by γ-rays with increasing doses glycosidic bond cleavage prevails over crosslinking and the created network again becomes soluble. The presence of oxygen in the system, during gamma irradiation, drastically diminishes the maximum gel fraction. It was observed also for CMC, HEC and MC. It is due to the reaction of oxygen with macroradicals, which transform into peroxy-macroradicals, and subsequently decompose with rupture of main chain of the macromolecule [19].

Concentration and length of the initial polymer chains affect the results of irradiation, what is depicted in Fig. 7. Higher initial average molecular weight of the polymer enhances the share of gel in the produced hydrogel. Comparable results, with a strong dependence on the initial molecular weight and irradiation conditions were obtained for all examined polymers.
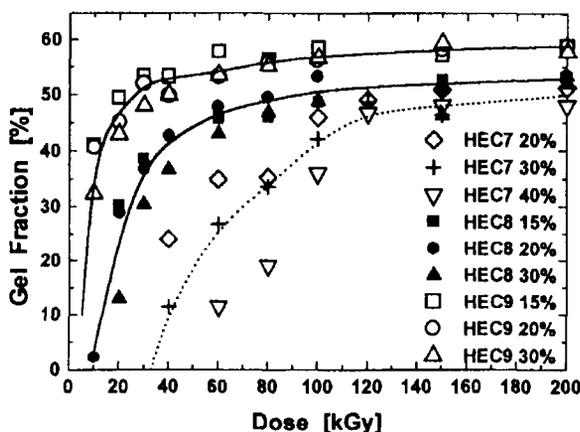

Fig. 7. EB irradiation of HEC of various molecular weight in deoxygenated aqueous solution.

Hydrogels of CMC with a DS of 2.2, as well as those formed from other cellulose ethers, exhibit swelling properties related to an initial concentration of polymer in solution and to applied dose. It is presented in Fig. 8. Swelling ability is the highest for hydrogels at low doses and drastically reduces with dose increasing. For formation of gel from linear polymer statistically one crosslink bond per chain is necessary. Such network is weak and susceptible for breaking but, because of relatively low number of intermolecular bonds, is able to high expansion by holding the water into its voids. With subsequent increasing the density of crosslinks, due to additional irradiation, the absorption ability of the gel decreases. The hydrogel structure becomes more tightly connected and rigid.

Hydrogels of cellulose derivatives undergo degradation by cellulase enzyme. The results for CMC with a DS of 2.2 prepared by γ-irradiation at from 50% aqueous solutions are shown in Fig. 9. Hydrogels with lower

density of crosslinks (formed by lower dose) degrade faster than that crosslinked more tightly (higher dose). Samples formed by absorption of the
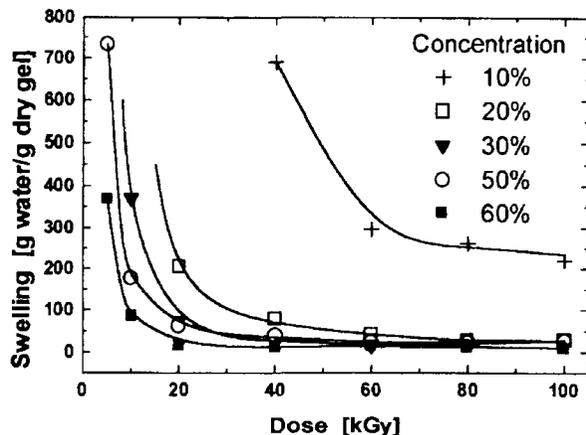

Fig. 8. Swelling in water of CMC 2.2 hydrogels formed by EB irradiation of deoxygenated aqueous solutions.

energy of 20 kGy disintegrate completely after 95 hours. For gels irradiated with a dose of 40 kGy and above the degree of degradation does not exceed 60% after 96 hours of incubation.
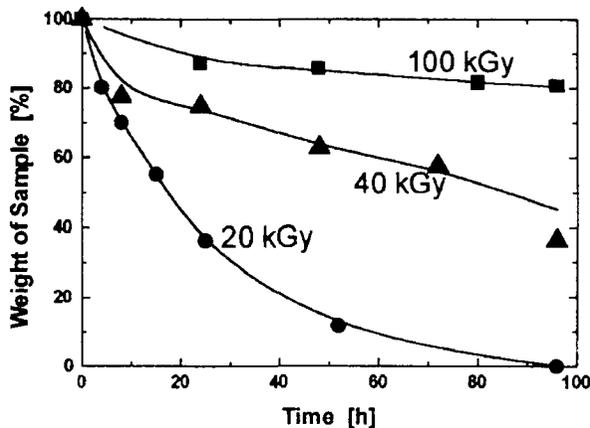

Fig. 9. Enzymatic degradation of CMC 2.2 hydrogel formed in 50% γ-rays; cellulase enzyme in acetic acid – NaOH buffer, pH 5.0, at temperature 37°C.

Microbial degradability was evaluated by measuring of carbon dioxide produced from decomposed polymeric material. Samples of CMC with DS of 1.29 and 2.2, also cellulose as a reference material, were used in these experiments. The results are presented in Fig. 10. Cellulose undergoes the fastest degradation, which reaches ca. 80% after 1 month (after subtraction of CO_2 produced by pure compost). CMC decomposes much slower. CMC with a DS of 2.2 degrades after 1 month in 3.8% –

unirradiated and 8.4% – irradiated and CMC with a DS of 1.29 degrades in 12.3 and 18.7%, respectively. The derivative with a higher DS disintegrates slower. Side chains prevent the destruction of backbone by making the access of microorganisms to the vicinity of glycosidic bond difficult. Radiation treatment of the polymer improves its susceptibility for
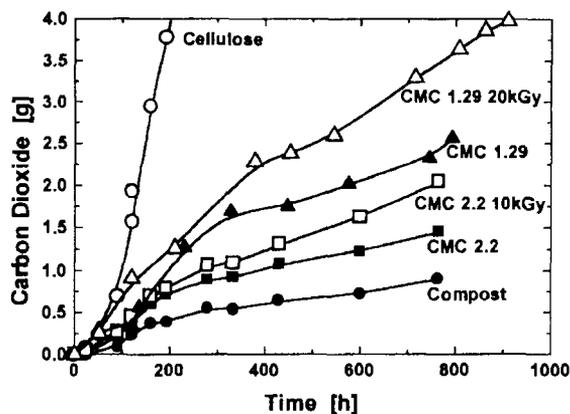

Fig. 10. Microbial oxidative degradation in compost soil of CMC 2.2 and 1.29, unirradiated and irradiated.

bacterial digestion. CMC with DS of 2.2 and 1.29 irradiated in 20% aqueous solution with dose 10 and 20 kGy, undergoes faster decomposition despite some crosslinks were introduced. The gel fraction of examined hydrogels was 15% for CMC with a DS of 2.2 and 47% for CMC with a DS of 1.29. At the base of these results we can state that hydrogels made from cellulose ethers by irradiation are degradable.

4. CONCLUSIONS

On the basis of our experimental work it can be concluded:
- Cellulose ethers in concentrated aqueous solutions undergo crosslinking initiated by ionizing radiation.
- Resulted material exhibits typical properties of hydrogels, such as relation of crosslinking degree on absorbed dose, ability to swell to equilibrium state, an increase of the mechanical properties, etc.
- Domination of radiation crosslinking over degradation is possible only for cellulose ethers characterized by high degree of substitution and irradiated in very concentrated solutions.
- Domination of crosslinking over scission for cellulose ethers can be explained as a result of the increase of the probability of intermolecular bonds formation via radicals localized on side groups of cellulose main chain.
- Resulted hydrogels, similar to their origin polymers undergo biodegradation.

139

LITERATURE

[1]. Nichlson M.D., Merritt F.M.: W: Cellulose chemistry – its application. Eds. Th. Nevell, P. Zerorian, S. Haig. Hprwood Publ., Chichester 1989, p. 363.

[2]. Rosiak J.M., Ulanski P.: Radiat. Phys. Chem., 55 (2), 139 (1999).

[3]. Rosiak J.M., Olejniczak J.: Radiat. Phys. Chem., 42, 903 (1993).

[4]. Rosiak J.M.: J. Cont. Rel., 31, 9 (1994).

[5]. Tabata Y., Ito S., Tagawa S.: CRC Handbook of Radiation Chemistry. CRC Press, Boston 1991, XIV 742, Table XIV.15.

[6]. Charlesby A.: J. Polym. Sci., 15, 263 (1955).

[7]. Leavitt F.C.: J. Polym. Sci., 45, 536 (1960).

[8]. Leavitt F.C.: J. Polym. Sci., 51, 349 (1961).

[9]. Fei B., Wach R.A., Mitomo H., Yoshii F., Kume T.: J. Appl. Polym. Sci., 78, 278 (2000).

[10]. Wach R.A., Mitomo H., Yoshii F., Kume T.: J. Appl. Polym. Sci., 81, 3030 (2001).

[11]. Wrick M.G.: J. Polym Sci., Part A, 6, 1965 (1968).

[12]. Guido S.: Macromolecules, 28, 4530 (1995).

[13]. Brown W., Henley D., Ohman J.: Macromol. Chime., 63, 49 (1963).

[14]. Neely W.B.: J. Polym. Sci., Part A, 1, 311-320 (1963).

[15]. Olejniczak J., Rosiak J.M., Charlesby A.: Radiat. Phys. Chem., 37, 499 (1991).

[16]. JP 97293597.

[17]. von Sonntag C.: Adv. Carbohydr. Chem. Biochem., 37, 7 (1980).

[18]. Nagasawa N., Yoshii F., Mitomo H., Kume T.: Polym. Degrad. Stab., 63(3), 279 (2000).

[19]. Ulanski P., Bothe E., Rosiak J.M., von Sonntag C.: Macromol. Chem. Phys., 195, 1443 (1994).

---

[1] Specially designed computer program was kindly provided by Professor J.M. Rosiak of the Institute of Applied Radiation Chemistry, Łódź, Poland (http://mitr.p.lodz.pl/biomat/).

II. PRODUKCJA I METROLOGIA ŹRÓDEŁ PROMIENIOWANIA