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Radiation crosslinking of biodegradable hydroxypropylmethylcellulose

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Abstract

In general, cellulose and its derivatives irradiated with ionizing radiation in solid state or in dilute aqueous solution undergo mainly degradation by the cleavage of glycoside bonds in its main chain. Hydroxypropylmethylcellulose (HPMC) with different degree of substitution (1.9 and 1.4) was irradiated with electron beam (EB) radiation at ambient temperature and different doses (0–100 kGy) and concentrations (0.5–60 wt%). Irradiation of HPMC in aqueous solutions at reasonable concentrations (paste-like condition) resulted in the formation of gels. Gel content was found to increase with increase of radiation dose and decrease of HPMC concentration within the range studied. Ten and 30 wt% concentrations of HPMC irradiated at 30 Gy dose were chosen as the working systems for further experiments. HPMC with higher degree of substitution gave higher gel contents at every concentration and irradiation doses. HPMC gels (1.9) swelled by absorbing more than 2500 g of water per gram of dry gel at a low applied dose. Swelling experiments of HPMC gels were carried out in different solvents, at different pHs and temperatures. Experimental results showed that HPMC has both hydrogel and organogel characters showing pH dependence only at pH values greater than 8.0. HPMC gels are also highly swollen at low temperatures, gradually deswelling as temperature rises, usually sharply over a limited temperature range similar to temperature-sensitive hydrogels. To investigate the radiation induced degradation of HPMC at low concentrations, viscosity of degraded samples was measured using rotational viscometer. Viscosity of HPMC samples after irradiation became smaller with increasing dose because of the cleavage of glycoside bonds. Biodegradation study of crosslinked HPMC gels was carried out with cellulase enzyme in buffer solutions. The enzymatic degradation tests showed within 24 h, the weight loss of HPMC gel obtained at 30 kGy irradiation was 95%. It has also been observed that biodegradation of HPMC with high degree of substitution was relatively slow than that of HPMC with low degree of substitution due to its structural properties.

Keywords: Hydroxypropylmethylcellulose; Electron beam irradiation; Paste-like; Biodegradation

1. Introduction

The growing problem of non-biodegradable plastic waste and the resulting general shortage of landfill availability; and the need for the environmentally sensitive use of resources together with the CO_2 neutrality aspects are two main reasons for the interest in biodegradable plastics and polymers (Simon, Müller, Koch, & Müller, 1998). Biodegradable products should not only fulfill their task excellently but after use and disposal should degrade easily in the soil by the action of naturally occurring microorganisms. Nowadays, utilization of high-energy radiation (gamma or electron beam) is commonplace in the modification of biodegradable plastics (Song, Yoshii, & Kume, 2001). Irradiation of polymers is generally aimed at introducing a desired amount of crosslinking (increasing molecular weight of polymer) or chain scission (decreasing molecular weight of polymer). Crosslinking will cause an increase in tensile strength, elongation, modulus of elasticity, hardness and softening temperature. On the other hand, chain scission decreases these properties.

Cellulose ethers are high-molecular-weight compounds wherein the hydrogens of the hydroxyl groups of cellulose have been partially replaced by alkyl or substituted-alkyl groups in order to modify the character of the native cellulose. Such modification may range from mere alteration of the surface characteristics of a textile, through solubility in various solvents, to thermo plasticity.

The average number of hydroxyls in the anhydroglucose unit that are substituted in a particular product is known as

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the degree of substitution (DS). The DS value may range from 0 (cellulose itself) to a maximum of 3.0 (fully substituted cellulose). In certain instances, the added substituent may also contain a hydroxyl group, and this hydroxyl of pendant chain may react with the reagents more readily than the hydroxyls of the cellulose. Thus, if ethylene oxide is the reagent, poly(ethylene oxide) chains result. The term molar substitution (MS) was coined to describe the total number of moles of such a reagent that become attached to the cellulose or to the chain. Such a compound may, for example, have an MS of four, but its DS may be only one, and in no case can its DS exceed three. The length of the pendant chain will be MS/DS = 4/1, or 4 units. If a DS value that permits solubility in organic solvents is reached, this may also confer thermoplasticity upon the product (Doelker, 1993). Cellulose ethers may contain a variety of substituent groups, based on varying degrees of substitution, and accordingly are soluble in a variety of solvents.

Hydrogels are two- or multi-component systems consisting of a three-dimensional network of polymer chains and water that fills the space between macromolecules. Their ability to absorb water is due to the presence of hydrophilic groups such as $-OH$, $-CONH-$, $-CONH_2$, $-COOH$, and SO_3H (Kost, 1996). Hydrogels can be considered of physical or chemical nature according to the class of bonds existing between individual polymer chains; physical hydrogels have weak hydrogen bonds or electrostatic interactions, while in chemical hydrogels chains are cross-linked as a result of covalent bonds between polymer chains. The interchain crosslinks can be obtained either by reaction with chemical reagents or by means of ionizing radiation (Bray & Merril, 1973; Chen, Bao, & Zhang, 1985).

As compared to conventional methods of preparation, the use of ionizing radiation in hydrogel preparation have some advantages, which include easy process control, possibility of joining hydrogel formation and sterilization in one technological step, no need to add any initiators, cross-linkers, etc. which are possibly harmful and difficult to remove, no waste, relatively low running costs which altogether make irradiation the method of choice in the synthesis of hydrogels, especially for biomedical applications. Also from the point of view of radiation chemistry, cross-linking of polymers, including hydrogel formation, belongs to one of the most successful applications of this branch of science (Güven, Şen, Karadağ, & Saraydın, 1999; Rosiak & Ulanski, 1999). Therefore, the main areas of applications of hydrogel materials prepared with high-energy irradiation include: drug delivery system, wound dressing, injectable polymers, implants, contact lenses, stimuli responsive systems.

Although, high-energy irradiation provides a clean and efficient method for gel formation, it can also lead to degradation of polymer chains and loss of viscosity (Peppas, 1987). Polysaccharides, including cellulose derivatives, generally degrade by breaking of glycosidic linkage under ionizing radiation. But in some cases, chemical gels can be made using high-energy radiation under mild conditions as paste-like that do not degrade polysaccharides. Fei, Wach, Mitomo, Yoshii, and Kume (2000) studied degradation and crosslinking of different type of cellulose derivatives using high-energy radiation. They showed that in dilute solutions and also in solid form cellulose molecules are degraded by high-energy radiation but crosslinked under special conditions.

HPMC is used whenever there is a need to thicken, gel, emulsify, suspend, stabilize, get water retention and good workability, etc. For example, HPMC can be successfully applied in building materials as providing excellent workability and water retention; in paint removers, adhesives and glues, polymerization, printing inks, cosmetics, paints and coatings as thickening agent; in ceramics as providing water retention and lubricity; in agriculture and textiles as binders (Choe, 2000).

In this study, we aimed to synthesize biodegradable hydroxypropylmethylcellulose (HPMC) hydrogels having different DS in *paste-like condition* (neither solid nor aqueous) by using high-energy radiation from electron accelerators. Swelling properties were investigated in different environmental media such as pH, temperature, organic solvent, etc. Viscosity of degraded HPMC samples was investigated using rotational viscometer. Biodegradation of HPMC was carried out in enzymatic medium under the attack of cellulase.

2. Experimental

2.1. Materials

HPMC was used as received as a sample from Shin-Etsu Chemical Co. Ltd (Japan). The properties of HPMC samples are collected in Table 1. $H_3PO_4-NaH_2PO_4-Na_2HPO_4$ (pH 1.68–8.0) and $Na_2B_4O_7-NaOH$ (pH 9.0–10.01) buffer solutions used in the swelling experiments were purchased from Kanto Chemical Co., Inc. (Japan). At pH 11.00, the pH of medium was adjusted using 0.02 M $CH_3COOH-NaOH$

Table 1
The properties of HPMC samples (Shin-Etsu Chemical Co, 2001)

Chemical name		Hydroxypropylmethylcellulose	
Type		HPMC 60SH	HPMC 90SH
Methoxyl group ($-OCH_3$)	DS	1.9	1.4
	%	28.0–30.0	19.0–24.0
Hydroxypropoxyl group ($-CH_2CHOHCH_3$)	MS	0.25	0.20
	%	7.0–12.0	4.0–12.0
Viscosity (mPa s)		4270	4370
Weight-average molecular weight (g/mol)		3.1×10^5	3.5×10^5

buffer system. Swelling experiments were also carried out in different solvents having different polarities. All solvents ($CHCl_3$, CCl_4, C_2H_5OH, CH_3OH) used for swelling experiments were supplied from Wako Chemical Co., Inc. (Japan). The cellulase enzyme C-0901, from *Penicillium funiculosum*, was obtained from Sigma Chemical Co. (USA).

2.2. Preparation of crosslinked HPMC samples

HPMC was mixed homogeneously with water to give certain concentration which is varying from 0.5 to 60 wt%. The dispersed materials were kept for a few days at room temperature to ensure complete dissolution and uniform distribution of polymer chains. Higher concentration solutions (≥ 30 wt%) were very thick gels almost like solid. After few days, HPMC solutions were poured between two PTFE sheets to form film using IKEDA Cold Press and then placed into poly(vinylidene chloride) bag to avoid the penetration of oxygen during irradiation, after removal of the air by a vacuum pump. The HPMC samples were irradiated with an electron beam (EB) generated from a Cockcroft-Walton type accelerator (maximum voltage and current are 2 MV and 30 mA, respectively). The irradiation was carried out at 1 mA beam current and acceleration energy of 1 MV at an apparent average dose rate of 1.4 Gy/s. The material used in EB irradiation was in the shape of film with a thickness of 0.5 mm. The thickness of samples with covering sheet and package was less than 1 mm, which guaranteed the uniform penetration of beam and distribution of energy throughout the entire material.

2.3. Viscosity of degraded HPMC samples

To investigate the degradation of HPMC at very low concentrations, the viscosity of HPMC solutions (0.05–0.25 wt%) after irradiation were measured by using rotational viscometer (Tokimec Viscometer Model TV-20) at 30 °C. The viscosities of unirradiated samples were also measured and results were presented as a ratio of the viscosity of irradiated samples to unirradiated samples with changing irradiation dose.

2.4. Determination of gel fraction and degree of swelling of HPMC samples

Irradiated HPMC samples were dried in air and in a vacuum oven and weighed. To remove uncrosslinked polymer, the samples were extracted with water for 48 h and then dried again to determine gel fraction (Eq. (1))

$$\text{Gel fraction (\%)} = \frac{w_g}{w_0} \times 100 \qquad (1)$$

where w_0 is the initial weight of dry gel and w_g is the weight of dry gel after water extraction.

Dried HPMC hydrogels (W_0) were accurately weighed and transferred into water. Water uptake with respect to time was obtained by periodically removing a sample from water, quickly blot drying and reweighing (W_t). Degree of swelling ($S\%$) was calculated as follows

$$\text{Degree of swelling (\%)} = \frac{w_t - w_0}{w_0} \times 100 \qquad (2)$$

Swelling experiments were carried out in different solvents, temperatures and pH values.

2.5. Biodegradation studies

Enzymatic degradation of irradiated HPMC samples (10, 30 and 40 wt% irradiated to 30 kGy dose) was investigated using cellulase enzyme (at a concentration of 0.025 mg/ml from preliminary tests). The degradation experiments were performed at 37 °C, in $CH_3COOH–NaOH$ buffer at pH 5.0. Before measuring the initial weights, HPMC samples were cut into pieces approximately 0.5 cm × 0.5 cm and dried under vacuum at 40 °C for 24 h. Then the samples were placed into small vials containing 2.5 ml of enzyme solution and shaken for reaction at different periods of time. After the reaction samples were taken out from the vials, then washed with distilled water and dried in vacuum to constant weight. The biodegradation was observed by measuring the ratio of weight loss to the initial weight of the sample. Weight loss was calculated from the decrease of weight of the sample before and after the enzymatic degradation test.

3. Results and discussion

3.1. The effect of irradiation on HPMC samples

The effects of ionizing radiation on polymeric materials can be manifested in one of three major ways. The polymer may undergo one or both of the two possible reactions: those that are molecular weight increasing in nature, or molecular weight reducing in nature. Or, in the case of radiation-resistant polymers, no significant change in molecular weight will be observed. The conventional term for irradiation-induced increase in molecular weight is cross-linking. The corresponding term for irradiation-induced decrease in molecular weight is chain scission (or degradation).

Interactions of high-energy radiation with polysaccharides result in dehydrogenation, oxidative degradation, and depolymerization reactions and destruction of the basic monomer units. It is known that after irradiation cellulose molecules are altered by breaking of glycosidic linkages and the introduction of carboxyl and carbonyl groups (Nitzel, 1984). With increasing dose there was an increasing formation of these groups and the yields were slightly greater when cellulose was irradiated in air as compared with irradiation in an oxygen-free atmosphere.

The degradation of cellulose was studied using different radiation sources. These studies showed that when cellulose is irradiated by γ-radiation, neutrons and also X-rays, chain scission occurs to give rise to carbonyl- and carboxyl-groups (Charlesby, 1955; Leonhardt et al., 1985; Mares & Arthur, 1969). However, in most cases, the results obtained during their tests could not be described in relation to EB irradiation. EB irradiation of crosslinkable plastics has yielded materials with improved dimensional stability, reduced stress cracking, higher service temperatures, reduced solvent and water permeability, and significant improvements in other thermomechanical properties. In EB irradiation, the concentration of radicals in the system is assumed to be significantly higher than during γ-irradiation for a given dose due to high dose rates involved. For the formation of a crosslinking bond, the presence of two radicals on adjacent chains is required. Their subsequent recombination results in the formation of a chemical bond between two polymeric chains. Thus, high dose rate is more efficient for crosslinking reaction.

It is known that cellulose derivatives exposed to high-energy irradiation either in solid state or in dilute aqueous solution lead to degradation (Arthur, 1973; Fei et al., 2000). Degradation of HPMC in dilute aqueous solution was studied using rotational viscometer. Fig. 1 shows the degradation of HPMC with low DS (HPMC 90SH) as a function of dose. Here, V_o and V_{irr} denote the dynamic viscosity of aqueous solutions of HPMC samples before and after irradiation, respectively. As it can be seen, the viscosity of HPMC samples after irradiation decreased sharply with increasing dose and leveled-off at around 40 kGy dose. Wach, Mitomo, Yoshii, and Kume (2002) observed similar behavior in aqueous solutions of hydroxypropylcellulose (HPC) after irradiation. In dilute aqueous solutions, although the chain mobility is unrestricted, the distance between macroradicals become large to form crosslinking bond, therefore, degradation occurs predominantly. Restricted mobility during irradiation in solid is the main cause of scission when macromolecules bearing of radicals are immobilized by the surrounding matrix of semi-crystalline phase. The rate of viscosity reduction is lower for solid state than for solution irradiation. It also proves that the presence of water accelerates radiation-induced reactions through indirect effect.

Although, in dilute aqueous solution and in solid form cellulose derivatives undergo degradation, some evidence of high energy initiated crosslinking of cellulose derivatives has already been reported (Desai & Shields, 1970; Fei et al., 2000). When HPMC is irradiated at moderate concentration, reactions leading to intermolecular crosslinking prevail and insoluble gel is formed. Fig. 2 shows gel fraction versus dose curves for different concentration of HPMC 90SH. As can be seen from figure, the gel fraction increases with absorbed dose, steeply at the beginning of gelation, and levels off asymptotically to the maximum value around 40 kGy. At the investigated region of concentrations there is no significant discrepancy in the gelation for both HPMC samples. The maximum gel fraction is independent of the initial molecular weight of the polymer and reaches around 80% at 60 kGy of the absorbed energy. At 40 kGy dose, gel fraction versus concentration of HPMC curves are shown in Fig. 3. Gel fraction first increased with HPMC concentration up to 10% and reached to a maximum value, then gradually decreased. The reason of this observation can be explained

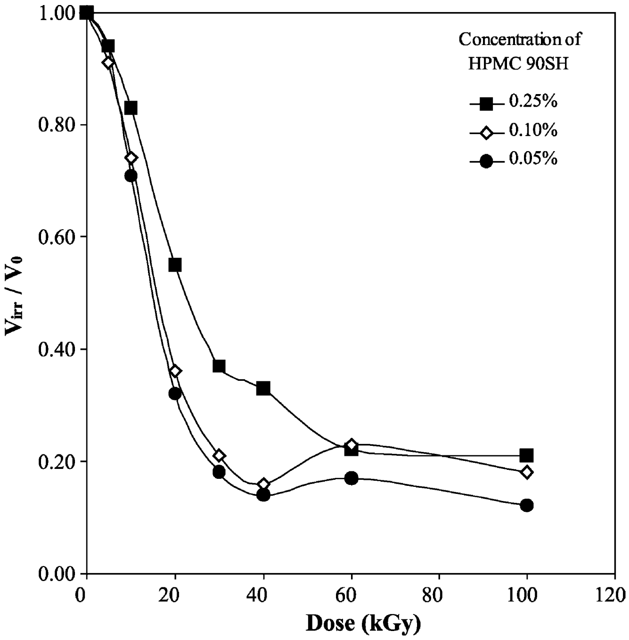

Fig. 1. Degradation of HPMC 90SH in dilute aqueous solutions by electron beam irradiation, V_{irr}; the viscosity of degraded samples after irradiation and V_o; the viscosity of original sample.

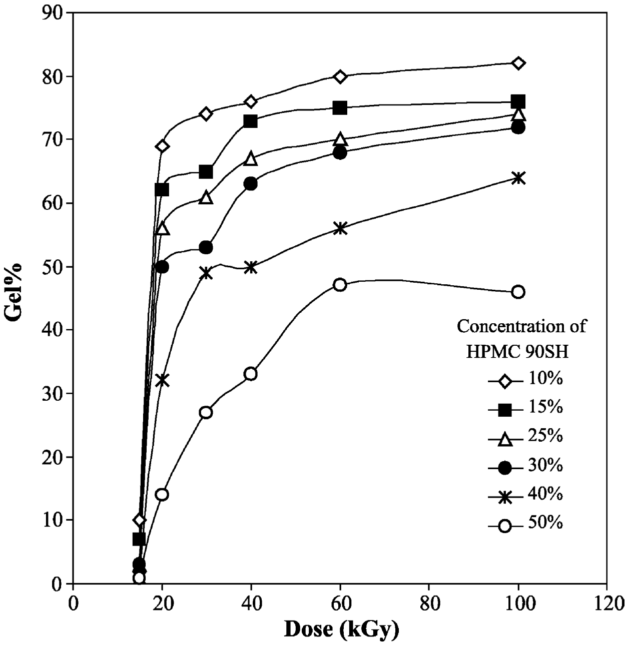

Fig. 2. The change of extent of gelation of HPMC 90SH aqueous solutions with dose. The initial concentrations of HPMC solutions are given in the figure.

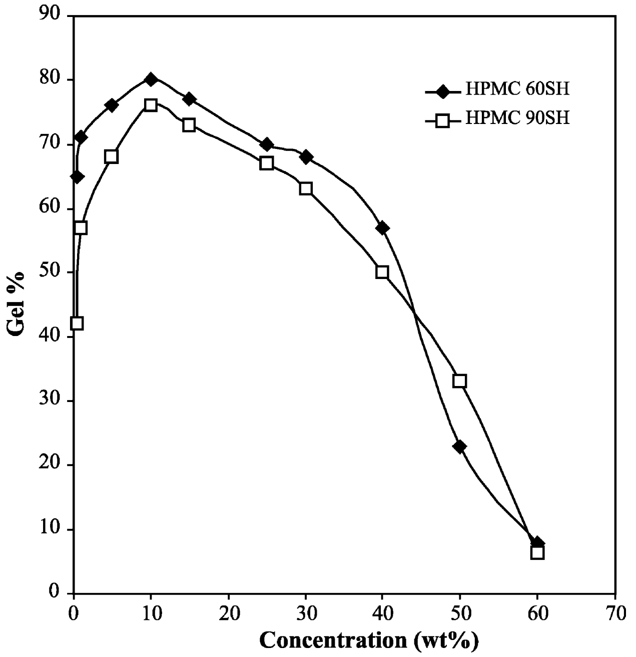

Fig. 3. The concentration dependence of maximum gel values obtained for both HPMC samples irradiated at 40 kGy dose.

by water effect on irradiation of HPMC. Up to 10 wt% concentration of HPMC gel fraction increased with increasing concentration due to the amount of water increases the probability of combining of macroradicals in dilute solutions. Around 10 wt% concentration of HPMC water ensures reasonable distance between macroradicals to form crosslinking bond. At this stage, it is important for crosslinking that the polymer is homogeneously dissolved in water. It is well known that cellulose has a highly crystalline structure even if some hydroxyl groups are replaced by other substituent groups. During irradiation, crosslinking bond forms in the amorphous region of cellulose. The crystalline part of cellulose degrades under irradiation (Park, 1963). The amorphous or disordered region of cellulose is accessible to water. Water normally breaks the hydrogen bonds in the amorphous part of cellulose and acts as a plasticizer allowing flexibility of the polymer chain and is not a barrier to the coupling of macroradicals. Beyond 10 wt% concentration of HPMC, gel fraction is decreased by increasing concentration of HPMC due to the high crystalline structure, which prevents the accessibility of water. And also at high concentrations the amount of water is not sufficient to provide the beneficial indirect effect to enhance the combination of macroradicals. Wach et al. (Fei et al., 2000; Wach et al., 2002) studied the high-energy radiation effects on various cellulose derivatives including carboxymethylcellulose (CMC) and HPC. They observed that maximum gel fraction was obtained in 50–60 wt% concentration for both cellulose derivatives. The reason of this discrepancy between HPMC and these cellulose derivatives was explained by chemical structure and DS.

Since crosslinking and scission occur simultaneously in the polymer during irradiation, the yield of crosslinking, $G(x)$, and degradation, $G(s)$ have an influence on the results of irradiation. The G value is the number of crosslink bonds or scission acts per 100 eV of absorbed energy. The yield values and gelation doses (D_g)—minimum energy required starting the gelation process—were estimated by gel–sol analysis on the basis of the Charlesby–Pinner equation (Charlesby, 1960):

$$s + s^{0.5} = \frac{p_0}{q_0} + \frac{1}{q_0 \bar{P}_n D}$$

where s is the sol fraction, p_0 and q_0 are the fractions of ruptured and crosslinked main chain units per unit dose (proportional to the radiation chemical yields of degradation and crosslinking $= G(s)/2G(x)$), respectively, $\bar{P}_n$ is the number average degree of polymerization of unirradiated polymer, and D is absorbed dose. A plot of $s + s^{0.5}$ against $1/D$ should be linear, with the intercept at $1/D = 0$ equal to p_0/q_0, that is, to $G(s)/2G(x)$.

If $\bar{P}_n$ is known, q_0 can be calculated from the slop of the plot and used, with the value of the intercept, to calculate $G(x)$. The chain scission ($G(s)$) and crosslinking ($G(x)$) yields obtained from the Charlesby–Pinner equation are collected and given in Fig. 4 in the form of $G(s)/G(x)$, ratio versus concentration of HPMC for both samples. This ratio, which measures relatively the extent of chain scission against crosslinking shows an interesting dependence on HPMC concentration. At low and high concentrations the ratio is high showing the prevalence of chain scission over

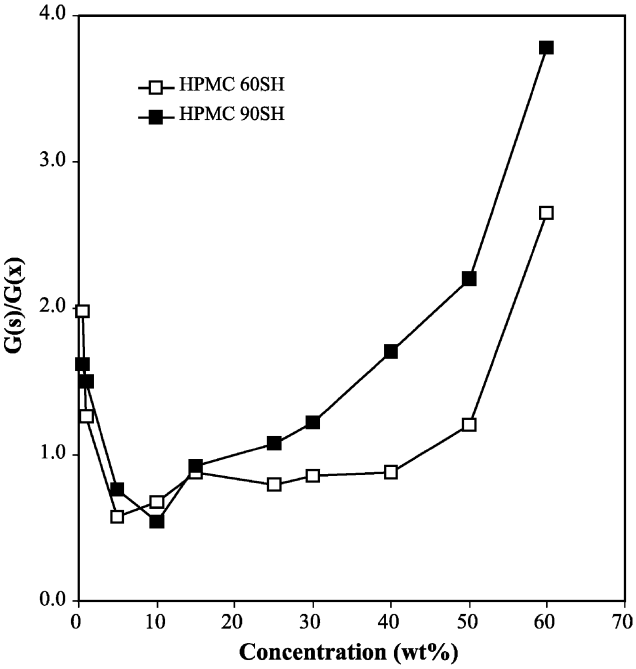

Fig. 4. The change of $G(s)/G(x)$, ratio of chain scission to crosslinking yields for two HPMC samples used in this work with initial polymer concentration.

crosslinking. In the moderate concentration range, $G(s)/G(x)$ is around one for both samples which coincides with the high gel values reported earlier.

3.2. Swelling properties of HPMC

HPMC gels were characterized in terms of their degree of swelling. The degree of swelling much depends on crosslink density hence irradiation dose. The relationship between the degree of swelling and dose for gels obtained at different concentrations are shown in Fig. 5 for HPMC 60SH. It can be seen from figure, that the higher the irradiation dose, the lower the degree of swelling within the concentration range studied in this work, at doses above D_g the crosslink density increases with dose. This reduces the average chain length between crosslinks, restricting the chain motion and extension. Volumetric expansion of the network reduces as a function of increasing crosslink density.

Swelling experiments were performed in organic solvents besides water. Fig. 6 shows the typical time dependence of the swelling ratio in water and some organic solvents. The HPMC gels swelled rapidly with immersing time and attained equilibrium value at around 25 h in water and 5 h in organic solvents for the geometries and sizes considered in this work. Having comparatively hydrophobic methoxyl and hydroxypropoxyl groups, HPMC is soluble in some organic solvents and also in water-organic solvent mixtures. Initial swelling rate and equilibrium swelling value of gels depend strongly on the thermodynamic quality of the solvent. Polarity and hydrogen bonding ability of solvents play decisive role in swelling HPMC gels.

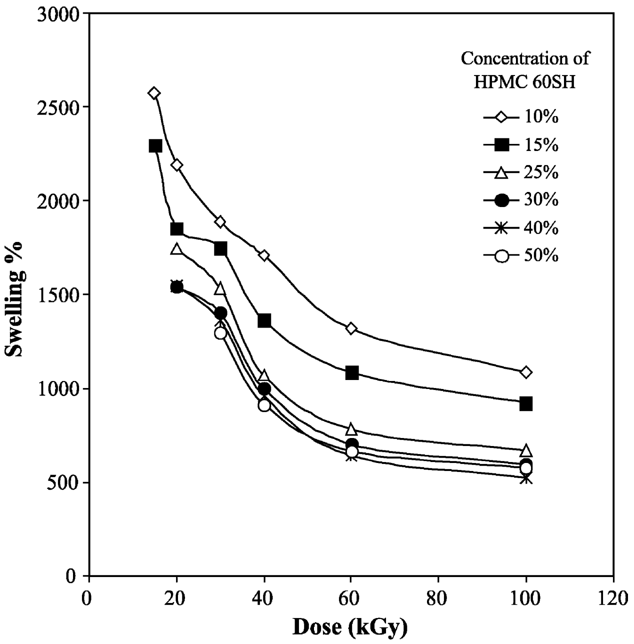

Fig. 5. The degree of swelling-dose curves for HPMC 60SH gels prepared from different initial concentrations as given in the figure.

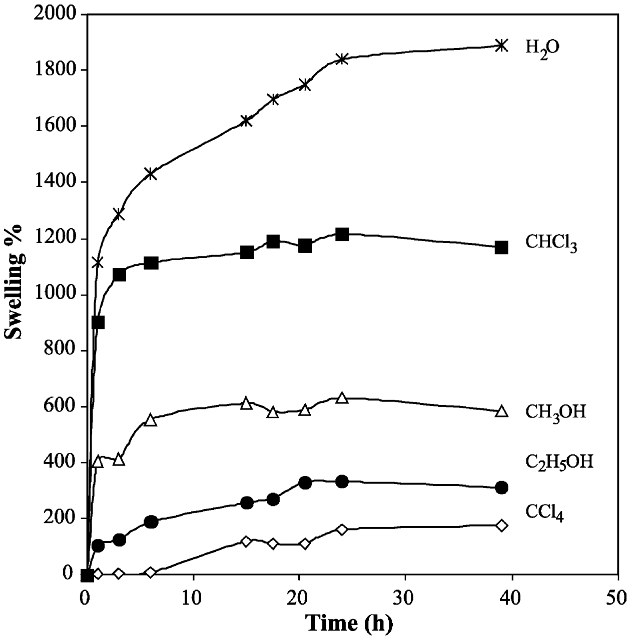

Fig. 6. Kinetics of swelling behavior of HPMC 60SH gels obtained at 10 wt% concentration, 30 kGy in different organic solvents.

Among the solvents used nonpolar CCl_4 gives the lowest and highly polar and strong H-bonding solvent water causes the highest extent of swelling. In order to have a quantitative measure for the thermodynamic quality of the solvents used, their solubility parameters (δ) are considered and used in the construction of Fig. 7.

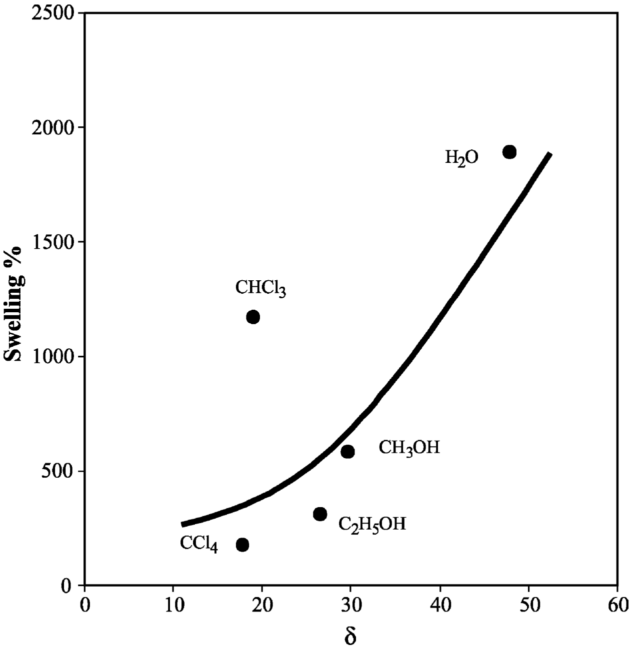

Fig. 7. The dependence of maximum degree of swelling on the solubility parameters (Brandrup & Immergut, 1989) of solvents used in Fig. 6 for HPMC 60SH prepared from 10 wt% concentration irradiated to 30 kGy $\delta(CCl_4) = 17.8$, $\delta(CHCl_3) = 19$, $\delta(C_2H_5OH) = 26.6$, $\delta(CH_3OH) = 29.7$, $\delta(H_2O) = 47.9$.

The increase in equilibrium value of swelling of HPMC gels follows nicely the δ values of solvents with the exception of the swelling value corresponding to $CHCl_3$.

Swelling behavior of HPMC gels were also investigated at different pHs ranging from 2.0 to 11.0. HPMC is a nonionic polymer, which does not show any polyelectrolyte behavior. The general behavior observed in Fig. 8 is that under identical conditions HPMC 90SH shows higher swelling than that of HPMC 60SH at every pH which is due to lesser DS of OH groups in the backbone. The swelling of gels are almost pH independent of 2.0–7.0. A significant increase in swelling is observed at pH values from 8.0 to 11.0, in alkaline medium. The possibility of chain cleavage or alkaline cellulose formation due to replacement of –OH by $-O^-Na^+$ is rather low due to mild solution conditions. The steep increase observed in swelling takes place at pH values of 8.0 and 9.0 for HPMC 90SH and 9.0, 10.0 and 11.0 for HPMC 60SH. This can be explained by the effect of anion used in the preparation of buffer solutions. It is known that (Savage, 1965) perborate salts enhance the solubility of hydroxyethylcellulose. We therefore assume that the increase in swelling in the presence of tetraborate is due to the fortuitous change brought about in solvent quality of water.

Temperature is one of the most significant parameters affecting the phase behavior of gels. The volume-phase transition of a thermo-sensitive gel was first reported by Hirokawa, Tanaka, and Matsuo (1984) in poly(*N*-isopropylacrylamide) gel in water. Thermo-sensitive behavior is caused by the balance between hydrophobic interaction of the polymer network and water. For polymers showing lower critical solution behavior at higher temperatures the polymer network shrinks and becomes more closely packed while the water molecules excluded from the polymer network. From preliminary UV–vis spectroscopic studies, we found that an aqueous solution of HPMC precipitated or gelled when heated to a certain temperature, but it reverted to the original solution state on subsequent cooling. The gelation or precipitation temperature changed depending on the type of HPMC, its concentration and the rate of heating. Fig. 9 shows the temperature dependence of swelling behavior of HPMC gels. As it is seen from the figure, both HPMC gels showed almost the same behavior with increasing temperature. The main difference in their swelling behavior is relatively higher swelling ratios of highly substituted HPMC. A similar behavior has been reported for HPC crosslinked with glutaraldehyde (Suto & Kawano, 1999) and HPMC crosslinked with divinylsulfone (O'Connor & Gehrke, 1997).

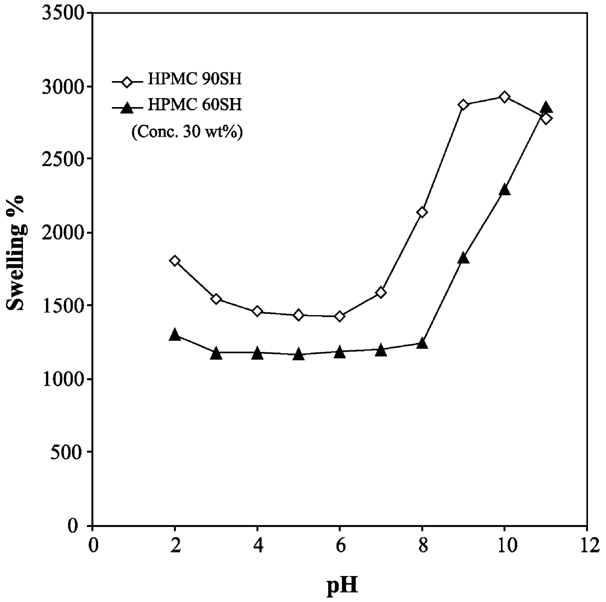

Fig. 8. The influence of pH on the degree of swelling of HPMC gels prepared from 30 wt% solution irradiated to 30 kGy.

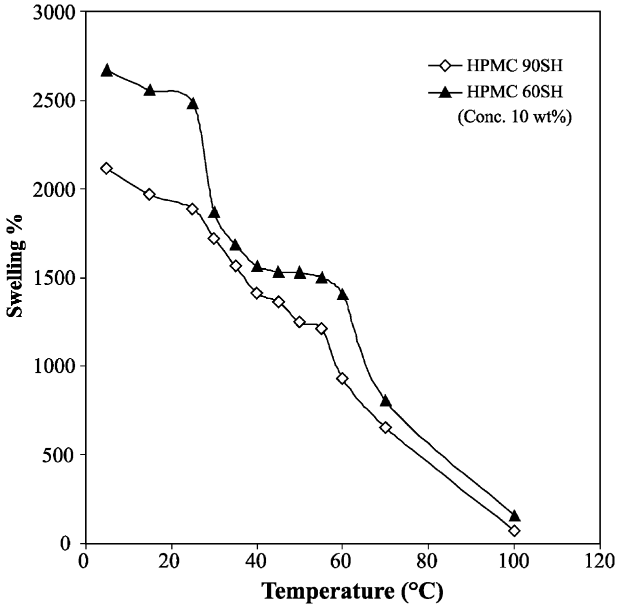

Fig. 9. Temperature dependence of the degree of swelling of HPMC gels prepared from 30 wt% solution irradiated to 30 kGy.

3.3. Enzymatic degradation

The problem of non-biodegradable plastic waste becomes crucial in recent years especially with regard to environmental effects. A very desirable class of materials used for common purposes are biodegradable plastics and polymers. Traditional applications of synthetic polymers are mostly based on their relative inertness to biodegradation compared with natural macromolecules such as cellulose and proteins. Biodegradable polymers are considered as environmentally friendly polymers since these polymers are converted into CO_2 and H_2O when in contact with soil that contains microorganisms.

Enzymatic degradation is a more suitable method of degradation testing compared to other methods (microbial attack, soil burial tests, etc.) because the parameters of the test conditions can be controlled. The enzyme activity in the enzymatic degradation is affected by several factors such as temperature, pH, the type of buffer solution and presence of surfactants (Nugroho, Mitomo, Yoshii, Kume, & Nishimura, 2001). In this study, enzymatic degradation is expressed as the percentage in weight loss of degraded HPMC. Fig. 10 shows the weight loss curve of HPMC gels with high DS (1.9) for enzymatic degradation as a function of the reaction time. Degradation of the gels proceeded steeply during the first 4 h and became slower between 5 and 24 h. As it can be seen from figure, the weight loss values for 30 kGy irradiated 10 wt% concentration of HPMC gels was 35% after degradation for 24 h, while 30 and 40 wt% concentration of HPMC gels were degraded 85 and 95%, respectively, under the same conditions. These results are in conformity with gel fraction results. The gels with lower crosslink densities are affected more severely from the enzymatic degradation. The number of enzymatically scissioned chain segments with increase in gels with lower crosslinks. Also HPMC with high DS has more hydrophobic character and is less prone to enzymatic attack. As the level of substitution rises, the biodegradability is increasingly reduced because of obviously a certain number of unsubstituted glucose units must be present for the sterically demanding enzyme attack (Simon et al., 1998). Similar results were observed for HPMC gels with low DS (1.4), Fig. 11. In the enzymatic degradation curves for HPMC with low DS it was observed that the weight loss values for 30 kGy irradiated samples with different initial HPMC concentrations were all around 95% at the end of 24 h. The ease of enzymatic degradation of HPMC with low DS is simply due to the availability of higher number of attach sites, unsubstituted glucose residues as compared to highly substituted one.

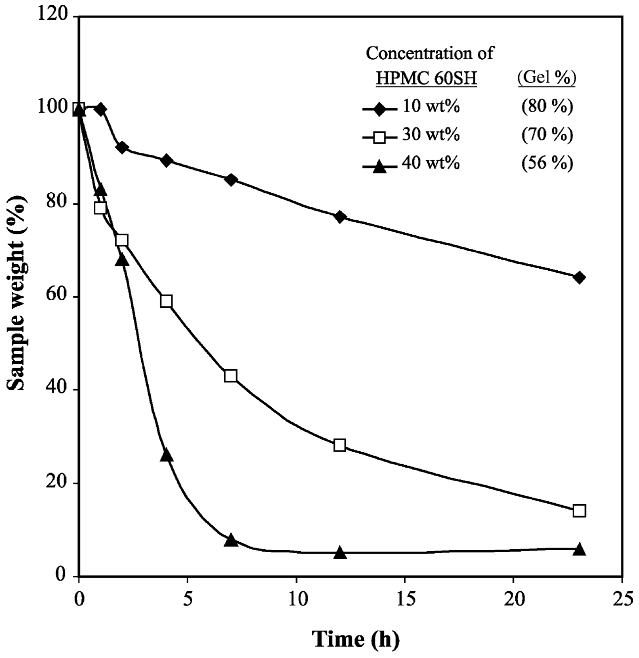

Fig. 10. The kinetics of weight loss due to biodegradation of HPMC 60SH obtained at the concentrations mentioned in the figure by the cellulase enzyme in CH_3COOH–NaOH buffer (pH 5.0).

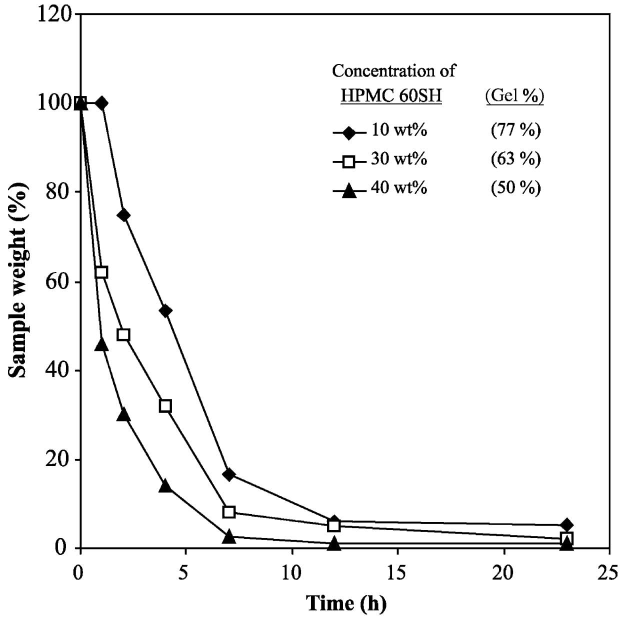

Fig. 11. The kinetics of weight loss due to biodegradation of HPMC 90SH obtained at the concentrations mentioned in the figure by the cellulase enzyme in CH_3COOH–NaOH buffer (pH 5.0).

The general trend observed for both Figs. 10 and 11 is that the rate of enzymatic degradation varied systematically with polymer concentration for a given substitution. The higher the gel content (lower HPMC concentration within the range studied here) the lower becomes the rate of degradation eventually reaching the same extent of degradation given that sufficiently long reaction times allowed.

4. Conclusion

HPMC gels were prepared by EB irradiation to investigate temperature and pH dependence of swelling and biodegradation properties. Upon irradiation, gel fraction values were found to increase with decreasing HPMC concentration for two samples with different DSs. Swelling properties were investigated in different media. HPMC showed both hydrogel and organogel character due to its hydrophobic and hydrophilic groups. No significant change in swelling has been observed for both gels at a pH range of 2.0–7.0. A significant increase in swelling, however, had taken place from pH 8.0 to 11.0 beyond which gels started rupturing. Thermally reversible HPMC gels swelled in cold water about 2000% while shrunk in hot water down to about 500% by volume. Tensile strengths of HPMC gels were increased with increasing dose before and after drying. In enzymatic degradation, HPMC gels with low DS degraded more easily than HPMC with high DS due to wider availability of unsubstituted glucose residues.

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