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Synthesis of antibacterial PVA/CM-chitosan blend hydrogels with electron beam irradiation

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Abstract

A series of excellent hydrogels were prepared from poly(vinyl alcohol) (PVA) and carboxymethylated chitosan (CM-chitosan) with electron beam irradiation (EB) at room temperature. Electron spectroscopy analysis of the blend hydrogels revealed that good miscibility was sustained between CM-chitosan and PVA. The properties of the prepared hydrogels, such as the mechanical properties, gel fraction and swelling behavior were investigated. The mechanical properties and equilibrium degree of swelling improved obviously after adding CM-chitosan into PVA hydrogels. The gel fraction determined gravimetrically showed that a part of CM-chitosan was immobilized onto PVA hydrogel. The further analyses of FTIR and DSC spectra of the prepared gels after extracting sol manifested that there was a grafting interaction between PVA and CM-chitosan molecules under irradiation. The antibacterial activity of the hydrogels against *Escherichia coli* was also measured via optical density method. The blend hydrogels exhibited satisfying antibacterial activity against *E. coli*, even when the CM-chitosan concentration was only 3 wt%.

Keywords: Carboxymethylated chitosan; Poly(vinyl alcohol); Irradiation; Hydrogels; Cross-linking; Grafting; Antibacterial activity

1. Introduction

Polymer modification by blending of two or more different polymers to obtain desired properties is now a practice. Some of the polymer blends exhibit superior and rare properties, unexpected from homopolymers. It is well known that physical, chemical and radiant methods can be applied to prepare polymer blends. Among them, radiation technique is a very convenient tool for the improvement or modification of polymer materials through cross-linking, grafting, or degradation. In this respect numerous studies have been conducted (Bhattacharya, 2000; Carenza, 1992; Guven, Sen, Karadag, & Saraydin, 1999; Rosiak & Ulanski, 1999). Recently, the blends between natural and synthetic polymers are investigated extensively because they can be used as biomedical and biodegradable materials (Carenza, 1992; Cascone et al., 2001; Crescenzi et al., 1997). In their utilization, many shapes and material properties are required such as hydrogels which have been widely used in the filed of biomedicine and pharmacy (Crescenzi et al., 1997; Rosiak & Ulanski, 1999; Rosiak & Yoshii, 1999).

Poly(vinyl alcohol) (PVA) is a water-soluble polyhydroxy polymer, used in practical applications because of its easy preparation, excellent chemical resistance and physical properties, and it is completely biodegradable and cheap (Martien, 1986). PVA hydrogels have been studied extensively but their properties need to be improved further for special applications (Huglin & Zakaria, 1986; Yoshii, Zhanshan, Isobe, Shinozaki, & Makuchi, 1999).

Chitosan, a copolymer of glucosamine and *N*-acetylglucosamine units linked by 1-4 glucosidic bonds, is obtained by N-deacetylation of chitin, which is one of the most abundant natural amino polysaccharide. Chitosan has a variety of applications in industrial pharmacy, and biotechnology (Koide, 1998; Majeti & Kumar, 2000). Some antibacterial and antifungal activities of chitosan and modified chitosan derivatives have been described (Hirano, 1995). However,

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chitosan shows its antibacterial activity only in acidic medium because of its poor solubility above pH 6.5. Thus, water-soluble chitosan derivatives which are soluble in both acid and basic physiologic circumstances might be good candidates for a polycationic disinfectant. Among them, carboxymethylated chitosan (CM-chitosan) has captured more interest due to its good antibacterial activity (Liu, Guan, Yang, Li, & Yao, 2001).

In order to improve or modify the properties of PVA hydrogels, chitosan was usually used to blend with PVA to form hydrogels via several methods (Canh, Binh, The, Trung, & Trung, 1999; Cascone et al., 2001; Kim, Kim, Lee, & Kim, 1992; Minoura et al., 1998). However, the blends are not easy to form homogenous structure at regular condition due to poor hydrophilicity of chitosan. CM-chitosan, which has good hydrophilicity at room temperature, exhibits good miscibility with PVA in aqueous media. It is well known that the miscibility of components of the blend plays an important role in the process of irradiation. It affects many properties of polymer blends after irradiation as well. From the practical point of view, CM-chitosan is expected to blend with PVA for modification and improvement of the properties of PVA hydrogels. In this paper, a series of PVA/CM-chitosan blend hydrogels prepared by irradiation technique is described, and the characteristic of the prepared hydrogels is studied in detail.

2. Experimental

2.1. Materials

PVA-117 (M_w : 74 000) was supplied by Kuraray Co. Ltd, Japan. CM-chitosan (M_w : 30 000) was obtained from Koyou Chemical Industral Co. Ltd, Japan, which has a deacetylation degree of 84% and a carboxymethyl group substitution degree of 0.91. Dimethyl sulfoxide (DMSO) used was of an analytical grade and distilled water was used for the preparation of hydrogels.

2.2. Preparation of the blend hydrogels

CM-chitosan powder was first dissolved in distilled water and then added to PVA solution, and continuously stirred to form homogeneous mixture with heating at 60–70 °C for 30 min. PVA in the final solution made up 10 wt%, and the content of CM-chitosan content varied from 1 to 10 wt%. The gel-like solution was poured into a petri dish for irradiation using a beam current of 1 mA and acceleration energy of 2 MeV generated by the Cockroft Walton electron accelerator.

2.3. SEM/EDS analyses of the hydrogels

The morphological structure of the blend hydrogels were studied by JSM-5600 scaning electron microscope of JEOL (with an attachment of EDS analyzer), Japan. Prior to examination, the samples were fractured in liquid nitrogen, the sections of the samples were coated with gold, then observed and photographed. The distribution pattern of CM-chitosan on the cross-sections of hydrogels was also measured by X-ray energy dispersion (EDS) analysis. The hydrogel samples were immersed in a 5 wt% $CuSO_4$ aqueous solution for 6 days at room temperature and then washed with deionized water. Prior to the measurement, the $CuSO_4$-stained samples were attached to a copper block cooled in liquid nitrogen, lyophilized and analyzed after gold-coating.

2.4. Mechanical properties of the hydrogels

In order to estimate the mechanical properties of cross-linked material, hydrogels were examined in relaxed state (after irradiation with the original water content). The hydrogels were cut into dumbbell (ASTM D-1822-L), and then tensile strength and elongation at break were measured by Strograph-R1 Material Tester (Toyoseiki Co. Ltd, Japan) at a cross-head speed of 50 mm/min. At least five measurements for each sample were recorded and a mean value was calculated.

2.5. Gel fraction

After irradiation, the sol part from samples was extracted by using following method: the hydrogel samples were first put into DMSO at room temperature for 72 h, and then washed by flow water for 1 h; After washing, the samples were soaked in distilled water for 48 h at room temperature. The remained gel was dried to constant weight at 50 °C. Gel fraction was measured gravimetrically

$$\text{Gel fraction (\%)} = W_g/W_o \times 100 \qquad (1)$$

where W_g is the weight of dry gel after extraction and W_o is the initial of dry gel.

2.6. Swelling of hydrogel

Hydrogel samples were immersed directly in distilled water at room temperature for the time required to achieve the equilibrium swelling (72 h), after that, the swollen hydrogels were dried at 50 °C to a constant weight. The equilibrium degree of swelling of the gel was caculated as

$$\text{Swelling} = W_e/W_d \qquad (2)$$

where W_e is the weight of gel at the equilibrium and W_d is the weight of dried gel after swelling experiment.

2.7. FTIR analyses of gel portion

The gel samples after extracting sol and the physical blends (containing 10% PVA, 3% CM-chitosan) as a reference sample without irradiation, were freeze-dried and pulverized. Infrared spectra with a resolution of 4 cm^{-1} of the samples as KBr pellets were recorded by Shimadzu FTIR-8100A spectrometer.

2.8. DSC analyses of gel portion

The melting points and melting enthalpies of the dry samples were studied using Perkin–Elmer Model DSC-7 differential scanning calorimetry (DSC) from 100 to 300 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.9. Antibacterial assessment

Antibacterial activity of the blend hydrogels against *E. Coli* B/r were evaluated by using the optical density method. Dry hydrogel film (0.05 g) was placed into 5 ml medium (nutrient broth from Difico, MI, USA) including 2% *E. coli* B/r culture where *E.coli* B/r grew in a logarithmic growth phase and then incubated at 37 °C for 48 h. During the incubation, the turbidity of the medium was measured at 650 nm every 2 h. All of the operation was done in aseptic condition or by aseptic technique.

3. Results and discussion

3.1. SEM/EDS analyses of the hydrogels

The blend samples were optically clear to the naked eye in spite of irradiation. They showed neither separation into two layers nor any precipitation when the CM-chitosan content is below 8 wt%.

The cross-section and surface of PVA/CM-chitosan blend hydrogel film were examined by scanning electron microscopy to verify the compatibility between PVA and CM-chitosan molecules. As shown in Fig. 1, the photographs of the cross-section of the blend hydrogel film showed a smooth and homogeneous morphology, suggesting high miscibility and blend homogeneity between PVA and CM-chitosan, when the content of CM-chitosan was below 8 wt%. These results are consistent with the SEM data of PVA/chitosan blend samples (Zheng, Du, Yu, Huan, & Zhang, 2001).

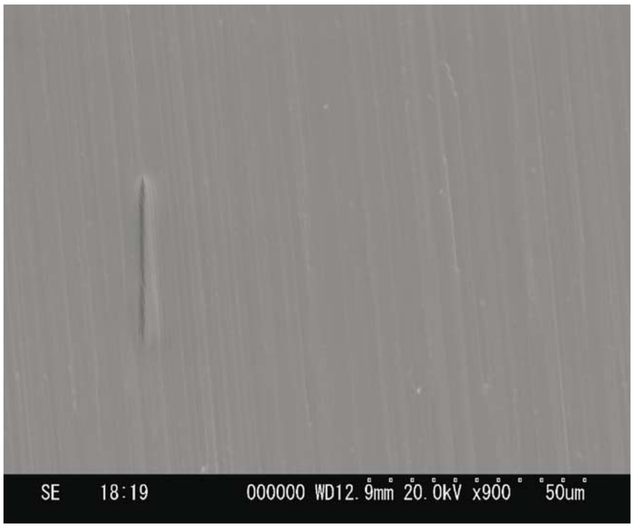


Fig. 1. SEM micrograph of the cross-section of PVA/CM-chitosan (3 wt% CM-chitosan) blend hydrogel film.

The two-dimensional distribution of the CM-chitosan components on the surface of the blend hydrogels was also investigated by analyzing the distribution pattern of $CuSO_4$-complexed amino groups in the CM-chitosan-containing hydrogels. As shown in Fig. 2, the CM-chitosan components in the blend hydrogel surface were distributed uniformly. Koyano, Koshizaki, Umebara, Nagura, and Minoura (2000) investigated the distribution of chitosan in the PVA/chitosan blend hydrogels. It was found that the chitosan could not easily make a uniform distribution in the blend hydrogels when chitosan content was low. In this study, it was found that the CM-chitosan could form a uniform distribution in the blend hydrogels with low CM-chitosan content (<8 wt%). This can be explained CM-chitosan is more hydrophilic than chitosan, so it can interact with PVA molecules more easily in the fabrication process of blend hydrogels. Furthermore, according to the results the distribution of CM-chitosan in the samples seems to be uniform at the molecular level. This implies that there might be some special interaction such as grafted reaction of CM-chitosan to PVA gels excluding hydrogen bonds between PVA and CM-chitosan molecular in the fabrication process of blend hydrogels by irradiation. Fig. 3 showed the copper distribution in the cross-section of blend hydrogel. It can also be seen that the copper ions form a uniform distribution in the cross-section.

Taken as a whole, the results of electron spectroscopy analysis demonstrate that good miscibility was sustained by the hydrogen bonds and intermolecular interaction between PVA and CM-chitosan.

3.2. Properties of PVA/CM-chitosan blend hydrogels

3.2.1. Mechanical properties of PVA/CM-chitosan blend hydrogels

The effects of the content of CM-chitosan in the PVA/CM-chitosan blend hydrogel on the mechanical properties are shown in Figs. 4 and 5. PVA/CM-chitosan blend hydrogels had upgraded tensile strength and elongation. Tensile strength increased with increasing CM-chitosan content in the blend systems and dose. The elongation at break increased with the increasing amount of CM-chitosan in the blend system, up to 5% of CM-chitosan. Then, it decreased beyond 5% CM-chitosan content but still remained higher than that of pure PVA gel. The elongation at break decreased with the increase the dose and showed opposite behavior when compared with the tensile strength. From the results of Figs. 4 and 5, it was found that PVA/CM-chitosan blend hydrogels had improved elasticity and

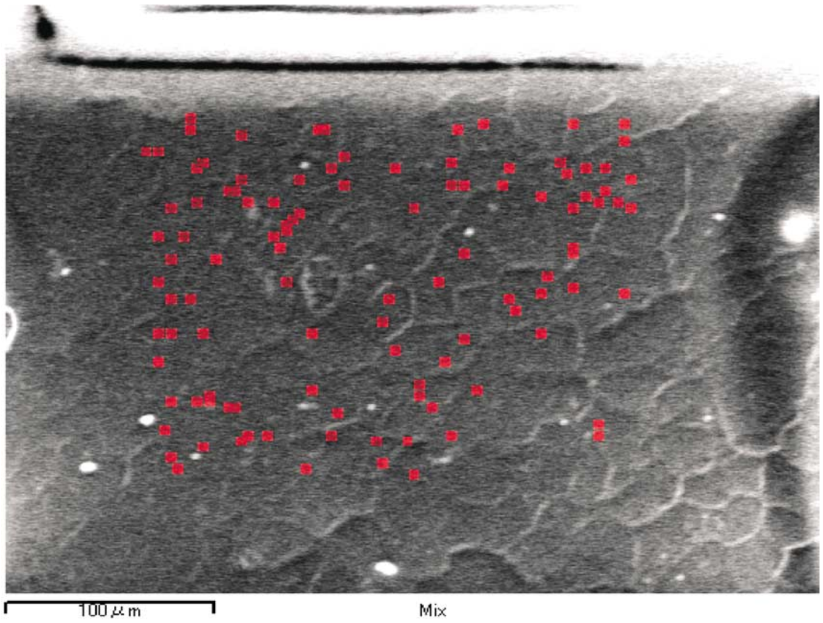


Fig. 2. Two-dimensional distribution of copper on the surface of PVA/CM-chitosan blend hydrogel film (3 wt% CM-chitosan).

flexibility, so this kind of hydrogel is recommended as wound dressing material.

3.2.2. Swelling of the hydrogels

The changes in swelling of PVA/CM-chitosan blend hydrogels as a function of content of CM-chitosan in the blend system and the dose are shown in Fig. 6. The swelling of hydrogels decreased with the dose, but increased when the CM-chitosan content was increased in the blend due to high hydrophilicity of CM-chitosan. CM-chitosan in the blend hydrogel plays an important role because it can improve both of the mechanical properties and swelling capacity of hydrogels.

3.2.3. Gel fraction of PVA/CM-chitosan hydrogels

The changes of the gel fraction of PVA/CM-chitosan blend hydrogels versus the dose as a function of CM-chitosan content in the blend system are shown in Fig. 7. The gel fraction of PVA/CM-chitosan blend gels increased rapidly and then leveled off above the dose of 30 kGy. But at high dose, gel fraction decreased slightly due to the degradation of the gels. The gel fraction decreased with the increase of CM-chitosan content in PVA/CM-chitosan blend systems, but the results also showed that the part of CM-chitosan could not be removed by extraction.

In our previous work (Fei, Wach, Mitomo, Yoshii, & Kume, 2000; Wach, Mitomo, Yoshii, & Kume, 2001; Zhao, Mitomo, Nagasawa, Yoshii, & Kume, 2003), we discussed the irradiation-synthesis conditions of the hydrogels based on some water-soluble polysaccharide derivatives such as carboxymethylcellulose (CMC), carboxymethylchitin (CM-chitin) and CM-chitosan. It was found that irradiation could not induce cross-linking of pure CM-chitosan in aqueous solutions with low concentration of the polymer (below 10 wt%). In low concentrated aqueous solutions, the chains of CM-chitosan macroradicals were separated by water and placed at a distance from each other which prevented their intermolecular recombination. Then the yield of the cross-linking was insignificant, and the predominant radiation-induced reaction was scission of glycosidic bonds. In this

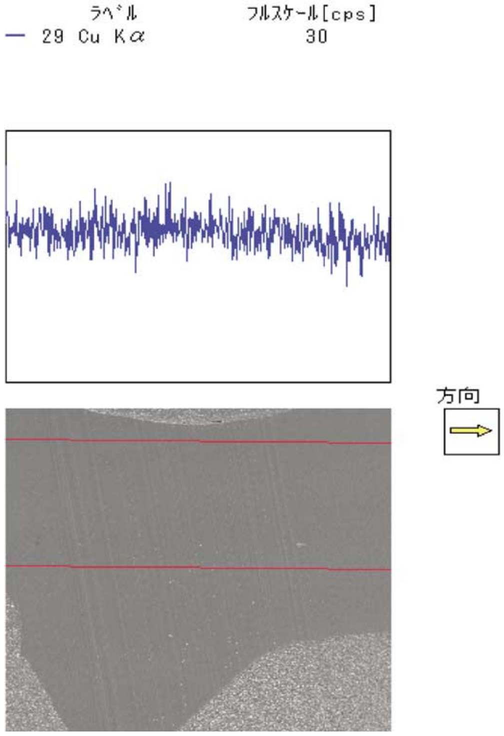


Fig. 3. EDS analysis of copper(II) ion distribution in PVA/CM-chitosan blend hydrogel (3 wt% CM-chitosan, cross-section).

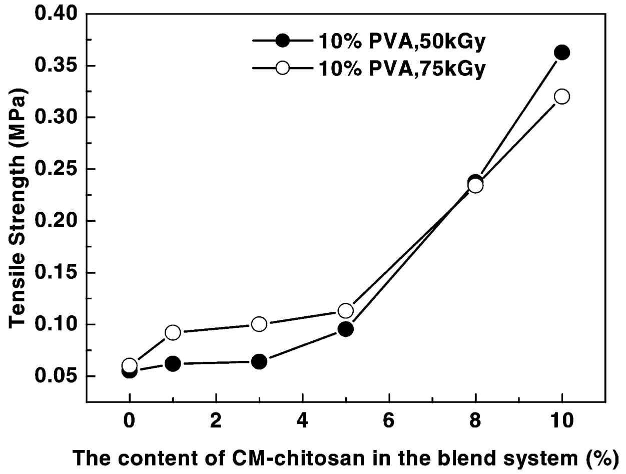


Fig. 4. Tensile strength of PVA/CM-chitosan blend hydrogels prepared by irradiation.

study, PVA/CM-chitosan/water blend systems were irradiated, PVA radicals reacted easily with the other PVA molecules to form cross-linked PVA network (Huglin & Zakaria, 1986). CM-chitosan macroradicals are considered to be separated by water and PVA molecules and placed apart from each other. However, CM-chitosan macroradicals were capable to contact with PVA chains around and then graft onto PVA network. This suggestion can be supported by the experiment result that the grafted chains were found at low concentrated PVA/CM-chitosan aqueous solution (2 wt%) after irradiation. Further studies will be done to support the conception.

Blend hydrogels of polysaccharides and synthesized polymer have been prepared and studied widely. Some researchers proposed that the chemical reaction between polysaccharide and synthesized polymer molecules occurred to bond polymers of two types. Polysaccharide repeating units contain reactive groups at C-2, C-3 and C-6 positions. Ju, Kim, and Lee (2001) reported a comb-type grafted alginate/poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels having PNIPAAm chains grafted on the backbone

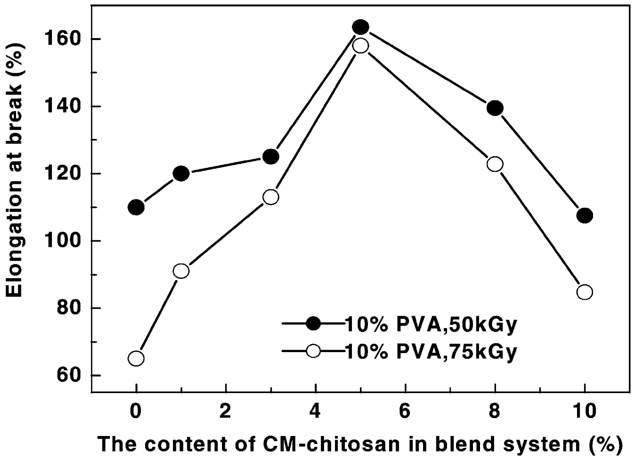


Fig. 5. Elongation at break of PVA/CM-chitosan blend hydrogels prepared by irradiation.

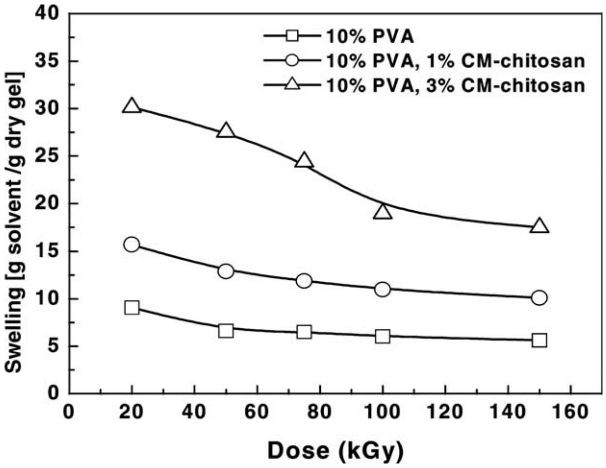


Fig. 6. Swelling of PVA/CM-chitosan blend hydrogels prepared by irradiation.

alginate network. Kim et al. (2002) blended chitosan and poly(dimethylsiloxane) (PDMS), and used UV irradiation to prepare the chitosan/PDMS gafted hydrogel. Recently, the grafting reaction between chitosan and PVA was reported, and it was found that C_2-C_3 bond of chitosan molecules was easily cleaved to yield an aldehyde and a free radical (Don, King, & Chiu, 2002). In addition, Zhai, Yoshii, Kume, and Hashim (2002) also reported the graft reaction between PVA and starch in PVA/starch blend gels prepared by irradiation. Therfore, the formation mechanism of the PVA/CM-chitosan blend hydrogels is also worthy of further investigation here.

3.3. Infrared spectral analyses of gel portion

In order to elucidate the formation mechanism of the PVA/CM-chitosan blend hydrogels, the FTIR spectra of formed gels after extraction of sol part were studied. The results are shown in Fig. 8. For comparison, the FTIR spectra of CM-chitosan and PVA/CM-chitosan physical blend without irradiation were also appeared. The PVA gel

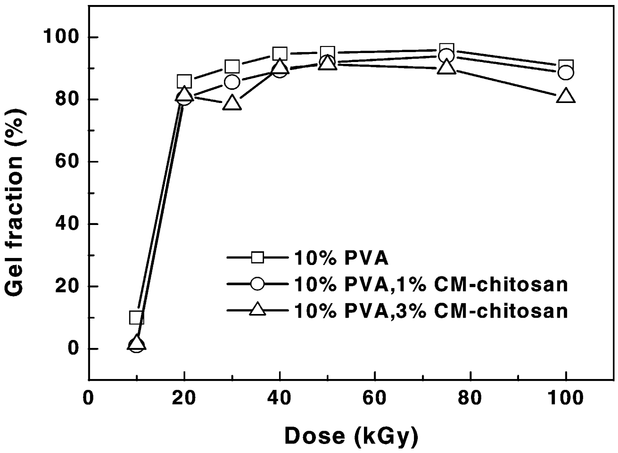


Fig. 7. Gel fraction of PVA/CM-chitosan blend hydrogels prepared by irradiation.

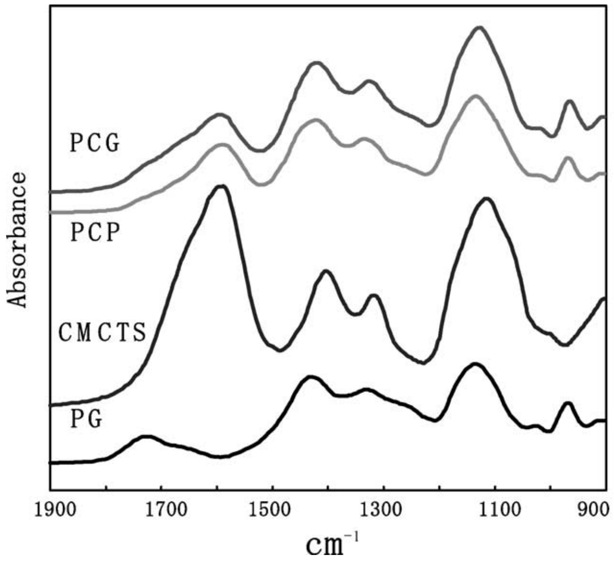


Fig. 8. FTIR spectra of gel portion of PVA, PVA/CM-chitosan gels prepared by irradiation at 50 kGy, PVA/CM-chitosan physical blend without irradiation, and CM-chitosan (CMCTS: CM-chitosan, PG: 10% PVA gel; PCG: 10% PVA/3% CM-chitosan gel; PCP: 10% PVA/3% CM-chitosan physical blend without irradiation).

produced at 50 kGy (without sol part) shows ca. 1452 and 1336 cm^{-1} peak contributing to the C–O–H bonds (δ(CH–OH) resonance) (Krimm, Liang, & Sutherland, 1956). For CM-chitosan, the bands at 1587–1625 cm^{-1} correspond to carboxy group and $-NH_3^+$, and make a broad peak in the spectrum (Liu et al., 2001). The spectrum of CM-chitosan also shows ca. 1414 cm^{-1} peak contributing to $-CH_2$-COOH group. The IR spectra of physical blend without irradiation and blend hydrogel produced at 50 kGy (without sol) are almost identical and both of them appear on obvious broad peak at 1587–1625 cm^{-1}, which is decreased but very similar to that of CM-chitosan. The peak confirms the contribution of CM-chitosan into the gel. This illustrates that the CM-chitosan was grafted onto PVA cross-linked chains. Moreover, the existence of CM-chitosan ensured that the blend hydrogels might be used to provide satisfying antibacterial activity in application. The following experiments will demonstrate it.

3.4. DSC analyses of gel portion

Thermal properties of the blend hydrogels were examined by DSC method. PVA exhibited a relatively large and sharp endothermic curve, with a peak at around 230 °C, while CM-chitosan studied in this work, which were amorphous, did not show any significant transitions in the temperature range of the DSC scan. Therefore, it was of particular interest to estimate how the thermal transition of PVA varied with blending at different irradiation conditions. Table 1 shows the results of DSC analyses of gel samples after extraction of sol part. The DSC results of unirradiated samples are also included as control. Before irradiation, after adding CM-chitosan in PVA the melting point of PVA only tended to be somewhat smaller, but its melting enthalpy decreased significantly. Similar results have been reported in the case when PVA was blended with some polysaccharides or their derivatives (Cascone et al., 2001; Kim et al., 1992; Park, Park, & Ruckenstein, 2001). This can be explained that the presence of these additives discounted relative crystallinity of PVA molecules. After irradiation, on increasing the dose, the melting points and melting enthalpies of both PVA gel and PVA/CM-chitosan blend gel decreased due to the cross-linking of PVA under irradiation, but at the same dose, the melting point and melting enthalpy of PVA/CM-chitosan blend gel were lower than that of pure PVA gel. It is well known that the melting point depression is caused by morphological and chemical modification. The morphological changes involve the thickness of the crystallites and the degree of crystallinity. The chemical changes are results of the cross-linking and grafting reactions (Yeom & Lee, 1996). In this work, it can be considered that irradiation was used instead the chemical cross-linker to induce grafting in the blend system. Of course, the chemical changes affect the morphological ones. If there is no grafting reaction between PVA and CM-chitosan, it is supposed that the DSC data of gel portion of the blend gel should be the same like that of pure PVA gel. Thus, it can be seen that CM-chitosan influenced the thermal behavior of PVA and it can be considered that the CM-chitosan might be grafted onto cross-linked PVA. Fig. 9 presents the DSC curves of the gel samples after extraction

Table 1
Melting point (T_m) and melting enthalpy (ΔH_m) of gel portion of PVA/CM-chitosan blend gels

Composition (CM-chitosan/PVA/H_2O)	Applied dose (kGy)	Gel fraction (%)	Melting point T_m (°)	Melting enthalpy ΔH_m (J/g)
0/10/90	0	0	228.32	56.50
0/10/90	20	87.61	219.04	50.38
0/10/90	50	95.78	218.54	43.62
0/10/90	75	97.76	217.12	40.12
0/10/90	100	95.21	213.78	39.82
3/10/87	0	0	228.02	37.24
3/10/87	20	81.67	219.01	27.02
3/10/87	50	90.86	217.33	24.75
3/10/87	75	87.23	214.63	26.81
3/10/87	100	82.45	208.50	23.44

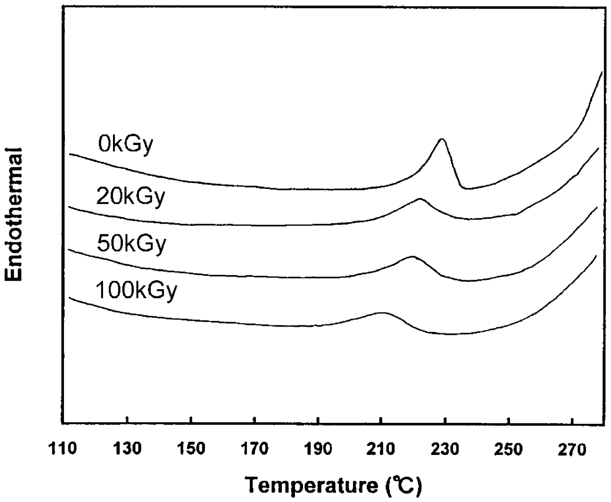


Fig. 9. DSC heating curves of gel portion of PVA/CM-chitosan blend hydrogels at different dose. The gel samples were prepared with a concentration of 10% PVA and 3% CM-chitosan.

of sol and physical blend for the blend ratio of 10% PVA/3% CM-chitosan at several doses. With increasing irradiation dose, the endothermic peak shifted to the lower temperatures and become broader. Fig. 10 presents the DSC curves of the gel samples after extraction of sol irradiated at 50 kGy with different CM-chitosan contents. The graphs reveal that endothermic peak shifted to the lower temperatures and become broader with increasing CM-chitosan content. These observations indicate that the ordered association of the PVA molecules in the gel part is strongly constrained by the presence of the CM-chitosan molecules. On the basis of the obtained results it can be concluded that the presence of CM-chitosan perturbs the formation of PVA crystallites, which can be caused by grafted chains.

In view of gel fraction, IR, DSC analysis of the PVA/CM-chitosan blend hydrogels (after sol extraction), it can be concluded that the grafting reaction of CM-chitosan molecules onto PVA chains occurred. When PVA/CM-chitosan blended mixture were exposed to irradiation, cross-linking of PVA, grafting of CM-chiotsan onto PVA and degradation of CM-chitosan to shorter chains took place simultaneously but eventually led to the formation of hydrogel. Before extraction of sol part, the PVA/CM-chitosan hydrogel can be treated as a combination of two kinds of network structure: (a) a semi-interpenetrating network (semi-IPN), wherein unreacted CM-chitosan chains were trapped within the PVA matrix; (b) a grafted network, wherein CM-chitosan was immobilized onto PVA matrix by grafting. Schematic representations of these network structures are proposed in Fig. 11. After extraction of unreacted material that was not incorporated into the network, the hydrogel based on CM-chitosan grafted onto cross-linked PVA was obtained.

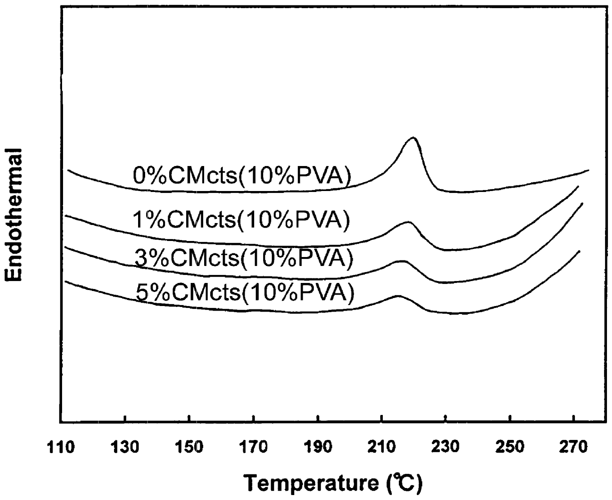
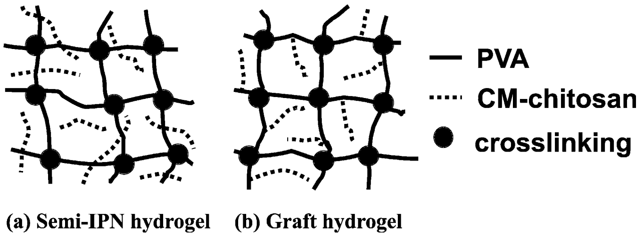


Fig. 10. DSC heating curves of gel portion of PVA/CM-chitosan blend hydrogels prepared at 50 kGy with different CM-chitosan contents.



(a) Semi-IPN hydrogel **(b) Graft hydrogel**

Fig. 11. Schematic illustration of structures for: (a) comb-type graft hydrogel and (b) semi-IPN hydrogel.

3.5. Antibacterial assessment

The antibacterial activity will be the most valuable property in the field of biomedical application, since hydrogels prepared for biomedical application have to sterilize or prevent from many microorganisms. Here, the PVA/CM-chitosan blend hydrogels made by irradiation are tested to confirm whether CM-chitosan can introduce the satisfying antibacterial activity to the blend hydrogels.

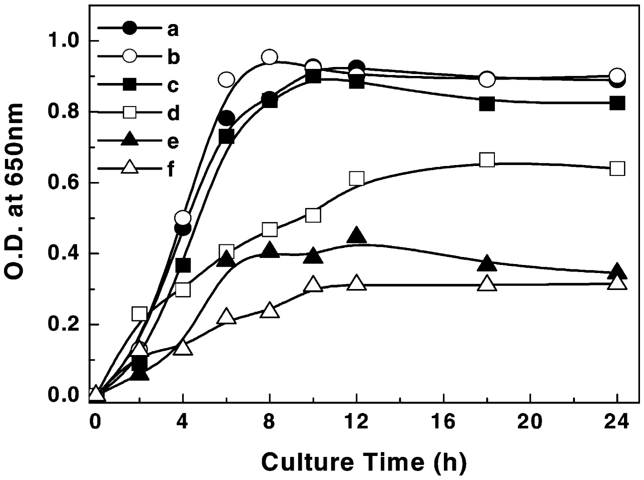


Fig. 12. OD versus culture time of medium (a), PVA gel (PVA 10%) (b), and blend gel gels with different CM-chitosan concentrations (c–f) against *E. coli.* (PVA 10%, CM-chitosan concentrations in (c–f) are 1, 3, 5, and 8%, respectively).

Fig. 12 shows the curves of optical density (OD) versus culture time for the blend hydrogel films against *E. coli*. Because the bacterial cell is opaque, the medium became turbid as the bacteria propagated. Therefore, the optical density can be used as a criterion measuring the activity of the samples. The smaller the OD of the medium, the higher was the antibacterial activity of the sample. It can be seen that the blend hydrogels exhibit significant antibacterial activity even when the CM-chitosan concentration was only 3 wt%. Compared to the pure medium and PVA hydrogel film, OD of the blend hydrogel films are much lower. Moreover, it was also found that the antibacterial activity of blend hydrogel films enhanced by increasing the CM-chitosan concentration in blend systems.

4. Conclusions

A series of excellent PVA/CM-chitosan blend hydrogels could be prepared by irradiation technique. Comparing to PVA hydrogels, the characteristics of blend hydrogels such as mechanical property and swelling capacity were significantly enhanced by the addition of CM-chitosan. Especially, it can provide satisfying antibacterial activity against *E.coli*, thus, can be widely used in the field of biomedicine and pharmacy. In addition, it was also found that there was a grafting reaction between PVA and CM-chitosan molecules besides the cross-linking of PVA molecules under irradiation.

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