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Effect of gamma irradiation on the condensed state structure and mechanical properties of konjac glucomannan/chitosan blend films

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ABSTRACT

Konjac glucomannan and chitosan blend films with different blend ratio were gamma irradiated up to 80 kGy, The mechanical properties achieved their maximum under 25 kGy dose, the tensile strength and breaking elongation of KC2 were enhanced about 40% and 30%, respectively. No change occurred in the primary group such as hydroxyl and acetyl of the blend films during irradiation. The effect of irradiation decreased with the increase of konjac glucomannan content, and the blend film KC2 irradiated by 25 kGy had the highest cystallinity. The miscibility of KGM and CHI in the blend film also played an important role in keeping its morphology, in addition to the content of chitosan when the films were irradiated. 25 kGy gamma irradiation was not only a useful sterilization method for the film biomaterial but also an efficient modification method for enhancing the properties of KC2.

1. Introduction

Gamma irradiation is an ionic, no-heat process that continues to receive attention as a preservation and functional modification agent in polymer research and application. Gamma irradiation had been applied to modification of the properties of konjac glucomannan (Prawitwonga, Takigamia, & Phillips, 2007), starch (Abu, Duodu, & Minnaar, 2006; Bao, Ao, & Jane, 2005; Rombo, Taylor, & Minnaar, 2004), chitosan (Chen, Song, Liu, & Fang, 2007; Choi, Ahn, Lee, Byun, & Park, 2002; Huang, Shen, Sheng, & Fang, 2005) and its blend film (Zhai, Zhao, Yoshii, & Kume, 2004). The effects of irradiation on these polysaccharides had been shown to include depolymerisation and degradation (Sokhey & Hanna, 1993), resulting in decreased viscosity or cross-linking (Nagasawa et al., 2004; Rombo, Taylor, & Minnaar, 2001), increased water solubility and acidity (Bao, Shu, Xia, Bergman, & McClung, 2001), and the gelatinization enthalpy was reported to increase (Rayas-Duarte & Rupnow, 1993; Rombo et al., 2001), or decrease (Bao & Corke, 2002).

Konjac glucomannan is a heteropolysaccharide derived from the konjac tuber. It consists of 1,4-linked β-D-mannose and β-D-glucose units in a molar ratio of 1.6:1 with a low degree of acetyl groups at the side chain C-6 position and having a molecular weight of 0.67–1.9 million on average (Li & Xie, 2004). It has been generally used in food, film-formation, chemical engineering as thickener, stabilizer, binder et al., and also been used in biomedical applications, for example, drug delivery (Pathak & Barman, 2003; Wang & He, 2000), cellular therapy (Majeti & Ravi, 2002), etc.

Chitosan is one of the most abundant natural polysaccharides containing nitrogen. It is the N-deacetylated derivative of chitin, a cationic polysaccharide composed of D-glucosamine and N-acetyl-D-glucosamine residues with 1,4-linkages (Majeti & Ravi, 2002; Xiao, Gao, Wang, & Zhang, 2000). Chitosan and its derivatives have been identified as hydrophilic, non-toxic, biodegradable, antibacterial and suitable as scaffold for tissue engineering (Lee et al., 2002; Madihally & Matthew, 1999; Shanmugasundaram et al., 2001; Zhang & Zhang, 2001). It had been used as artificial skin to accelerate wound and ulcer healing and as a biocompatible vehicle for sustained release of drugs (Oungbho and M¨uller, 1997). The positive surface charge and biocompatibility of chitosan enable it effectively to support cell growth (Zhang, Li, Gong, Zhao, & Zhang, 2002).

In previous work, a series of transparent blend films were prepared by blending konjac glucomannan with chitosan. The strong intermolecular hydrogen bonds existing between the amino groups of chitosan and the hydroxyl groups of konjac glucomannan in the blend films resulting in the enhancement of mechanical properties especially to the blend film KC2 (weight ratio of konjac glucomannan to chitosan = 8:2). And the MTT assay (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide methods) and cell morphology evaluation (such as smear method) proved

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that the KC2 blend films had good biocompatibility, making it possible to apply the KC2 blend film to biomaterial (Li, Kennedy, Peng, Yie, & Xie, 2006; Ye, Kennedy, Li, & Xie, 2006). Because the gamma irradiation is a general sterilization method for biomaterial. So the objectives of the work reported in this paper are (1) to demonstrate the effect of gamma irradiation dose on the structure and mechanical properties of konjac glucomannan/chitosan blend films; (2) to determination the proper irradiation dose.

2. Materials and methods

2.1. Materials

Konjac glucomannan was extracted and purified from the tuber of Konjac *Amorphophallus*. The tubers were sliced to about 8 mm in thickness and then dried under heated air at 65 °C for about 6 h. The dried sheets were mill pulverized. The crude flour was immersed in 50% (v/v) aqueous methanol for 3 h and then dried at 50 °C under reduced pressure. Then, the raw konjac flour was extracted with benzene-absolute alcohol and trichloromethane-n-butanol (4:1, v/v) (Sevag method) for five times, respectively. The fat- and protein-extracted flour was swollen with a mixture of distilled water [30% H_2O_2 (5:1, v/v)] and heated at 40 °C for 20 min; After environmental cooling to room temperature, the hydrosol was centrifuged at 20,000 × *g* for 20 min. Then, acetone was added to the supernatant with stirring. After being filtered with a 120 mesh filter cloth, the white cotton-like precipitate was squeezed and dried by vacuum freeze drying (Li & Xie, 2004). The viscosity-average molecular weight (*Mv*) of the konjac glucomannan thus obtained was determined by viscometry was 9.89×10^6 according to the Mark–Houwink equation $[\eta] = 5.96 \times 10^2 Mv^{0.73}$ at 25 °C (Li, Xie, & Kennedy, 2006).

The chitosan was purchased from Wuhan Tianyuan biomaterial Co. (Wuhan, China). Its degree of deacetylation was measured to be 85% by the method of Jiang (2002), and the viscosity-average molecular weight (Mv) of the chitosan as determined by viscometry was 1.68×10^6 according to the Mark–Houwink equation $[\eta] = 1.424 \times 10^{-3} Mv^{0.96}$ at 25 °C.

2.2. Preparation of blend films

Konjac glucomannan was dissolved in distilled water, and the insoluble residue was filtered out to give a remaining concentration of 1 wt%. Chitosan was dissolved in a 0.8 wt% acetic acid solution to a concentration of 1 wt%. The solutions of konjac glucomannan and chitosan with different mixing ratios [9/1, 8/2, 60/40, 40/60 and 20/80 konjac glucomannan/chitosan (w/w)] were cast onto polystyrene plates and dried at room temperature. A series of blend films were obtained and coded as KC1, KC2, KC4, KC6, and KC8. The films obtained from pure konjac glucomannan and chitosan was coded as KGM and CHI.

2.3. Irradiation of the blend films

The blend films were sealed in polyethylene bags and were irradiated at Hubei Academy of Agricultural Sciences, China. Using a ^{60}Co source (dose rate of 1.4 kGy h^{-1}), target doses were 10, 25, 40, 60 and 80 kGy, at room temperature, respectively. Control (0 kGy) and irradiated samples were stored in desiccators. These samples was code as the film name-irradiation, for example, the KC2-25 means the blend film KC2 irradiated by 25 kGy.

2.4. Characterization of films

The powdered films were blended with potassium bromide and laminated, and the IR spectra were recorded with a Nicolet (USA) Nexus 470 FTIR spectrometer. Film samples of about 100 μm thickness were coated with gold in 0.1 τ vacuum degree. The cross-section morphologies were observed on a Hitachi X-650 SEM. The X-ray diffraction (XRD) curves of the films were recorded with a Rigaku (Japan) D/max-RB X-ray diffractometer and used a CuKα target at 40 kV and 50 mA. The diffraction angle ranged from 60° to 5°. The crystallinities of the films were calculated from $X_c = F_c/(F_c + F_a) \times 100\%$, where X_c is the crystallinities, F_c and F_a are the areas of crystal and noncrystalline regions, respectively. The tensile strength (σ_b) and breaking elongation (ε_b) of the films were measured on an electron tensile tester CMT-6104 (Shenzhen Sans Test Machine Co., Ltd., Shenzhen, China) with a tensile rate of 250 mm/min according to the Chinese standard method (GB/T4456-96).

3. Results and discussion

3.1. Mechanical properties of konjac glucomannan/chitosan blend films

The study of mechanical properties was of primary importance for determining the performance of materials, especially that of film materials. The tensile strength (σ_b) dependence of the irradiation dose (Fig. 1) was such that the tensile strength increased with increase of irradiation dose, and the maximum value appeared at 25 kGy for all the blend films and the pure chitosan film. Fang, Yu, and Zhou (1997) reported the decrease of the tensile strength and breaking elongation when pure chitosan was gamma irradiated at 5–25 kGy both in air and nitrogen atmospheres. However, the 2.6 times increase of the tensile strength and 20% decrease of breaking elongation was observed when the chitosan conduits were sterilized by 25 kGy gamma rays (Cao et al., 2005). The increase of both tensile strength and breaking elongation of the pure chitosan

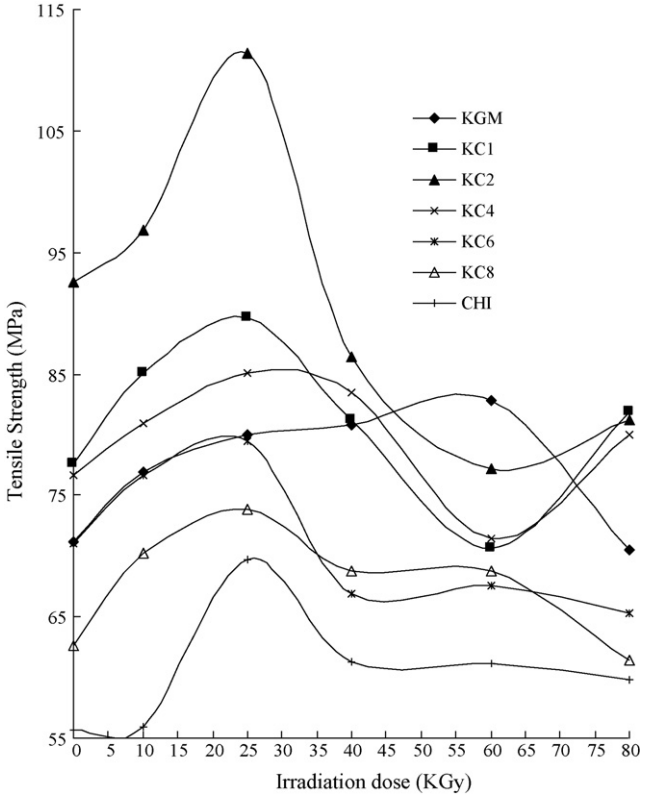

Fig. 1. The effect of radiation dose on tensile strength of konjac glucomannan/chitosan blend films.

film was also observed when the film was gamma irradiated for 14–18 kGy (Yang, Yang, Li, Zhao, & Zhang, 2003). The main reason for these difference might be the difference of preparation method on the chitosan film, when the film was treated by the alkali, the mechanical properties decreased, conversely, the tensile strength could be increased.

As for the blend film KC2, which had been proved to be the best miscibility and the maximum tensile strength in the previous work (Ye et al., 2006), the amplitude of tensile strength was more remarkable and achieved its maximum value at 111.33 MPa (2 times that of the pure chitosan film without irradiation) when irradiated by 25 kGy. The considerable enhancement in tensile strength of blend films indicated increase of intermolecular interactions between konjac glucomannan and chitosan due to the low dose gamma irradiation. As for the blend film composed by chitosan and starch (Zhai et al., 2004). The tensile strength and the breaking elongation did not changed markedly when it was modified by 30 kGy gamma irradiation, the main difference might be such a blend film belonged to a microphase separation system; however the KC2 was a kind of miscible system.

Increase in the irradiation dose on the blend films and the pure films furthermore, the tensile strength of all the films (except the pure film of konjac glucomannan) decreased sharply, and the color of the films turned to brown. This meant that the high irradiation dose decreased the mechanical properties of the konjac glucomannan/chitosan blend films due to the molecular chain degradation of chitosan (Kang, Dai, Zhang, & Chen, 2007; Kume, Nagasawa, & Yoshii, 2002; Nagasawa, Mitomo, Yoshii, & Kume, 2000; Wasikiewicz, Yoshii, Nagasawa, Wach, & Mitomo, 2005).

The change of breaking elongation with the irradiation dose of the konjac glucomannan/chitosan blend films is shown in Fig. 2. Breaking elongation increased with the increase of irradiation dose and reach the maximum at 10 or 25 kGy for all the blend films and the pure konjac glucomannan films. The high irradiation dose could decrease the breaking elongation just as that of tensile strength. As for the pure chitosan film, its breaking elongation decreased for all irradiation doses. This meant that the addition of konjac glucomannan to the chitosan film could improve the blend film mechanical properties markedly when the biomaterial was sterilized by gamma irradiation. The change of breaking elongation of konjac glucomannan/chitosan blend films was also similar to that of starch/chitosan blend films (Zhai et al., 2004).

The blend film KC2 had increased breaking elongation and tensile strength when the irradiation dose was 25 kGy. So it was deduced that low dose irradiation could be an efficient method to modify the konjac glucomannan/chitosan blend film.

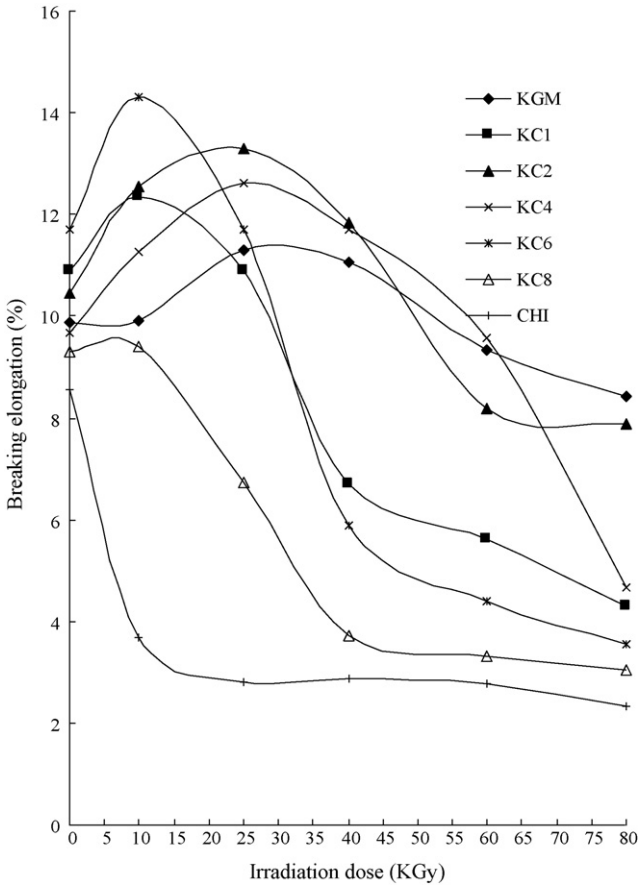

Fig. 2. The effect of radiation dose on breaking elongation of konjac glucomannan/chitosan blend films.

3.2. FTIR analyses of konjac glucomannan/chitosan blend films

The IR spectra of the films of konjac glucomannan, chitosan, KC1, KC2, KC4, KC6 and KC8 irradiated at 0–80 kGy gamma ray were shown in Figs. 3–9. In Fig. 3 the absorption band at 3441 cm^{-1} and the peaks at 2924 cm^{-1} were assigned to the stretching of –OH groups and C–H of methyl in konjac glucomannan; the characteristic absorption bands of mannose in konjac glucomannan appeared at 886 and 804 cm^{-1}. The broad peak at 1638 cm^{-1} were assigned to stretching of C–O of the associate hydroxy group (which meant the C–O in the C–O–H). The spectra of konjac glucomannan irradiated in air with irradiation dose lower than 25 kGy did not show any significant difference in comparison with the spectrum of unirradiated konjac glucomannan. That indicated that the chemical structure was not much altered by absorption of such a dose. When the samples were irradiated with higher dose of 40, 60 and 80 kGy. The broad band between 3660 and 3000 cm^{-1} still did not change except the peak strength increased slightly; this result might be due to the absorption of H_2O (Zhai et al., 2004). Little increase of absorbance in the range 1740–1700 cm^{-1} indicated that carbonyl and carboxyl groups could not become formed efficiently at such an irradiation dose. Little changes of three bands at 1152, 1090 and 1035 cm^{-1} was observed, So it could be deduced that little C_1–O–C_4 groups decayed when irradiated at 80 kGy.

In Fig. 4, The absorption band at 3445 cm^{-1} was assigned to the stretching of N–H groups bonded to –OH in chitosan; the peaks at 1371 cm^{-1} were assigned to the characteristic bending absorption band of amino group and the stretching of acrylamide III; the peaks at 1077 cm^{-1} were assigned to the characteristic absorption

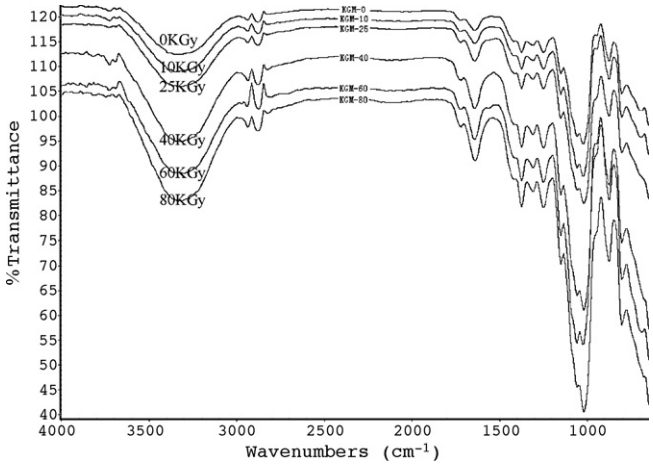

Fig. 3. FTIR spectra of konjac glucomannan film after irradiation.

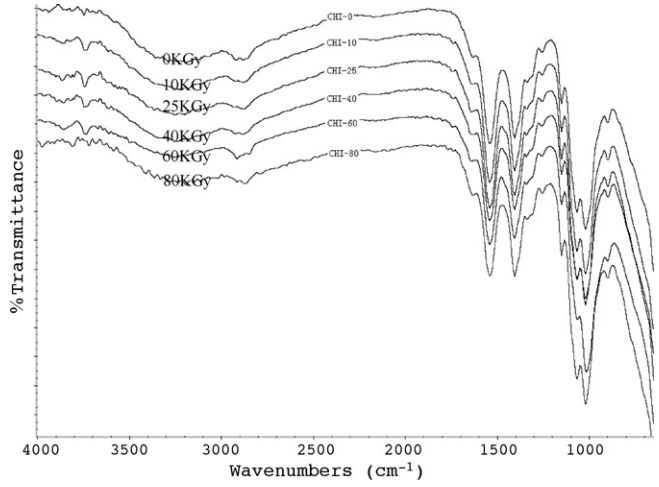

Fig. 4. FTIR spectra of chitosan film after irradiation.

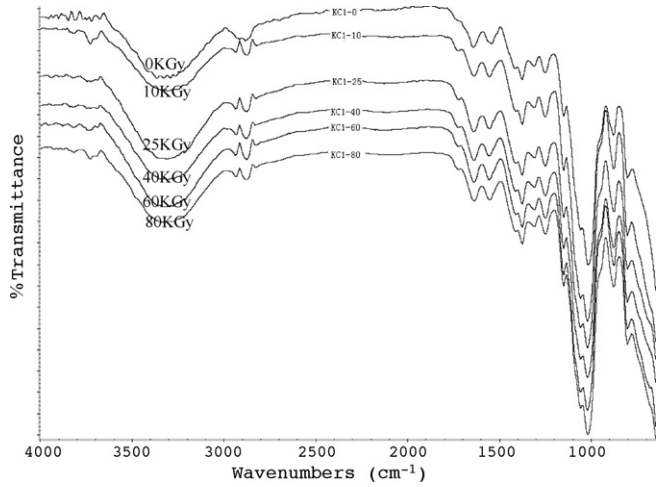

Fig. 5. FTIR spectra of KC1 film after irradiation.

band of C_6–OH. The spectra of chitosan irradiated between 10 and 80 kGy did not show any significant difference in comparison with the spectra of unirradiated chitosan. That also indicated that the chemical structure was not much altered by absorption of such a dose.

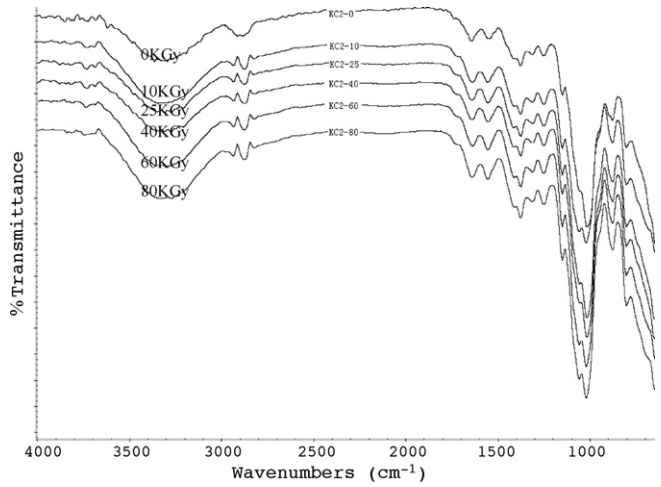

Fig. 6. FTIR spectra of KC2 film after irradiation.

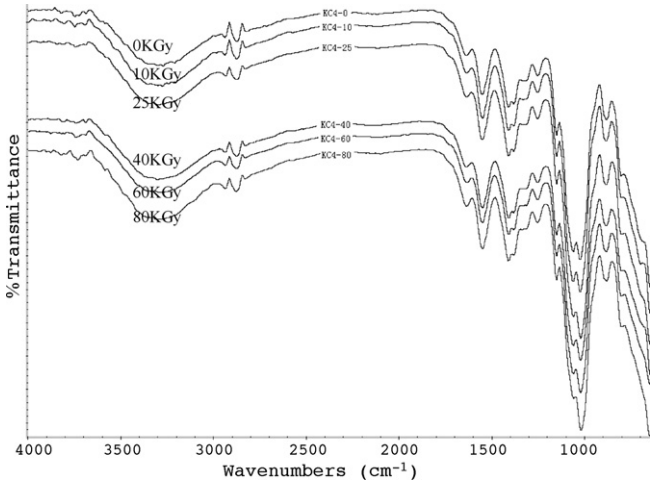

Fig. 7. FTIR spectra of KC4 film after irradiation.

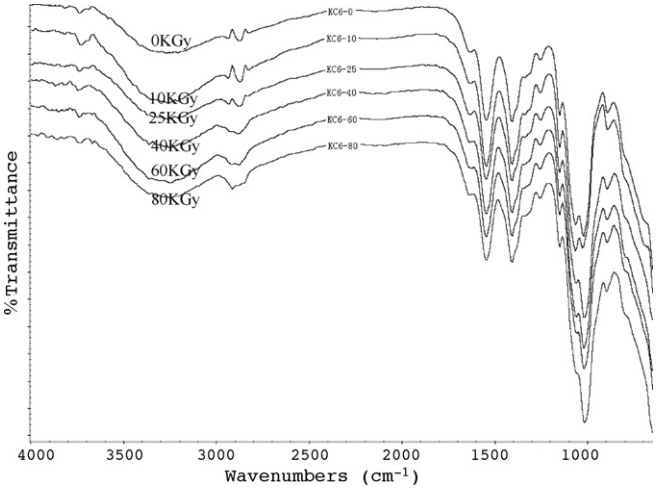

Fig. 8. FTIR spectra of KC6 film after irradiation.

Compared with the spectrum of pure konjac glucomannan and chitosan, the absorption band around 3440 cm^{-1} broadened and shifted to a lower wave number with the increase of konjac glucomannan, indicating the gradual increase of intermolecular hydrogen bonds between chitosan and konjac glucomannan. The

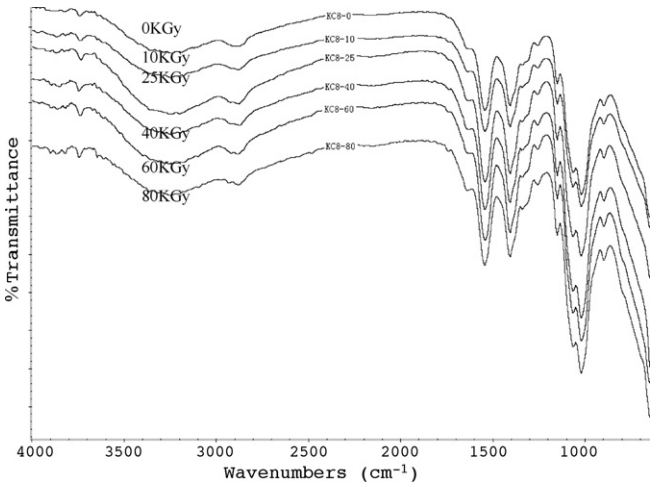

Fig. 9. FTIR spectra of KC8 film after irradiation.

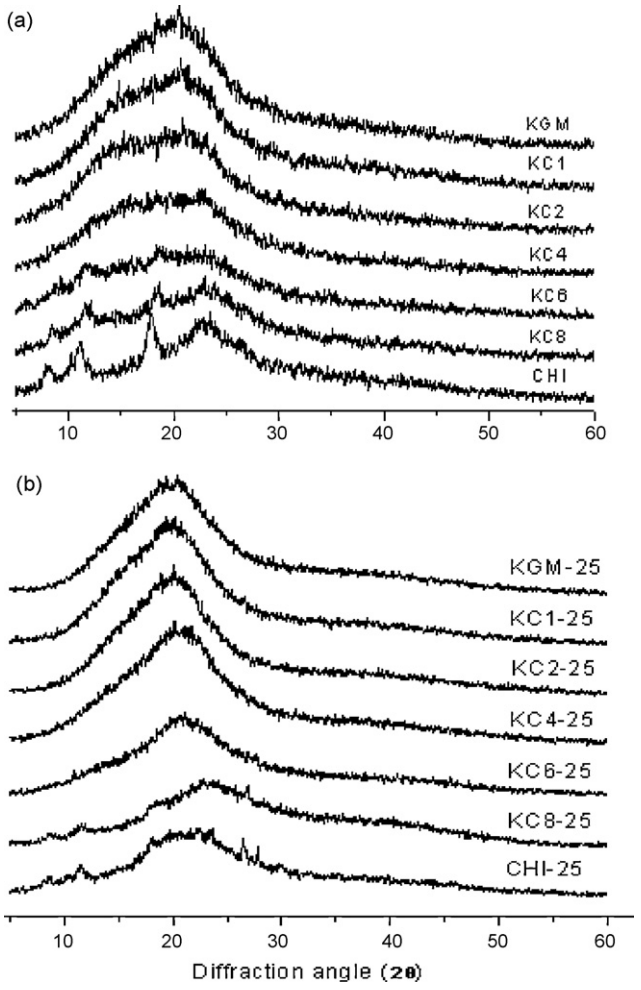

Fig. 10. X-ray diffraction patterns of konjac glucomannan/chitosan blend films. (a: 0 kGy; b: 25 kGy) the ordinate is diffraction intensity (CPS) however the ordinate is often ellipsised, because the diffraction patterns is combined in the figure, the ordinate cannot be marked out. Thank you.

stretching of carbonyl (existed in the acetyl) at 1723 cm^{-1} of konjac glucomannan disappeared; and the stretching of intramolecular hydrogen bonds at 1638 cm^{-1} in konjac glucomannan coupled and shifted to a lower wave number, suggesting the new hydrogen bonds between chitosan and konjac glucomannan molecules in the blend films occurred. In Figs. 5–9, the IR spectra of all the blend films with different blend ratios and irradiated by different irradiation doses did not change, which meant that the blend films did not form new chemical bonds. So it proved that the free radical polymerization between konjac glucomannan and chitosan could not be happened.

3.3. X-ray analyses of konjac glucomannan/chitosan blend films

The WXRD curves of KGM, CHI, KC1, KC2, KC4, KC6 and KC8 films irradiated by 25 kGy were shown in Fig. 10. The pure konjac glucomannan film showed a noncrystalline state and only had a very broad peak around $2\theta = 20.0^\circ$ (Fig. 10a), after irradiation by 25 kGy, the XRD pattern of konjac glucomannan film changed little (Fig. 10b), which indicated its irradiation stability and was consentaneous with its changes of mechanical properties.

Four crystal peaks at around $2\theta = 7.8^\circ$, 11.1°, 17.8° and 23.4° could be recognized in the XRD pattern of chitosan (Fig. 10a), after irradiation by 25 kGy, the XRD pattern of chitosan film changed evidently (Fig. 10b), the four crystal peaks strength decreased, and

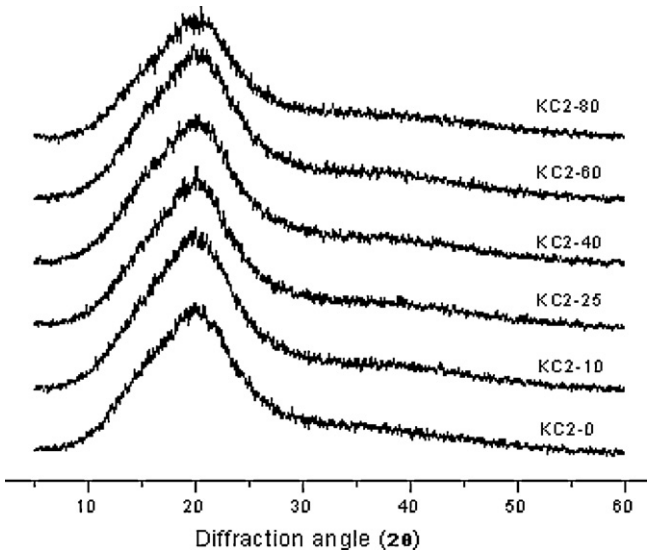

Fig. 11. X-ray diffraction patterns of KC2 blend films by different dose irradiation. The ordinate is diffraction intensity (CPS) however the ordinate is often ellipsised, because the diffraction patterns is combined in the figure, the ordinate cannot be marked out. Thank you.

at the same time three new crystal peaks formed at $2\theta = 26.5^\circ$, 27.8° and 29.8°. The blend film KC8 and KC6 also had similar changes, which meant that the condensed state structure of chitosan and the blend film changed in a molecular rearrangement method.

With increase of konjac gluconmannan content, the diffraction peak corresponding to 11.1° of chitosan in the blend films became gradually lowered, and the diffraction angle neared more and more to 20.0° accordingly. The same regularity could be drawn in regard to diffraction peak around $2\theta = 7.8^\circ$, 17.8° and 23.4°. As for the blend film KC2, the three new crystal peaks could not be found only because of its low content of chitosan (20%), however the crystallinity of KC2 increased evidently from 43.3% to 47.4% after 25 kGy irradiation. It indicated that the changes of crystalline structure and the improvement of crystallinity resulted in better mechanical properties.

The WXRD curves of KC2 film irradiated by 0, 10, 25, 40, 60 and 80 kGy are shown in Fig. 11. The KC2 film only had a very broad peak around $2\theta = 20.0^\circ$, after being irradiated by different doses of gamma ray, no new crystal peaks could be found even for that irradiated by 80 kGy. The only notable change was the cystallinity, it increased from 43.3% (0 kGy) to 45.5% (10 kGy), 47.4% (25 kGy), and then decreased gradually to 46.4% (40 kGy), 45.5% (60 kGy) and 40.1% (60 kGy). The blend film KC2 had the maximum value.

3.4. SEM observation of konjac glucomannan/chitosan blend films

The compatibility of the two kinds of polymer could be evaluated by the homogeneous and compact degree of the blend film, i.e. the blend would be homogeneous and compact when the two kinds of high polymer had a good miscibility. The scanning electron micrographs of the pure and blend films irradiated by 25 kGy are shown in Fig. 12. The cross-section morphologies of the chitosan film shows unevenness and little holes, which indicated that the pure chitosan film suffered to a little degradation at 25 kGy irradiation. The cross-section morphologies of the blend films KC8, KC6 and KC4 had evidently separate zone or hollow in different degree, microscopic phase separation in the blend films and irradiation chemical sensitivity of chitosan might be the main reason for this representation. The phase separation decreased again on the increase of the konjac glucomannan content. When the com-

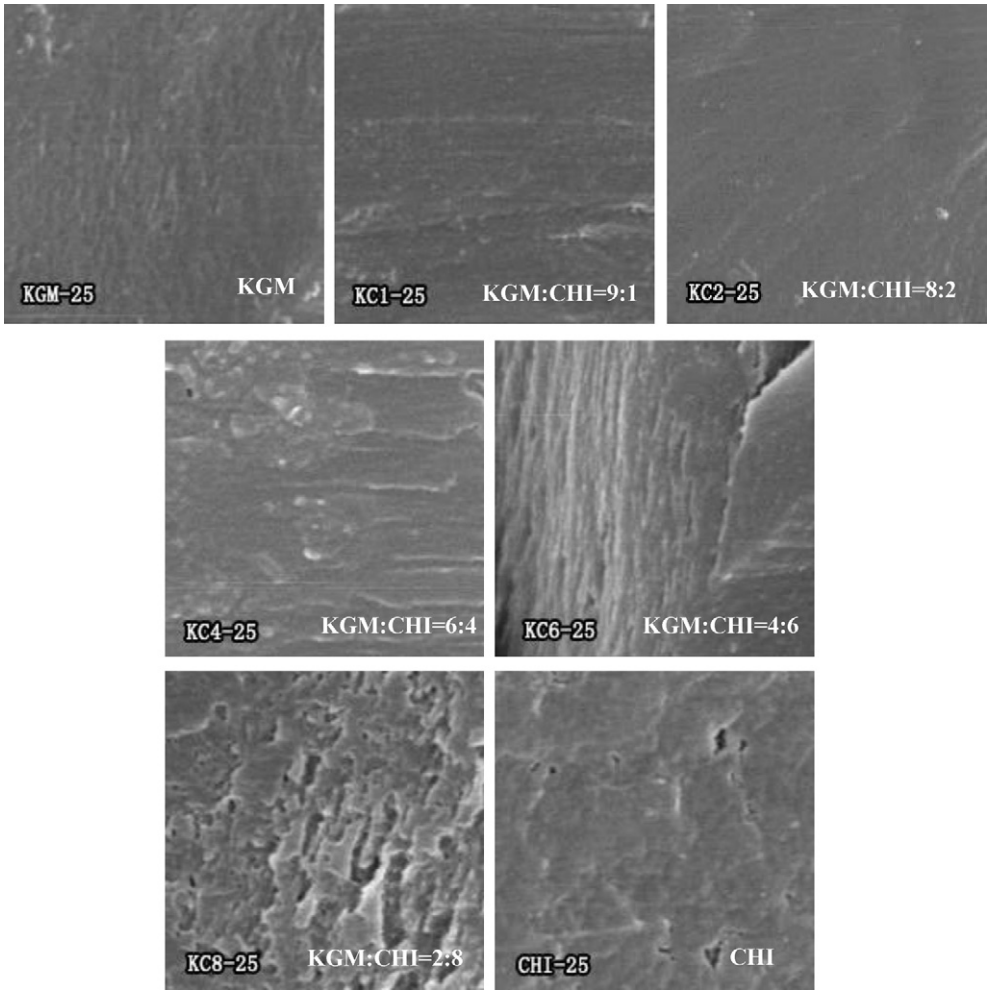

Fig. 12. SEM photographs of cross-section of the konjac glucomannan/chitosan blend films irradiated at 25 kGy (5000×).

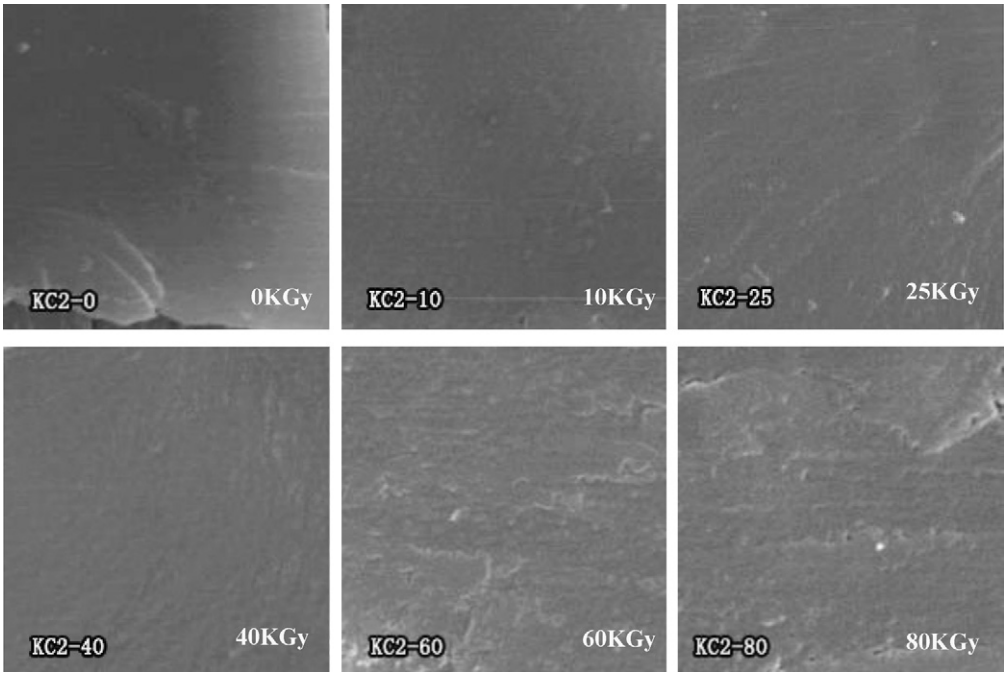

Fig. 13. SEM photographs of cross-section of the KC2 blend films irradiated by different dose gamma ray (5000×).

posite ratio of konjac glucomannan to chitosan was 8:2 by weight, the blend film KC2 showed smooth and homogeneous cross-section morphology when irradiated by 25 kGy gamma ray, suggesting that the high miscibility of the blend films and the irradiation inactivity of konjac glucomannan kept the perfect morphology, and contributed to the increase of mechanical properties. A little undulation in the blend film KC1 might be caused by the poor miscibility (Ye et al., 2006).

SEM of the KC2 blend films irradiated by different doses are shown in Fig. 13. The film before irradiation had a smooth and homogeneous cross-section morphology, when the films were irradiated by 10, 25 and 40 kGy. The cross-section morphology of KC2 did not change perceptibly and still were fine and close suggesting that the low dose irradiation did not destroy the film structure. However when the film was irradiated by 60 and 80 kGy gamma ray, some hollowing and channeling occurred, and the cross-section turned to rough and uneven, just as the blend films of starch/chitosan (Zhai et al., 2004).

4. Conclusion

Little change in the mechanical properties was observed as the konjac glucomannan film while prominently change was observed in chitosan film when the films were irradiated by 0–80 kGy gamma ray. The mechanical properties achieved their maximum under the 25 kGy dose, the tensile strength and breaking elongation of blend KC2 which had the best miscibility was enhanced about 40% and 30%, respectively after 25 kGy dose irradiation. IR analysis showed that no change happened in the primary group such as hydroxyl, acetyl, and acetylamino of the blend films after irradiation, the IR spectra of irradiation modified films were consistent with those of the films without radiation, suggesting that the improvement of the mechanical properties did not result in the free radical polymerization of konjac glucomannan and chitosan. XRD analysis indicated that new crystallite regions appeared and cystallinity changed. The effect of irradiation decreased with the increase of konjac glucomannan content, and the blend film KC2 irradiated by 25 kGy had the highest cystallinity. The results indicated that konjac glucomannan has a remarkable inhibition on the deterioration of the chitosan blend film during irradiation. SEM analysis indicated that the miscibility of the blend film also played an important role in its morphology besides the content of chitosan when the films were irradiated by gamma ray, the favorable miscibility could help to keep complete of blend film (e.g. KC2), and low irradiation dose did not change the morphology perceptibly. So it could be concluded that gamma irradiation could affect the crystalline structure of the blend film, sequentially influencing its microstructure, and finally brought about changes of its mechanical properties. The blend film KC2 improved its mechanical properties when it was sterilized by gamma irradiation, which meant 25 kGy gamma irradiation was not only a useful sterilization method for biomaterial but also an efficient modification method for enhancing the mechanical properties of KC2.

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