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Synergetic degradation of konjac glucomannan by γ-ray irradiation and hydrogen peroxide

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ABSTRACT

Konjac glucomannan (KGM) samples were irradiated with ^{60}Co γ-rays with a radiation dose of 50 kGy in the presence and absence of hydrogen peroxide. The average molecular weight (Mw) and polydispersity index (PDI) of untreated and degraded samples were measured by gel permeation chromatography (GPC), revealing that γ-rays and hydrogen peroxide had a synergetic effect on degradation. Structures of untreated and degraded products were characterized with ultraviolet–visible (UV) and Fourier-transform infrared (FT-IR) spectroscopies, and X-ray diffraction (XRD). Results showed that there was no significant change in the main chain of KGM following degradation, although the crystallinity of KGM decreased. A synergetic effect of γ-rays and hydrogen peroxide was also found in the structural characterization of KGM. The physical properties of KGM changed markedly following degradation, which may increase its application potential. The mechanism of degradation of KGM in the presence and absence of hydrogen peroxide was also investigated.

1. Introduction

Konjac glucomannan (KGM) is a high molecular weight water-soluble non-ionic (neutral) polysaccharide extracted from the tubers of *Amorphophallus konjac* C. Koch (Nishinari, 2000; Nishinari, Williams, & Phillips, 1992), and is composed of β-(1 → 4) linked D-mannose and D-glucose in a molar ratio of 1.6:1 or 1.4:1, with about 1 in 19 units being acetylated. KGM may contain short side branches at the C-3 position of the mannoses, and acetyl groups are randomly present at the C-6 position of sugar units (Kato and Matsuda, 1969; Katsuraya et al., 2003; Maeda, Shimahara, & Sugiyama, 1980).

KGM has been used as a health food in Japan and China for decades because it is non-caloric. KGM exhibits unique properties such as high viscosity, excellent gel- and film-forming abilities (Jian, Zeng, Xiong, & Pang, 2011; Lu, Wang, & Xiao, 2008; Mao, Klinthong, Zeng, & Chen, 2012; Wu et al., 2012; Ye, Kennedy, Li, & Xie, 2006), good biocompatibility and biodegradability (Prawitwonga, Takigamia, & Phillips, 2007; Ye et al., 2006), and its ability to lower blood cholesterol and sugar levels and promote weight loss, intestinal activity and immune function (Chua, Baldwin, Hocking, & Chan, 2010). As a result, it has been used in various applications (Zhang, Gan, Xie, & Xiao, 2005a; Zhang, Xie, & Gan, 2005b), such as food additives (Iglesias-Otero, Borderías, & Tovar, 2010), packing and preservative materials (Liu, Hu, & Zhuo, 2004), release-controlling materials (Wang & He, 2002) and wood adhesives (Umemura et al., 2003). The deficiencies of KGM include low solubility, poor stability of its sols and low mobility of its solutions, which have markedly limited its applications. With the rapidly growing demand for renewable resources, it is worth improving the properties of KGM. Physical, chemical and biological modification has been widely used to improve its functional properties (Cheng, Karim, & Seow, 2007; Li, Xia, Wang, & Xie, 2005; Luo, Liu, Zhang, & Lin, 2009; Pang et al., 2012; Shen, Li, Zhang, Wan, & Gao, 2012; Shinsaku, Shigetomo, Naruhiro, & Yoshinory, 2002; Tian, Dong, & Chen, 1998; Wu, Lin, Luo, & Chen, 2009; Xiao, Gao, Li, & Zhang, 1999; Xie, Feng, Cao, Xia, & Lu, 2007; Xu, Luo, Lin, Zhuo, & Liang, 2009; Xu, Sun, Yang, Ding, & Pang, 2007; Yao et al., 2011; Zhang & Jiang, 2004). Modified KGM has been applied in a wide range of situations including colon-specific delivery (Liu et al., 2004), field-flow fractionation (Benincasa, Cartoni, & Fratte, 2002), ion exchange and adsorption (Luo & Feng, 2004).

Synergetic degradation uses two or more kinds of degradation techniques together to improve degradation. Synergetic degradation is more efficient than physical, chemical or biological degradation alone, so it has been applied widely in the study of polysaccharide degradation (Kang, Dai, Zhang, & Chen, 2007; Mora et al., 2010; Nguyen, Dang, Nguyen, & Nguyen, 2011, 2012; Wang, Huang, & Wang, 2005; Yue, Yao, Wei, & Mo, 2008). Synergetic degradation by γ-ray irradiation and hydrogen peroxide has been used to degrade materials including chitosan (Kang et al., 2007; Nguyen

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et al., 2011, 2012) and sodium alginates (Sen & Atik, 2012). These studies showed that the degradation efficiency of γ-ray irradiation was obviously enhanced in the presence of hydrogen peroxide. However, the synergetic degradation of KGM by γ-ray irradiation in the presence of hydrogen peroxide has not been reported.

The purpose of this study was to develop an efficient method to prepare KGM oligosaccharides of different Mw and PDI by synergetic degradation. The mechanism of the synergetic effect, and the structural characteristics and physical properties of the resulting products, were also investigated. Our results may contribute to the further application of modified KGM.

2. Materials and methods

2.1. Materials

KGM was purchased from San Ai Konjac Food Co. (Yibin City, China), which had been purified by washing with aqueous methanol solution before air-drying (the purity of KGM is above 98.5%). Hydrogen peroxide was purchased from Guangzhou Kezhan Chemical Industry Co. (Guangzhou, China). All other chemicals including hydrogen peroxide were of reagent grade.

2.2. Pre-treatment and γ-ray irradiation

50 g KGM powder was sealed in polyethylene bags. 10 g KGM powder was dissolved in 1 L distilled water, then stirred by magnetic stirrer half an hour at 50 °C. Another 10 g KGM powder was dissolved in 1 L hydrogen peroxide solution (concentration was 1%, v/v), then stirred by magnetic stirrer half an hour at 25 °C. All these samples were irradiated by ^{60}Co γ-ray irradiation at 50 kGy dose (about 25 kGy per day) at Radiation Center of Guangzhou Huada Biological Technology Co. (All samples needed to deoxygenate before γ-ray irradiation in the test of the color change of samples). Another 10 g KGM powder was dissolved in 1 L hydrogen peroxide solution (concentration was 1%, v/v), then degraded naturally two days as control. All wet samples were dried by vacuum freeze dryer (Shenzhen Yuanzhou Technology Co., Shenzhen, China) after above 90% of distilled water was lost by evaporation.

2.3. Physical properties

2.3.1. Average molecular weight (Mw) and polydispersity index (PDI)

The Mw and PDI were determined by a 515-gel permeation chromatography (Waters, USA). The eluent was 0.1 mol/L NaCl aqueous solution and the temperature of the columns was kept at 30 °C. The flow rate was maintained at 0.6 mL/min. The sample concentration was 0.1% (w/v).

2.3.2. Solubility

All samples (0.10 g) were dispersed in 24.90 g of crushed ice under an ice-water bath at 0 °C with vigorous stirring for approximate 1.0 h until crushed ice thawed thoroughly. Then sample solution were centrifuged at 4000 rpm for 20 min. 10.00 g of the upper solution was dried in an oven at 105 °C until constant recorded as *m*. The solubility was calculated based on the following equation:

$$\text{Solubility}(\%) = \frac{2.5 \times m}{W} \times 100$$

where *m* refers to the weight of soluble section in 10.00 g upper solution, *W* refers to the total weight of samples. Experiment was taken three times and draw average number (Du, Li, Chen, & Li, 2012).

2.3.3. Viscosity

All samples were dissolved in distilled water to a certain concentration and then used a Physical MCR (MCR301, Anton Paar, Austria) to determined the viscosity at 25 °C.

2.3.4. Thermal analysis

Thermogravimetric analysis of samples were conducted with TG-209 instrument (Netzsch, Germany) under nitrogen atmosphere with a flow capacity of 20 mL/min. The scan was carried out at a heating rate of 10 °C/min from room temperature to 700 °C. The weight of samples were about 3.2 mg.

2.3.5. Morphology

All samples were fixed on a cylindrical microscope stub covered with carbon strip and coated with a thin layer of gold, then the morphology and surface topography of samples were observed by a field emission scanning electron microscope (Quanta 400, Phylips, Holand). Accelerating voltage was 20 kV, the distance was 10 mm, and the lens diaphragm was 30 μm.

2.4. Structural characterization

2.4.1. Ultraviolet–visible spectra (UV)

UV–vis spectra of samples were carried out via a UV-2550 spectrometer (Shimadzu, Japan) in the range of 200–400 nm. The concentration of samples were 0.05% (w/v).

2.4.2. Fourier transform infrared spectra (FT-IR)

The FT-IR spectra were taken on KBr pellet on a Vetor 33 FT-IR spectrometer (Bruker, Germany). The spectra were obtained in the wavenumber range 400–4000 cm^{-1}.

2.4.3. X-ray diffraction (XRD)

X-ray diffraction was performed with a D 8 ADVANCE X-ray diffractometer (Bruker, Germany). The X-ray diffraction patterns with Cu Kα radiation (λ = 0.154178 nm) at 40 kV and 40 mA were recorded from angles of 5°–60°, and scanning rate was 0.2°/s.

3. Results and discussion

3.1. Mw and PDI

The Mw and PDI of different samples are depicted in Fig. 1. The Mw and PDI of a sample degraded with hydrogen peroxide alone were similar to that of the untreated sample; in other words, hydrogen peroxide alone did not degrade KGM efficiently. The Mw of samples degraded with irradiation alone (6.58×10^4 Da) and synergetic degradation (6.48×10^4 Da) is much lower than that of the untreated sample (4.80×10^5 Da). The PDI of the sample subjected to synergetic degradation decreased to 1.19 from 1.44 for the untreated sample, whereas the PDI of the sample degraded with irradiation alone increased from 1.44 to 1.48. The decreased Mw of the samples degraded by irradiation may have been caused by scission of the carbohydrate backbone, as may the increased PDI of the sample degraded with irradiation alone, because it was incomplete and less selective in this case (Luo, Yao, Zhang, & Lin, 2012). The PDI of the sample subjected to synergetic degradation decreased significantly, possibly because scission occurred more exactly and effectively in the presence of hydrogen peroxide. Overall, these results suggest that γ-ray irradiation and hydrogen peroxide had a synergetic effect on degradation of KGM.

In the case of degradation by hydrogen peroxide alone, hydrogen peroxide was able to generate free radicals such as HOO$^-$, HO$^\bullet$, and $^\bullet$O$_2{}^-$. However, such radicals did not directly affect the Mw and PDI of the sample degraded with hydrogen peroxide alone.

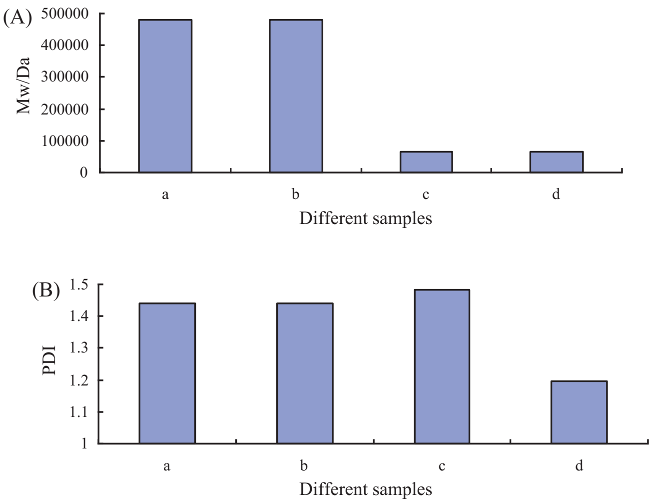


Fig. 1. The Mw (A) and PDI (B) of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

For degradation using radiation alone, degradation is ascribed to the direct action of radiation on the KGM chains: $R+(hv)\rightarrow R^{\bullet}$, $R^{\bullet}\rightarrow R_1+R_2$. These actions were not selective and incomplete, so KGM was degraded to different degrees, and the PDI of this sample increased even though the Mw decreased.

In the synergetic degradation of KGM using both γ-ray irradiation and hydrogen peroxide, the mechanism involves the formation of hydroxyl radicals ($^{\bullet}OH$) through the radiolysis of water and hydrogen peroxide as follows (Kang et al., 2007; Nguyen et al., 2011; Sen & Atik, 2012):

$$H_2O + (hv) \rightarrow e^{-}{}_{aq},\ H^{\bullet},\ {}^{\bullet}OH,\ H_2O_2,\ H_2,\ H_3O^{+}$$

$$H_2O_2 + (hv) \rightarrow 2^{\bullet}OH$$

Furthermore, during irradiation, $e^{-}{}_{aq}$ and $H^{\bullet}$ can react with H_2O_2 as follows:

$$e^{-}{}_{aq} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^{-}$$

$$H^{\bullet} + H_2O_2 \rightarrow H_2O + {}^{\bullet}OH$$

The concentration of $^{\bullet}OH$ radicals increased during irradiation via the above reactions. Thus, the formation of hydroxyl radicals is enhanced in the presence of hydrogen peroxide. Hydroxyl radicals are a powerful oxidative agent that could react with KGM by abstracting carbon-bound hydrogen atoms. The resulting carbohydrate radicals could induce direct breakage of the β-1,4-glucosidic linkages by rearrangement (Ulanski and von Sonntag, 2000), which causes the Mw to decrease rapidly. Therefore, treatment of KGM with radiation in the presence of hydrogen peroxide allows its molecular weight to be reduced effectively and exactly.

3.2. Solubility

The solubility of KGM in water is very poor even though it is a hydrophilic molecule, which has markedly limited its application. Like most polysaccharides, the solubility of KGM may increase as its Mw decreases. The solubility of different samples is depicted in Fig. 2. The solubility of samples degraded with irradiation alone and both irradiation and hydrogen peroxide increased obviously compared with that of the untreated sample. This is because the particles in these samples are more porous than those in the untreated sample. According to Ratcliffe, Williams, Viebke, and Meadows (2005), the solubility of samples is related to their intermolecular association through hydrogen bonding. This implies that the increase of solubility may be caused by decreased hydrogen bonding, which hinders intermolecular association and enhances solvation. Compared with the solubility of sample degraded with irradiation alone (95.41), that of the sample subjected to synergetic degradation increased (97.17), which supports the conclusions drawn from the Mw and PDI of the samples.

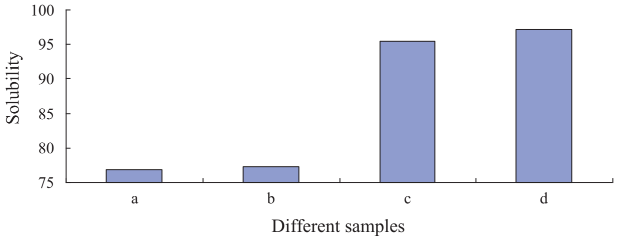


Fig. 2. The solubility of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

3.3. Viscosity

Viscosity is an important index of high molecular weight polysaccharides, and affects their commercial application. The viscosities of different samples are depicted in Fig. 3. The viscosity of all samples increased as their concentration was increased, for example, the viscosities of the untreated samples at 0.5, 1.0, 1.5 and 2.0% are 26.4, 37.9, 234 and 583 Pa s, respectively. The viscosities of samples degraded with irradiation decreased significantly. The viscosity of the untreated sample in 2.0% aqueous solution is 583 Pa s, while that of the sample subjected to synergetic degradation in 5.0% aqueous solution is only 1.04 Pa s. Such decrease of viscosity is expected because of the decreased Mw of the samples following degradation (Kishida, Okimasu, & Kamata, 1978; Xu et al., 2007). Similar behavior was observed for chitosan (Wang et al., 2005; Yue et al., 2008). Comparing curves *c* and *d* reveals that the viscosity of the sample subjected to synergetic degradation is lower than that of the sample degraded with irradiation alone at the same concentration. That is, the viscosity of the sample subjected to synergetic degradation decreased more than that degraded with irradiation alone. This finding is also consistent with the Mw and PDI of the samples presented above.

3.4. Thermal analysis

Thermogravimetric analysis (TGA) has been widely used to evaluate the thermal properties of materials. As illustrated in Fig. 4, all of the samples were involved in three steps of degradation. The first step involved the removal of moisture at low temperature, the second was to decrease in weight, which is the major step, and

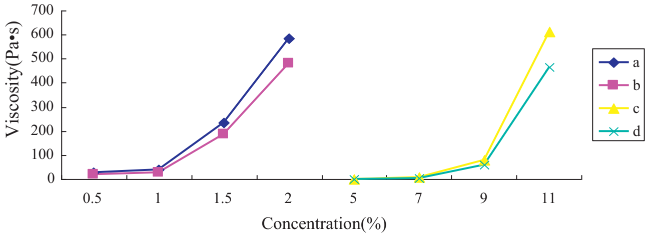


Fig. 3. The viscosity of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

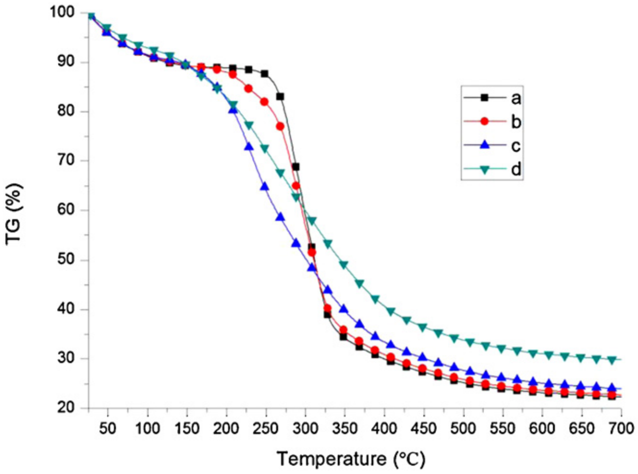
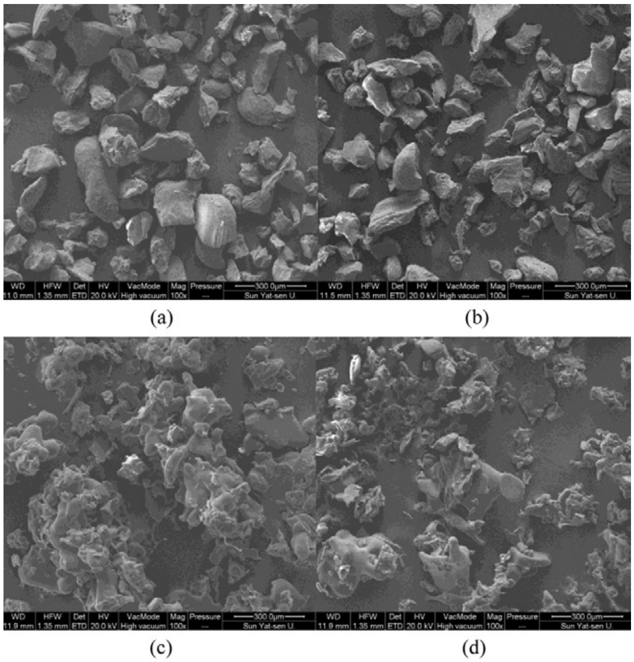


Fig. 4. TG curves of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

the final step involved the loss of a small amount of water. Approximately 10% of the weight was lost in the first step. This resulted from the loss of moisture, which was present in the untreated sample because of its extensive hydrogen bonding (Lin, Chang, Gupta, & Shu, 2010). The end temperatures of the first step for the untreated sample, those degraded with hydrogen peroxide alone and irradiation alone, and the sample subjected to synergetic degradation are 181.0, 178.0, 126.0 and 113.0 °C, respectively. Therefore, the synergetic effect between γ-ray irradiation and hydrogen peroxide occurred during cleavage of the hydrogen bonds of KGM. The weight loss of about 60% in the second step is attributed to a complex process including degradation of saccharide rings and disintegration of macromolecule chains in the samples (Yu et al., 2007). The weight losses of the untreated sample, those degraded with hydrogen peroxide alone and irradiation alone, and the sample subjected to synergetic degradation are 65, 64, 60 and 56%, respectively. These findings are ascribed to cleavage of some saccharide rings and macromolecule chains during irradiation, and again a synergetic effect was observed in the presence of hydrogen peroxide. After three steps of degradation, the weight losses of the untreated sample, those degraded with hydrogen peroxide alone and irradiation alone, and the sample subjected to synergetic degradation were 77.74, 77.30, 76.05 and 70.21%, respectively. Overall, the thermal stability of degraded samples was higher than that of the untreated one. The thermal stability of the sample subjected to synergetic degradation was markedly higher than that of the other samples.

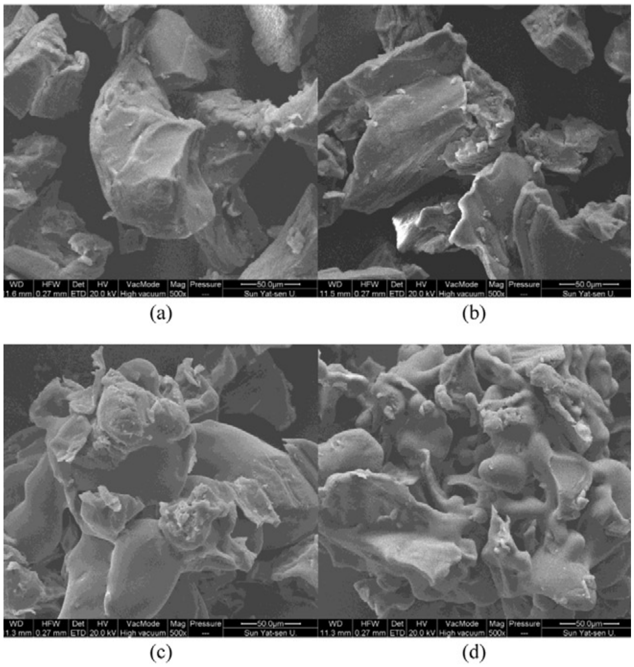
3.5. Morphology

The morphologies of the different samples are presented in Fig. 5, showing a flake-type structure with diverse particle sizes and shapes. The untreated sample and that degraded with hydrogen peroxide alone contained obvious particles and a relatively coarse, rigid surface. Following irradiation, the particles disappeared and the surface became porous. Such pores might be caused by hydrogen bond dissociation or the degradation of macromolecular chains (Luo et al., 2012). The images clearly show that the irradiated samples were less dense and more porous than unirradiated ones. The main reason for the increased porosity may be the decrease in Mw induced by irradiation. The surface morphologies of samples treated with irradiation alone and synergetic degradation were extremely similar. This is because the Mw of the sample subjected to synergetic degradation did not decrease sufficiently to distinguish its surface morphology from that degraded with irradiation alone despite its lower Mw.


(a) (b)

(c) (d)

100×


(a) (b)

(c) (d)

500×

Fig. 5. The morphology of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

3.6. UV spectroscopy

UV spectra of the different samples are illustrated in Fig. 6. An absorption band appeared at about 265 nm following degradation, and its intensity increased for samples treated with γ-ray irradiation alone and synergetic degradation, especially for the latter. Similar results have been reported for other polysaccharides (Choi et al., 2009; Wasikiewicz, Yoshii, Nagasawa, Wach, & Mitomo, 2005;

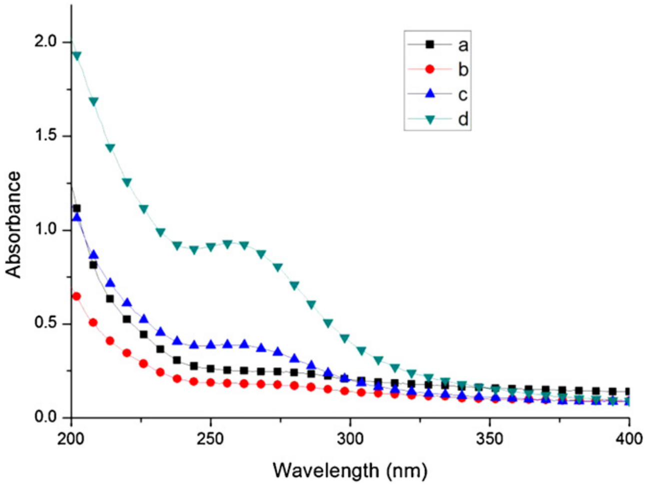


Fig. 6. The UV spectra of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

Yordanov & Karakirova, 2007). Ulański and Rosiak (1992) ascribed this peak to double bonds (carbon–oxygen) formed after main chain scission and hydrogen abstraction followed by ring opening of the polysaccharide. Like sucrose that can form free radicals by high energy radiation treatment (Nakajima & Otsuki, 1990), KGM can generate free radicals under γ-ray irradiation (Xu et al., 2007). These free radicals can combine with different groups and induce chain scission. A double bond then forms through rearrangement. This process is consistent with the observation of a new absorption band at about 265 nm.

A previous study showed free radical reactions of samples degraded by irradiation were enhanced in the presence of hydrogen peroxide. Increased free radical reactions might cause the number of double bonds to increase, so the intensity of the peak in the spectrum of the sample subjected to synergetic degradation increased.

3.7. *FT-IR spectroscopy*

FT-IR spectroscopy is used to study the vibrations of molecules and polar bonds between different atoms. Structures of polysaccharides, such as monosaccharides, glycosidic bonds and functional groups, can be analyzed by FT-IR spectroscopy (Mathlouthi, Seuvre, & Birch, 1986; Zhang, 1994). The FT-IR spectra of the different samples are depicted in Fig. 7. The spectra of the untreated and degraded samples were almost completely identical, because no new chemical groups were introduced into the structure. The similarity of the spectra means that the backbone of KGM did not change during the different treatments. However, the intensity of some of the absorption peaks changed depending on the degradation treatment.

The stretching vibration modes of the O—H group appear as a broad band at about 3398 cm^{-1}. Peaks at 2936, 1383 and 1066 cm^{-1} were assigned to stretching vibrations of —CH_2— groups (Xu et al., 2007; Yu et al., 2007). The peak at 1024 cm^{-1} was assigned to the characteristic absorption band of the C—O vibration. The intense peak at 1640 cm^{-1} was attributed to the in-plane deformation of water molecules (Zhang et al., 2001).

The peak at 1732 cm^{-1} was assigned to the stretching vibrations of C═O groups. The intensity of this peak increased remarkably for the samples treated with irradiation alone and synergetic degradation compared with that of the untreated sample, particularly that subjected to synergetic degradation. This suggests that C═O groups formed during these treatments. These results are consistent with the results from UV measurements.

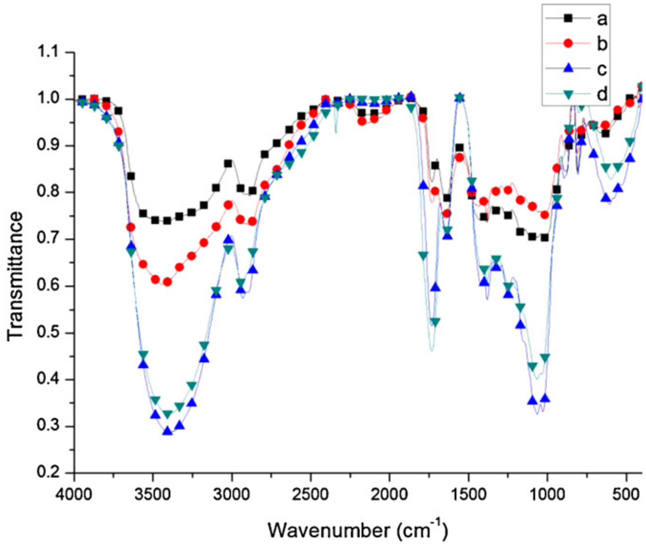


Fig. 7. The FT-IR spectra of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

The peaks at 2150 and 875 cm^{-1} were assigned to the asymmetric stretching vibration of cumulative double bonds and β-glycosidic bonds, respectively. Both of these peaks disappeared in the spectrum of the sample subjected to synergetic degradation. This is because hydrogen peroxide can stimulate γ-ray irradiation to produce more oxygen atoms and hydroxyl radicals. These substances are highly reactive, which may promote ring opening. The cumulative double bonds then readily decompose following ring opening. In addition, hydroxyl radicals could attack the β-1,4-glycosidic bonds, causing them to decompose.

3.8. *X-ray diffraction*

X-ray diffraction patterns of the different samples are depicted in Fig. 8. The untreated and degraded samples exhibit fairly similar diffraction peaks consistent with an amorphous structure. A relatively sharp diffraction peak was observed at about 20.3° in

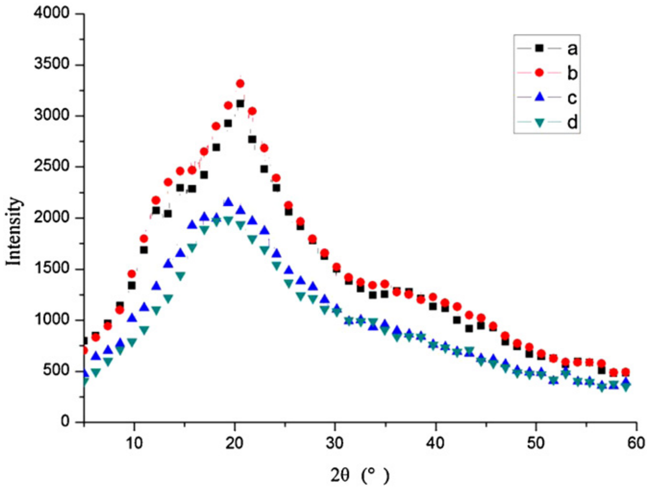


Fig. 8. The X-ray diffraction spectra of different samples (a, untreated sample; b, sample with H_2O_2 degradation alone; c, sample with irradiated degradation alone; and d, sample with synergetic degradation).

the untreated sample. The intensity of this peak decreased for the degraded samples, especially for those degraded by irradiation. The untreated and hydrogen peroxide-degraded samples showed weak peaks at 11.8° and 36.9°. These peaks were absent in the patterns of samples degraded with irradiation.

Irradiation changed the crystal structure of KGM. The decreased intensity of the diffraction peaks indicated that the proportion of crystalline material in the irradiated samples decreased after degradation. Although hydrogen peroxide alone does not change the crystal structure of KGM, it can help γ-ray irradiation to change the crystal structure of KGM. Therefore, the synergetic effect was observed in the diffraction patter of KGM, because the degradation caused both the Mw and crystallinity of KGM to decrease (Luo et al., 2012).

4. Conclusions

KGM was efficiently degraded by γ-ray irradiation in the presence of hydrogen peroxide through a synergetic effect. This synergetic effect assisted cleavage of the β-1,4-glycosidic bond of KGM, promoting chain scission and the formation of carbonyl groups. The mechanisms of degradation by irradiation in the presence and absence of hydrogen peroxide differ significantly. The PDI of the samples shows that scission induced by irradiation may be more exact and effective in the presence of hydrogen peroxide than without it.

Structural characterization of the samples indicated that the backbone of KGM still existed in the degraded products, but the crystallinity of KGM was reduced by synergetic degradation. The Mw, PDI, and viscosity of the samples decreased while their solubility increased remarkably after synergetic degradation.

Degradation of KGM by γ-ray irradiation in the presence of hydrogen peroxide is a very promising technique to produce KGM of different Mw on a large scale. More importantly, the PDI of the products approached 1.0, so the composition of the products formed by synergetic degradation is consistent.

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