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X-ray photoelectron spectroscopy analysis on surface modification of Konjac glucomannan membrane by nitrogen plasma treatment

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ABSTRACT

In order to improve the surface property of Konjac glucomannan (KGM) film, the nitrogen plasma modification was carried out using ion beam injection machine. The surface atomic composition was evaluated by X-ray photoelectron spectroscopy analysis afterward. It was observed that the atomic concentration ratio of wO/wC increased using plasma treatment. The molecular chain degraded and acetyl was partly removed. Hydroxyl was partly replaced by primary amide group. Generation of new functionality groups suggested that plasma treatment might be an effective means to modify the physical property of KGM film.

1. Introduction

Konjac glucomannan (KGM) is an essential polysaccharide that is the main component of the konjac flour produced from the tubers of morphophallus konjac C. Koch. It consists â-1-4-linked glucose and mannose units, with mole ratio of 1:1.5 to 1:1 (glucose:mannose) (Jian, Wang, Yao, & Pang, 2010). KGM has a high thickening ability in water, which leads to gel and film formation during its processing (Pang, Lin, Zhang, Tian, & Sun, 2003). KGM is also biocompatible with other macromolecules (Wang, Yao, Jian, Sun, & Pang, 2010). So it has been commercially used as food, pharmaceutical and biological materials. However, KGM always has several defects, such as high molecular weight, strong hydrophilicity, and lower stability in the solution. So its application might be always limited (Pang et al., 2003).

In order to extend KGM's applied range, many chemical modifications have been done (Jian, Zeng, Xiong, & Pang, 2011). However, chemical reagent residue was always concerned using the chemical modifications, although some of them improved KGM's performances (Yu, Gan, He, Yuan, & Chen, 2003). On the other hand, chemical modifications have been turned out to be nonselective, tedious or expensive (Vesel, 2008). If KGM can be modified in a controlled manner, several end-use applications can be improved. Plasma modification technology is a dry chemistry process with high energy efficiency but cost-effectiveness (Ly et al., 2010). It might be an effective means for the incorporation of appropriate functional groups onto biomolecules, which could be widely applied in the biological materials preparation (Ding et al., 2007).

In this paper, nitrogen plasma was injected into KGM film by ion beam injection machine to change the character of the KGM film. While, the atomic composition on the surface of plasma treated film was analyzed by X-ray photoelectron spectroscopy.

2. Materials and methods

2.1. Preparation of KGM film

KGM were obtained from commercial sources, and purified by the method mentioned in the literature (Jian, Yao, Wang, Guan, & Pang, 2010). The purity of final product was 98%. Three gramme purified KGM was dissolved 300 ml completely. The solution was heated at 60 °C for 10 min, then poured into a square glass plate with side length of 30 cm, and placed for 3 h. Afterward, it was placed into a vacuum oven and dried at 60 °C for 10 h to make the KGM film. Before the nitrogen plasma treatment, the film was cut out into the round shape with the diameter of 10 cm.

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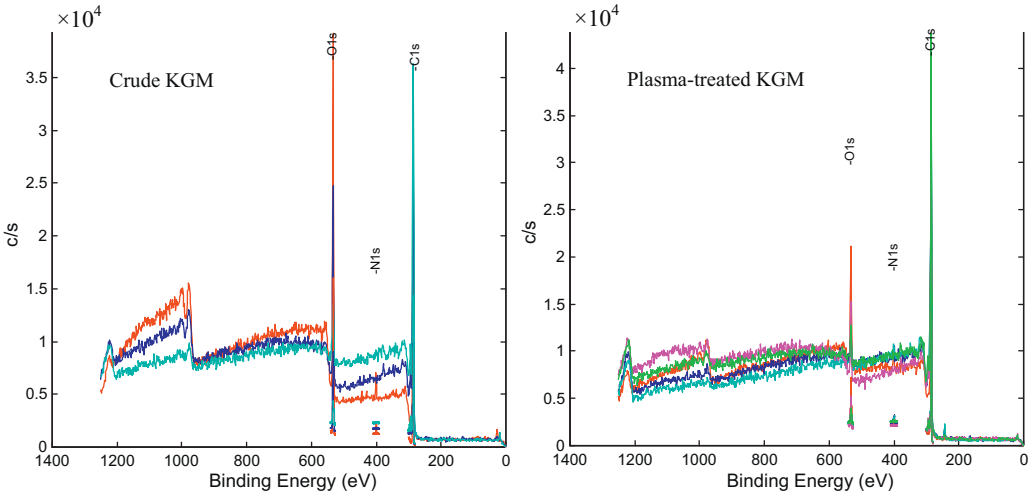

Fig. 1. Survey XPS spectra of KGM film surface.

2.2. Injection of nitrogen plasma

Nitrogen plasma (N^+) was injected into KGM film by an Ion Beam Injection Machine (Institute of Plasma Physics, Chinese Academy of Sciences, China). The parameters for plasma treatment were set as follows: nitrogen ion beam energy: 25 keV, pulse duration: 15 s, pulse interval: 10 s. Ion dose was 2000 units, and the density of per unit was 2.6×10^{13} ions cm^{-2}.

2.3. X-ray photoelectron spectroscopy analysis

The surface atomic compositions of virgin and plasma-modified KGM were evaluated using a Physical Electronics, Inc. PHI 660 Scanning Auger Microprobe (SAM). The virgin KGM was detected in three positions: 0 nm, 10 nm and 50 nm. The plasma-modified KGM was detected in 5 positions: 0 nm, 10 nm, 50 nm, 200 nm and 500 nm. Using the database for polymeric compounds (Beamson & Briggs, 1992), the binding energy assignments were done.

2.4. Statistical analysis

All experiments were carried out in triplicates. Means and standard deviations of the data were calculated for each treatment. Analysis of variance (ANOVA) was carried out to determine any significant differences ($P < 0.05$) among the applied treatments by the SPSS package (SPSS 10.0 for windows).

3. Results and discussion

3.1. Surface atomic composition of KGM

KGM is composed mainly by carbon, nitrogen, and hydrogen atoms. To detect the injection depth of N^+ and its population in plasma-treated KGM film, X-ray photoelectron spectroscopy (XPS) was used to evaluate the atomic composition in different depths of virgin and plasma-treated KGM film, respectively. The typical survey XPS spectra of virgin and plasma treated KGM was shown in Fig. 1. The atomic composition was shown in Table 1. Obviously, the nitrogen atom was mainly populated in the depth of 0–50 nm in the plasma treated KGM, i.e. N^+ could reach the depth of 50 nm in KGM film. Its content in 500 nm depth was nearly 0.66%. As for the crude KGM, the nitrogen atomic content was lower, only 0.16% in 50 nm depth. The trace content of nitrogen atom in crude KGM might be the result of the contamination during operation and should be neglected. An interesting finding was also found that the ratio of carbon to oxygen increased using plasma treatment, which indicated that oxygen atom may be removed or replaced by nitrogen during the plasma process.

Table 1
Elemental composition of KGM film.

	Crude KGM			Plasma-treated KGM		
Depth	C1s	N1s	O1s	C1s	N1s	O1s
0 nm	65.31	0.60	33.98	82.91	2.46	14.63
10 nm	78.84	0.52	20.65	91.27	3.96	4.77
50 nm	91.57	0.16	8.26	93.61	3.05	3.34
200 nm	–	–	–	88.47	0.66	10.88
500 nm	–	–	–	94.09	0.52	5.40

3.2. Analysis of C1s spectra

Binding energy is relevant to the atom and its radicel (Charpentier, Maguire, & Wan, 2006). The surface atomic composition was evaluated by the binding energy and chemical shift of C1s. Using the database for polymeric compounds (Beamson & Briggs, 1992), the binding energy assignments were done. Referring to the literature (Ma, Manolache, Sarmadi, & Denes, 2001), the carbon atom in plant polysaccharide could be divided into four combination types, i.e. C1, C2, C3, and C4. As shown in Fig. 2, 4 fitting peaks for C1s were observed in both virgin and plasma-treated KGM. Their binding energy and assignments were shown in Table 2. It could be observed that the content of acetyl in KGM decreased after the nitrogen plasma treatment. It could be speculated that acetyl was one of the attack points of N^+. Decrease in the content of bond C—O—C suggested that glycosidic bond was partly broken, which leads to the degrade of the molecular chain. To our interest, as indicated by the results, the content of C—OH bond was also decreased, which could be speculated that the hydroxy in sugar moieties fell off during the plasma treatment process. Based on the change of the ration of 4 carbon groups, it could be concluded that acetyl, glycosidic bond, and hydroxy in sugar moieties were the attack points of N^+.

3.3. Analysis of O1s spectra

The high resolution of O1s XPS spectra and its binding energy was shown in Fig. 3 and Table 3, respectively. Clearly, there were two fitting peaks in O1s curve. The peaks indicated two different

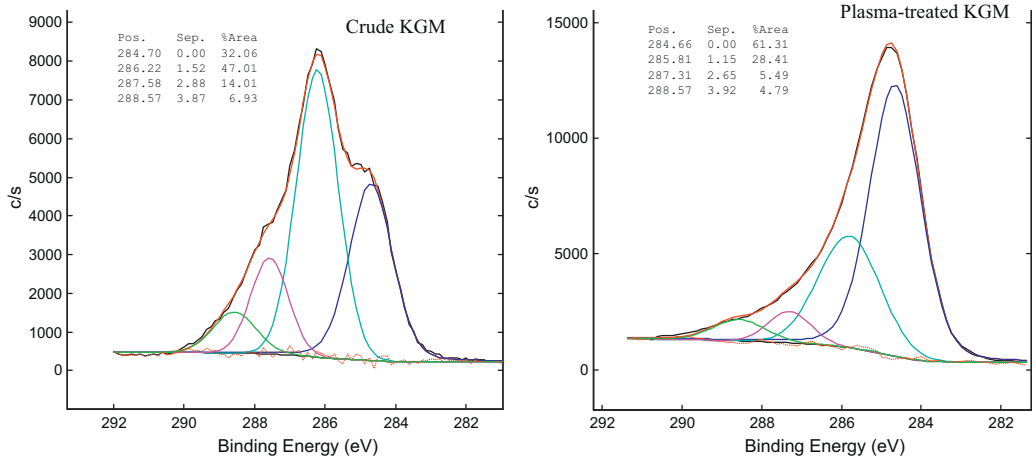

Fig. 2. C1s peak fitting of KGM.

Table 2
Position and assignments of C1s peaks.

KGM					KGM treated by N^+				
Peak no.	Position	Separation	Area%	Assignment	Peak no.	Position	Separation	Area%	Assignment
C1	284.70	0.00	32.06	—C—C/—C—H	C1	284.66	0.00	61.31	—C—C/—C—H
C2	286.22	1.52	47.01	—C—OH	C2	285.81	1.15	28.41	—C—OH
C3	287.58	2.88	14.01	—C—O—C—	C3	287.31	2.65	5.49	—C—O—C
C4	288.57	3.87	6.96	—C=O	C4	288.57	3.92	4.79	—C=O

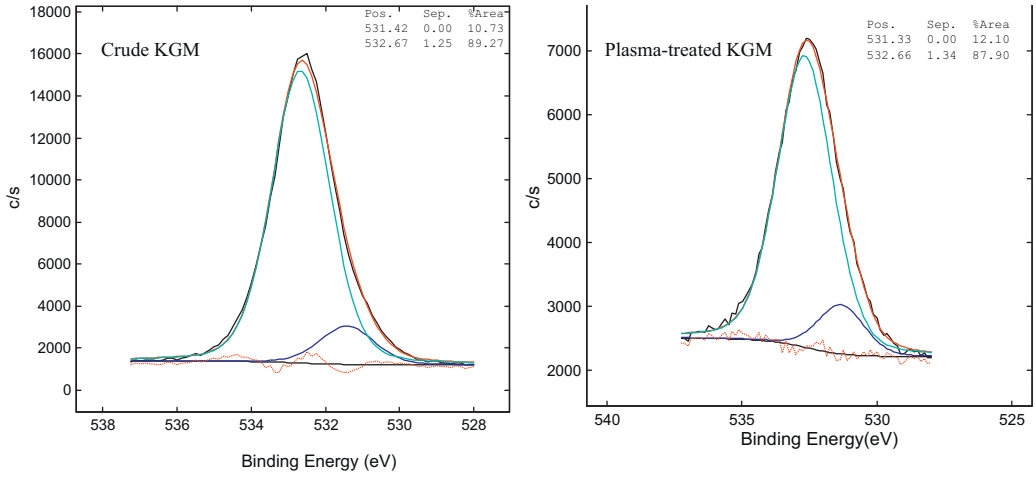

Fig. 3. O1s peak fitting of KGM.

types of oxygen linkages. The lower binding energy (531.42 eV) stands for oxygen (labeled as O1) bonded to carbon in double bond (C=O), and the higher one (labeled as O2) (532.66 eV) was produced by the C—O bond. It was found that the oxygen was mainly in single bond no matter how plasma treated. The content of the oxygen in single bond decreased slightly, which might be the result of removal of the C—OH bond. This result was consistent to the analysis of C1s spectra.

3.4. Analysis of N1s spectra

Fig. 4 shows the high resolution N1s spectra for plasma-treated KGM. The peaks obtained by Gaussian fitting indicated two different types of nitrogen linkages. A detailed analysis of the two chemical linkages and the corresponding peak ratio were represented in Table 4. The N1s spectra of plasma-treated KGM was deconvoluted with two peaks for C—NH_2 (399.01 eV, labeled as

Table 3
Position and assignments of O1s peaks.

KGM					KGM treated by N^+				
Peak no.	Position	Separation	Area%	Assignment	Peak no.	Position	Separation	Area%	Assignment
O1	531.42	0.00	10.73	—C=O	O1	531.33	0.00	12.10	—C=O
O2	532.67	1.25	89.27	—C—O	O2	532.66	1.33	87.90	—C—O

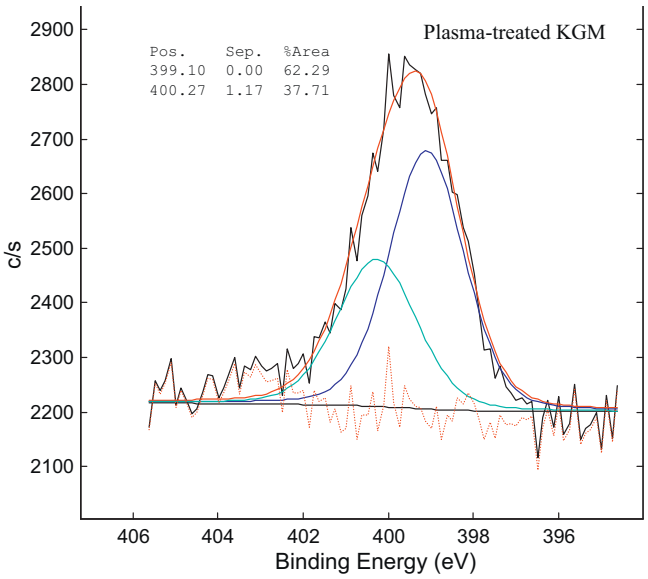

Fig. 4. N1s peak fitting of plasma treated KGM.

Table 4
Position and assignments of N1s peaks in plasma treated KGM.

Plasma treated KGM				
Peak no.	Position	Separation	Area%	Assignment
N1	399.10	0.00	62.29	—C—NH_2
N2	400.05	0.95	37.71	—NH—C=O

N1) and NH—C=O (400.05 eV, labeled as N2). The ratio of the two peak areas was about 1.65. This result suggested that the C—NH_2 bond was produced in saccharide ring after nitrogen plasma treatment. Combined with the analysis results of O1s spectra, it could be observed that the hydroxyl (—OH) in saccharide ring was replaced by primary amide (—NH_2) and acetyl reacted into amide linkage.

4. Conclusions

Nitrogen atom was mainly populated in the depth of 0–50 nm after the plasma treatment. The ratio of wC/wO increased because of the import of nitrogen atom. The significant changes of high resolution in C1s and O1s XPS spectra indicated that the surface of KGM was oxidized by energy transformation, and the molecular chain was degraded. Meanwhile, hydroxyl was partly replaced by primary amino-group, and acetyl was partly removed. Generation of new functionality in the KGM surface suggested that the physical properties of KGM might be changed using plasma treatment.

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