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## Synthesis and characterization of nitrokonjac glucomannan

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### ABSTRACT

Using Konjac glucomannan, which is abundant and renewable in nature as the raw material, Nitrokonjac glucomannan (NKGGM) was synthesized in the system which was mixed with fuming nitric acid, concentrated sulfuric acid and phosphoric anhydride. NKGGM is water resistant, but it can dissolve in organic solvent such as acetone. The nitrogen content, structure and properties of NKGGM were measured and characterized by elementary analysis, FTIR, SEM, X-ray Diffraction and TG-DSC. The results indicated: the nitrogen content of NKGGM could reach 13.59% due to the presence of  $-\text{ONO}_2$ ; a loose network structure was formed in NKGGM and it had a higher degree of crystallinity compared to original KGM; NKGGM decomposed at the temperature of 161 and it had a big exothermic peak; NKGGM had the properties of energetic material.

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### KEYWORDS

Nitration;  
Konjac glucomannan;  
Water resistant;  
Modification.

### INTRODUCTION

Due to potential limitation of petroleum resources as well as increasingly environmental concerns, polymers derived from renewable resources have attracted much attention as potential raw materials in the 21st century<sup>[1-6]</sup>. It is well known that the natural polymers are environmentally friendly and safe during use. Konjac glucomannan (KGM), one of the oldest and richest natural polymer on earth, can be derivatized to yield various useful products. It is a high molecular weight water-soluble non-ionic glucomannan found in tubers of the *Amorphophallus konjac* plant<sup>[7]</sup>. KGM is a linear random copolymer of  $\beta$ -(1 $\rightarrow$ 4) linked D-glucose and D-mannose in the molar ratio of 1:1.6 with a low degree of acetyl groups (approximately 1 acetyl group

per 17 residues) at the C-6 position<sup>[8-10]</sup>. There are a lot of very active primary hydroxyl  $-\text{CH}_2\text{OH}$  at the C-6 position of every constitutional unit<sup>[11]</sup>, under certain conditions, many chemical reactions can happen at this position, such as esterification<sup>[12]</sup>, etherification<sup>[13]</sup>, nitration<sup>[14]</sup>, graft polymerization<sup>[15-16]</sup> etc. From these reactions we can get the ramification of KGM with high energy and fine thermoplasticity. It is attractive for industrial use because of its renewability, biodegradability and low cost. At present, many investigation related to KGM are focused on isolating and characterizing properties of solution and solid, it is mainly used in biochemical, medical and food fields<sup>[17-20]</sup>. The investigation of konjac glucomannan used as an energy material has not been reported so far.

In this work we prepared the nitrokonjac

glucomannan(NKGM) in the system mixed with KGM, fuming nitric, concentrated sulfuric acid and phosphoric anhydride. And the nitrogen content, structure and properties of NKGM were investigated in detail.

## EXPERIMENTAL

### Materials

All chemical reagents used were obtained from commercial sources in Mianyang, China. And all are of analytical grade. The raw KGM sample(Rs) was a gift from Mianyang Konjac Co.(Sichuan, China) and was further purified by following procedures given in the literature<sup>[21]</sup>. A 1.5%(w/w) solution of KGM was prepared in water and the solution was centrifuged to remove the insoluble material. The supernatant liquid was poured into an equal volume of ethanol to precipitate KGM. The solid was then filtered, redispersed in water and freeze-dried. This yielded a fluffy white material, approximately 95% of the original powder, which was used for this study.

### Sample preparation<sup>[14]</sup>

4g of KGM and a mixture of 70ml of fuming nitric acid, 6ml of sulfuric acid, and 42g of P<sub>2</sub>O<sub>5</sub> were added to a round-bottomed flask equipped with a magnetic forced stirrer. The flask was placed in a ice-water bath and cooled for 2h. Then the reaction was controlled at 25°C for 60h. The resulting solution was poured into excess water to precipitate the NKGM, and the solid was filtered. This crude product was dissolved with acetone and then was precipitated and washed 3 times with water. After vacuum-drying at 50°C for 8h, 5.4g of white powdered NKGM was obtained.

### Characterization

The elemental analysis of KGM and NKGM was performed using on an element analyzer (Carlo Erba-1106, Italy).

The FT-IR spectra of the KGM and NKGM were recorded with a spectrometer (5700, Thermo Electron Co., USA) using KBr-pellets at room temperature, and the data were collected over 16 scans with a resolution of 4cm<sup>-1</sup>.

The surface of KGM and NKGM powder were coated with gold, and then were observed using a scan-

ning electron microscope (S440, Leica Cambridge LTD Co., Britain).

KGM and NKGM were analyzed using a D/max-3A X-ray(Health Physics Co., Japan) powder diffractometer equipped with a CuKα target at 35 kV and 60mA. WAXD patterns at a diffraction angle ranging from 2θ=3° to 75° were recorded using a scintillation detector.

Thermogravimetry(TG) and Differential scanning calorimetry(DSC) experiments were performed using a thermal analysis system(STA449C, NETZSCH Co., Germany) equipped with a high-temperature air heating apparatus. All the TG-DSC scans were carried out under air purge at a heating and cooling rate of 10°C/min. The aluminum sample pans for the TG-DSC measurements contained between 3 to 5 mg of the KGM and NKGM samples and were hermetically sealed.

## RESULT AND DISCUSSION

### Elementary composition and molecular structure

The elementary composition of KGM and NKGM is presented in TABLE 1:

TABLE 1 : Results of element analysis of KGM and NKGM

Elements	C	O	H	N
KGM	42.23	49.82	7.95	0
NKGM	23.83	60.15	2.43	13.59

The average degree of substitution of NKGM (DS) was calculated by formula (1):

$$DS = \frac{162 \times W_n}{14 - 45 \times W_n} \quad (1)$$

$W_n$  in formula (1) is the weight percentage of nitrogen. The DS value of NKGM was found to be 2.8.

The FT-IR spectra of KGM and NKGM are shown in figure 1. The broad stretching band of -OH groups around 3429cm<sup>-1</sup> for KGM was sharply decreased in

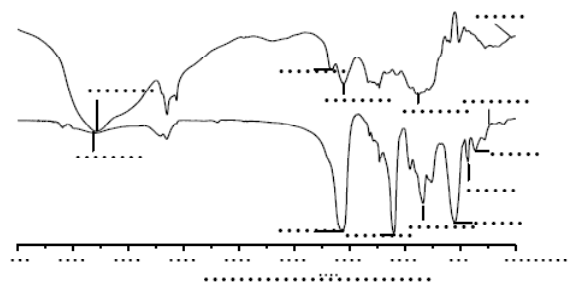


Figure 1 : FT-IR spectra of KGM and NKGM

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the spectrum of NKGM, indicating that the hydrogen atoms of -OH groups in KGM were substituted by -NO<sub>2</sub> groups. At the same time, the sharply decreased -OH groups which are hydrophilic explained why NKGM is insoluble in water. 1680~1640cm<sup>-1</sup> is the nonsymmetric vibrations of -O-NO<sub>2</sub>. Around 1280cm<sup>-1</sup>, it is the symmetric vibrations of -O-NO<sub>2</sub>. 1070~1000cm<sup>-1</sup> is the key chattering of ≡C-O-NO<sub>2</sub>. 840cm<sup>-1</sup> is the flexural vibration of C-O-NO<sub>2</sub>. 750cm<sup>-1</sup> is the rocking vibration of =C-O-NO<sub>2</sub>. And 690cm<sup>-1</sup> is the flexural vibration of ≡C-O-NO<sub>2</sub> in a flat<sup>[22]</sup>. Accordingly, the six obvious absorption bands, at 1655cm<sup>-1</sup>, 1280cm<sup>-1</sup>, 1070cm<sup>-1</sup>, 839 cm<sup>-1</sup>, 745cm<sup>-1</sup> and 690cm<sup>-1</sup> were assigned to the -O-NO<sub>2</sub> groups, indicating that water-insoluble nitrokonjac glucomannan had been synthesized.

### Surface structure of KGM and NKGM

The SEM micrographs of KGM powder and NKGM powder are shown in figure 2 and figure 3. The surface of KGM and NKGM are very different from each other. The pure KGM powders are spherical granules with ruleless aperture and small particle size. But after modified the NKGM powders are schistose with loosen and regular network structure. This indicate that the molecular chains of KGM are broken at the nitrification process and the -OH groups in the KGM molecular chains are exposed, it is helpful for the nitrification and the dehydration reaction of the molecular. Due to the strong dehydration agent P<sub>2</sub>O<sub>5</sub> and concentrated sulfuric acid, dehydration reaction happened inside and between the KGM molecular. This made the KGM molecular cross links with each other, the network structure was formed; and the insertion of -NO<sub>2</sub> groups made the network structure very loosen.

### Analysis of XRD

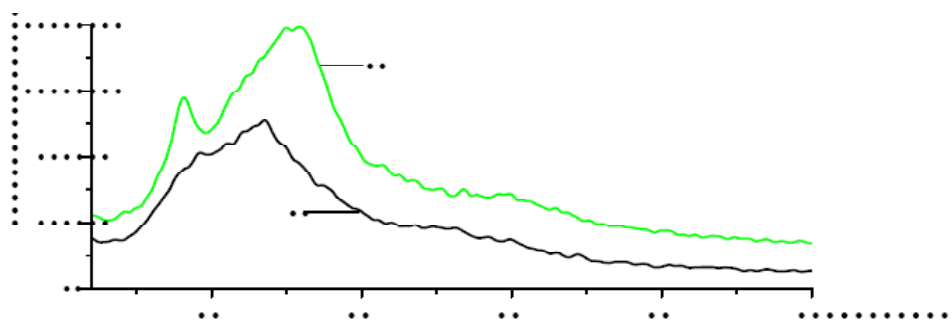


Figure 4 : XRD of KGM(A) and NKGM(B)

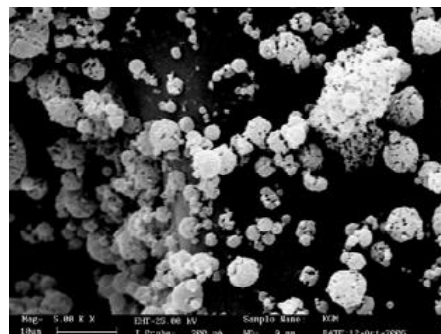


Figure 2 : SEM photographs of KGM

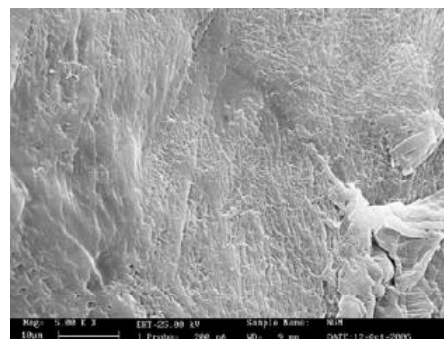


Figure 3 : SEM photographs of NKGM

Further evidence of configuration formation was obtained from X-ray diffraction. Figure 4(A) shows the X-ray diffraction patterns of KGM, it was almost amorphous and was very consistent with the hypothesis of N.Kishida<sup>[23]</sup>, which indicates that KGM is an amorphous powder which is built up with radial arranged micelle. But there is a strong peak at about 12.28°(2θ) in WAXS diffraction patterns of NKGM, and the peaks at 22.56 and 24.14 are notable, this indicate that the crystal intensity of NKGM is improved and an obvious crystal region is come into being, a β-Spectrum form is obtained<sup>[24]</sup>.

Mesophase formation in polymers is mainly attrib-

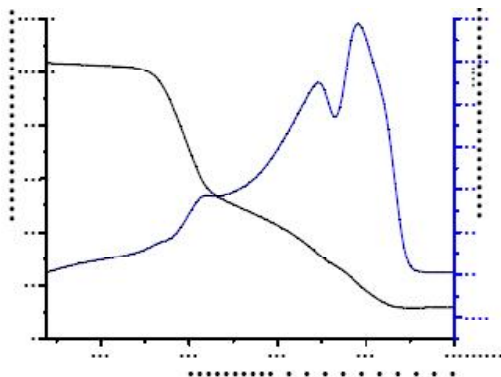


Figure 5 : The TG-DSC curve of KGM

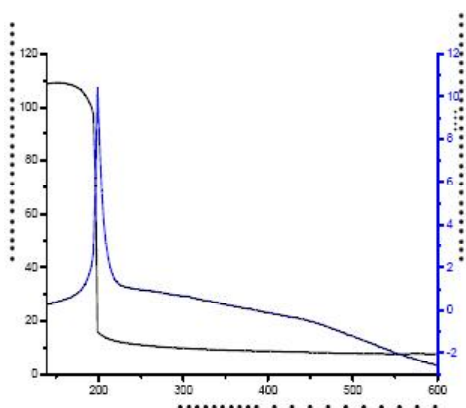


Figure 6 : The TG-DSC curve of NKGM

uted to the backbone rigidity as has been observed for several polysaccharides. The value of  $\alpha$ , in the Mark-Houwink-Sakurada(M-H-S) equation range from 0.5 for a Gaussian coil to 1.8 for rigid rods. The molecular weight( $M_w$ ) and conformation of NKGM were determined by H.Torigata<sup>[25]</sup> by the way of light scattering and viscosimetry. The  $M_w$  and M-H-S of NKGM are  $2.7 \times 10^5$  and  $1.160 \times 10^{-3}$  separately, and the  $\alpha$  values is 0.95, these can indicated that NKGM is a rigid molecular.

### Thermal properties

Thermogravimetry (TG) and Differential scanning calorimetry (DSC) have been widely used in energetic material for its security and compatibility; it is one of the main methods for evaluation of thermal characteristics of energetic material<sup>[26]</sup>. Figure 5 shows the TG-DSC curve of KGM; we can get from the figure that the decomposition temperature of KGM is 253, and the decomposition temperature of KGM can be divided into three stage: the first stage is 253~350, the weight loss

of KGM was 50.39%; Correspondingly, there's a faintish exothermic peak at the DSC curve, this is the exothermic decomposition of KGM. The result is well consistent with the findings of Y.Wang<sup>[27]</sup>. The second stage and third stage are 350~465 and 465~533, the weight loss are 22.4% and 15.28% respectively. And there are two obvious exothermic peaks at the DSC curve; they are the exothermic decomposition of KGM at high temperature. But we can see that the TG-DSC curve of NKGM is very different from KGM from **figure 6**. The decomposition temperature of NKGM is 161. Compared to KGM the decomposition temperature of NKGM is 92 lower. This indicate that the activation energy  $E$  of thermal decomposition of NKGM is dropped. It is due to the sharp decrease of -OH groups in the KGM molecular after modification and the decrease of hydrogen bonding between KGM molecular<sup>[28]</sup>. The weight loss of NKGM reaches 81.57% in a minor temperature range (194~199). And there is a narrow and speculate exothermic peaks at the corresponding DSC curve at 197.5. It is caused by the instantaneous combustion (explosion) of NKGM, this shows that NKGM possesses the property of energetic material.

### CONCLUSION

NKGM with high DS(DS=2.8) was obtained from the nitration. It is water resistant, but can dissolve in organic solvent such as acetone. The modified NKGM material has regular network structure, obvious crystal region, and enhanced crystallinity.

The decomposition temperature of NKGM is obviously decreased when compared with KGM. The insertion of -NO<sub>2</sub> groups changed the decomposition process of NKGM and promoted the burning speed evidently.

KGM is an abundant and renewable raw material, the blast temperature of its modified material NKGM is around 197.5 and it can be completely decomposed to NO<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O, which will do no harm to environment. Based on the property, NKGM would be used as a novel and green energetic material for the propellant and explosives.

**REFERENCES**

- [1] F.Degli-Innocenti, G.Bellia, M.Tosin, A.Kapanen, M.Itavaara; *J.Polymer Degradation and Stability*, **73(1)**, 101-106 (2001).
- [2] D.Darwis, H.Mitomo, F.Yoshil; *J.Polymer Degradation and Satiability*, **65(2)**, 279-285 (1999).
- [3] L.Wang, W.Ma, R.A.Gross, S.P.McCarthy; *J.Polymer Degradation and Satiability*, **59**, 161-168 (1998).
- [4] C.S.Wu; *J.Polymer Degradation and Satiability*, **80(1)**, 127-134 (2003).
- [5] D.Bikiaris, E.Pavlidou, J.Prinos, I.Alric, E.Borredon, C.Panayiotou; *J.Polymer Degradation and Satiability*, **60(3)**, 437-447 (1998).
- [6] R.A.Ruseckaite, A.Jimenez; *J.Polymer Degradation and Satiability*, **81(2)**, 353-358 (2003).
- [7] Vipul Dave, Mihir Sheth, Stephen P.McCarthy, Jo Ann Ratto, David L.Kaplan; *J.Polymer*, (39)**5**, 1139-11148 (1998).
- [8] M.Maeda, H.Shimahara, N.Sugiyama; *J.Agriculture Biology Chemistry*, **44(2)**, 245-252 (1980).
- [9] F.Smith, H.C.Srivastava; *J.Journal of American Chemical Society*, **39**, 1715-1718 (1959).
- [10] K.Kaname, O.Kohsaku, H.Kenichi; *J.Carbohydrate Polymers*, **53**, 183-189 (2003).
- [11] Z.Tian; *J.Adhesion In China*, **24(6)**, 33-35 (2003).
- [12] M.Hu, W.Hu, B.Xie; *J.Wuhan University Journal Natural Science Edition*, **3**, 101-109 (1994).
- [13] J.Pang, L.Xiao, L.Wang; *J.Linchan Huaxue Yu Gongye/Chemistry and Industry of Forest Products*, **23(4)**, 63-65 (2003).
- [14] S.Gao; L.Zhang; *Macromolecules*, **34**, 2202-2207 (2001).
- [15] N.Li, X.Luo; *J.China Plastic*, **19(11)**, 78-81 (2005).
- [16] Z.Liu, L.Chen, R.Zhou; *J.Polymer*, **46(16)**, 6274-6281 (2005).
- [17] C.Huang; *Acta Nutritional Sinico*, **2(4)**, 360-366 (1990).
- [18] K.Hannigan; *J.Food Engineering International*, **5(12)**, 21-25 (1980).
- [19] Y.Gu, J.Shi, Z.Hu; *J.Chinese Traditional and Herbal Drugs*, **30(2)**, 78-81 (1999).
- [20] C.Mao, N.Yu, Z.Gu; *J.Chinese Journal of Modern Applied Pharmacy*, **3(18)**, 12-17 (2001).
- [21] S.Zhang, S.Wu, Y.Yan; *J.Food Science*, **26(9)**, 275-277 (2005).
- [22] Z.Shao, W.Wang, F.Wang, F.Chen, H.Tan; *Chinese Journal of Explosives & Propellants*, **27(1)**, 36-39 (2004).
- [23] N.Kishida, S.Okimasu; *J.Agriculture Biology Chemistry*, **42(3)**, 669-670 (1978).
- [24] B.Li, B.Xie; *J.Scientia Agricultura Sinica*, **35(11)**, 1411-1415 (2002).
- [25] B.Li, C.J.Wang; *J.Guangzhou Food Science and Technology*, **19(4)**, 98-101 (2003).
- [26] S.Chu; 'Blasting Explosive Thermal Analysis [M]', Beijing, Science Press, 188-195 (1994).
- [27] Y.Wang, X.Zheng, J.Xie; *J.China Plastics Industry*, **2(34)**, 60-63 (2006).
- [28] R.Yan, H.Xu, S.Guang; *J.Chemical World*, **4**, 225-227 (2005).