

Synergistic degradation of konjac glucomannan by alkaline and thermal method



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ABSTRACT

The application of konjac glucomannan (KGM) in the food industry is always limited by its high viscosity. Hereby, low-viscosity KGM was prepared by alkaline-thermal degradation method. This process was demonstrated by the changes of average molecular weight and a kinetic model was developed. The results revealed that high alkalinity and high temperature had a synergetic effect on degradation. The structure of hydrolysates was evaluated by periodate oxidation and their fluidly properties were researched by rheology measurements. The degradation was divided into two regimes. The rate of the first regime (within 1 h) is higher than that of the second one (last 1 h). It is found that alkaline hydrolysis and deacetylation have a synergistic effect on the degradation under high alkalinity (pH 9.2) and low temperature condition (25 °C). Finally, rheology parameters showed alkaline-thermal degradation is a promising way that can be applied in practice to degrade KGM.

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1. Introduction

Konjac glucomannan (KGM), a kind of heteropolysaccharide with average viscosity molecular weight ranging from 10^5 to 10^6 (Chua, Baldwin, Hocking, & Chan, 2010; Li & Xie, 2004), is one of the highest viscosity polysaccharides and exhibits a typical shear thinning behavior (Yaseen, Herald, Aramouni, & Alavi, 2005). The viscosity of 1% (w/w) KGM solution could reach 30 000 cps (Takigami, 2000). Due to the unique high viscosity and gelling property, KGM is widely employed as emulsifier and stabilizer in the food, cosmetic and pharmaceutical areas, such as composite materials, biodegradable film and controlled release matrix (Alonso Sande, Teijeiro Osorio, Remuñán López, & Alonso, 2009).

However, the application of KGM as an additive in beverage and liquid transmission during food processing is limited by its high viscosity. It has been reported that KGM oligosaccharides have the potential bioactive benefits as the prebiotic and immunomodulator (Gao, Lou, & Liu, 2010; Jian et al., 2013). Partially hydrolyzed glucomannan polysaccharide could simulate better growth of *Bifidobacterium* and *Lactobacillus* (Al Ghazzewi, Khanna, Tester, &

Piggott, 2007). Therefore, lots of studies have focused on exploring efficient methods for degradation of glucomannan such as acid hydrolysis, enzymatic hydrolysis, physical and irradiation degradation, in order to get functional oligosaccharides or other commercial usages (Feng & He, 2008; Gao et al., 2010; Jian et al., 2013; Xu, Sun, Yang, Ding, & Pang, 2007; Yong chun, Qing-ruo, Ren, & Yan, 2005). Although many degradation methods are effective, they still possess several disadvantages. For example, the enzymatic degradation needs rigidly and mildly reactive environment and the enzymes are hardly separated from products, which increase the cost (Chen, Fu, & Ou, 2002). The alkaline degradation has been carried out into various polysaccharides, such as alginate (Haug, Larsen, & Smidsrod, 1967), but rarely studies well accessed on alkaline degradation of KGM.

KGM is composed of a linear chain of β -1,4-linked D-glucose, with side branches through β -1,6-glycosyl units (Chen et al., 2002; Li & Xie, 2004). The acetyl groups along the KGM backbone are located, on average, every 9–19 sugar units at the C-6 position (Nishinari, 2000). Deacetylation which formed by alkaline treatment has been demonstrated to improve the gelling properties of KGM by some researches. Under alkaline condition, deacetylation causes KGM molecular to transform from semi-flexible linear chain (with length of 1054.11 nm) to strong self-crimping elastic microsphere (with diameter of 40–50 nm) (Chen, Li & Li, 2011; Li, Kennedy, Jiang & Xie, 2006; Li, Xia, Wang & Xie, 2005). Therefore, it is necessary to take the effect of deacetylation into

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consideration when the regulation of alkaline degradation was evaluated comprehensively.

Actually, the temperature and molecular conformation also exert a leading role of alkaline degradation (Akbar, Iqbal, Massey, & Masih, 2012; Hansson & Hartler, 1970; Riedo, Scalarone, & Chiantore, 2010). Thermal treatment is a commonly degraded or assisted methods used for modification monosaccharides. For example, thermal treatment of chitosan (Zawadzki & Kaczmarek, 2010) or combined with oxidation degraded starch (Jankovic, 2013).

In the present study, the effects of deacetylation and temperature on alkaline degradation were evaluated. This comprehensive effect of alkaline and thermal treatment was investigated by analyzing oligosaccharides structure and recording the kinetic model of hydrolysis. The rheological properties of hydrolysates were characterized for molecular conformation and entanglement.

2. Materials and methods

2.1. Materials

Konjac glucomannan ($M_w \sim 980\,000$) was supplied by Nongxiang Biotech Co. (Wuhan, China) and used as received without further purification. All other chemicals were analytical reagents which were purchased from Sinopharm Chemical Reagent Co. (Beijing, China).

2.2. Alkaline-thermal degradation of KGM

0.3% (w/w) KGM solution was prepared by suspending KGM powder in distilled water and completely swelling at 25 °C for stirring 2 h. The value of pH with original KGM solution was 5.6. Then the degraded samples were controlled by adjusting pH and temperature. During degradation, 30 mL sample was collected every 30 min for analysis. The pH was adjusted into 7.2, 8.2, 9.2 by 0.1 M NaOH and the temperature was varied from 25 to 80 °C.

2.3. Molecular weight measurement

Viscosity average molecular weight of samples after hydrolysis was measured by an Ubbelodhe viscometer (Liangjing Co., Shanghai, China) at 25 ± 0.1 °C. The relative and specific viscosities (η_r and η_{sp}) were calculated according to

$$\eta_r = \frac{t}{t_0}, \quad \eta_{sp} = \eta_r - 1 \quad (1)$$

where t and t_0 is the flow time for the sample solution and the solvent, respectively. The viscosity-average molecular weight (M_η) was determined using the Mark–Houwink equation:

$$[\eta] = K \cdot [M_\eta]^\alpha \quad (2)$$

where K and α is the Mark–Houwink constants. According to the previous study (Li & Xie, 2004), the values of K and α are 5.96×10^{-2} and 0.73, respectively. The dried hydrolysates were dissolved in 0.2 M NaCl at room temperature. Before measurement, all solutions were purified by filtering through a 0.45 μm Millipore filter. All the measurements were carried out in six replicates.

2.4. Periodate oxidation

Sodium metaperiodate solutions were used at a concentration range of 0.0175–0.14 mM in accordance with the standard curve recommended for periodate oxidation measurement. The solutions of hydrolysate (3 mg/mL) and sodium metaperiodate (0.035 mol/L) were added into the reaction vessel, which was then stored in the dark place for 7 d (Kristiansen, Potthast, & Christensen,

2010). Subsequently, the absorbance was measured at 223 nm using a UV-1100 spectrophotometer (MAPADA, Shanghai, China). The standard curve was obtained: $y = 0.3965x$ ($R^2 = 0.9974$), where x is represented the consumption of sodium periodate (mol), and y is absorption measured by spectrophotometer.

2.5. Rheological measurements

The rheological measurements were carried out using a controlled stress rheometer (AR2000ex, TA, UK) with parallel plate geometry (40 mm, 1 mm gap). The alkali-thermal degraded products were equilibrated to room temperature for 30 min before measurement. Steady viscosity data were collected at shear rates from 0.01 to 300 s^{-1} at a constant temperature of 25 °C (Gaaloul, Corredig, & Turgeon, 2009). The apparent viscosity versus shear rate data was fit by the power law mode.

Small deformation oscillatory test was performed within the linear viscoelastic range controlled the strain of 0.5% which. Frequency sweep tests were performed at four different temperatures with frequency ranging from 0.1 to 100 rad/s. Temperature sweep tests were carried out at constant frequency (0.1 Hz) with heating from 25 to 90 °C by 1 °C/min and cooling back to 25 °C by 2 °C/min. The samples were covered with a thin layer of paraffin oil to prevent moisture loss. Measurements were carried out in triplicate. G' (storage modulus), G'' (loss modulus), and $\tan \delta$ (G''/G') were recorded respectively (Funami et al., 2009).

2.6. Statistical analysis

All the experiments were performed in triplicates and the results were reported as average value and standard deviation. A least significant difference (LSD) test with a confidence interval of 95% was used to compare the means.

3. Results and discussion

3.1. Molecular changes of KGM during the alkaline-thermal process

M_η can be a good indicator reflecting the rigidity of polymer chains. Hereby, the changes of M_η during the hydrolysis process under various temperature and pH conditions were monitored.

At the natural pH (5.6), M_η decreased slightly. The M_η decreased from 1.587×10^6 to 1.567×10^6 , 1.236×10^6 to 1.181×10^6 , 1.028×10^6 to 8.71×10^5 and 8.54×10^5 to 5.68×10^5 at 25 °C, 50 °C, 65 °C and 80 °C, respectively (Fig. 1). The data in Fig. 1 indicates that the M_η declined substantially with the pH rising, when the pH 9.2 reached a peak rate. At the same time, it suggests high pH accelerates the process of KGM degradation under the same temperature condition.

Temperature is also considered as one of the important factors affecting M_η during alkaline hydrolysis. At higher temperature, the decreasing trend is more obvious. Taking pH 9.2 as an example, after 2 h degradation, M_η decreased from 1.587×10^6 to 1.51×10^6 at 25 °C, while it decreased from 8.54×10^5 to 3.06×10^5 at 80 °C (Fig. 1). Overall, the decreasing of M_η at low temperature (25 and 50 °C) was much less than that at high temperature (65 and 80 °C). These results are similar to the previous studies about alkaline degradation of alginates (Haug et al., 1967). The alkaline degradation reaction is more pronounced under high alkalinity and high temperature condition. The change of M_η as a function of degradation time at higher temperature (65 and 80 °C) exhibited two stages. The cleavages into hydrolyzed products lead to a rapid decrease of M_η in short times followed by a slower rate. In the first stage, the M_η decreased sharply during the first hour of hydrolysis, which might be because the force of reaction does not rely on oxygen, but

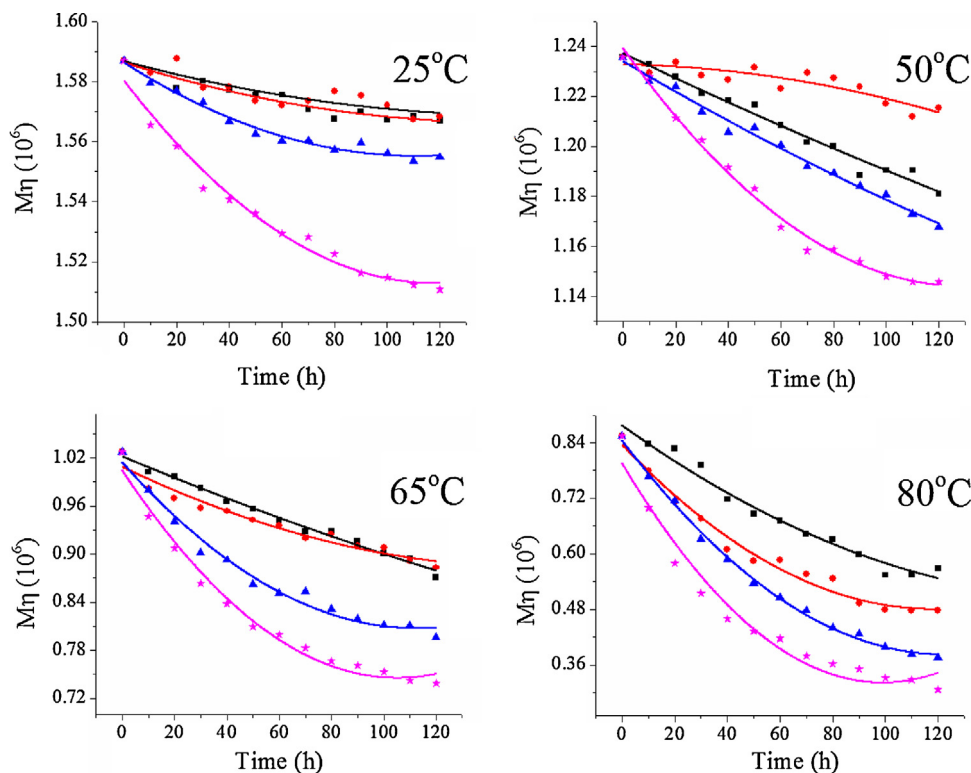


Fig. 1. The M_η variations of KGM solutions as a function of degradation time at different temperature and pH: ●: pH 5.6; ■: pH 7.2; ▲: pH 8.2; and ★: pH 9.2.

starts on the carboxyl end group. In the second stage, the degradation might be attributed to oxidative reaction. It produced new carboxyl end group to sustain the first stage (Akbar et al., 2012).

Hence, assisted alkaline could improve the efficiency of thermal degradation. Consequently, it is essential to understand the mechanism of alkaline degradation on this complex effect. Partially, reducing glucose units of polysaccharide chains will be transformed to their C2-epimers in alkaline solution. The classical transformation is a base-catalyzed enolization, which may revert to the starting aldose or be converted to epimers of the original aldose (Haug et al., 1967).

3.2. Kinetics study of KGM hydrolysis

The kinetics of alkaline-thermal hydrolysis of KGM has a similar pattern with that of other polysaccharides, such as alginate, κ -carrageenan (Haug et al., 1967; Whistler & BeMiller, 1958). Here, KGM is a kind of half-flexibility molecular with suitable density for crystalline region and amorphous region. To compare the degradation rate of other similar polysaccharides, the first-order degradation kinetics was assumed, which is a generally accepted model for random hydrolysis processes. The first-order kinetics for polymer degradation can be simply given by

$$\frac{dL}{dt} = -kL \quad (3)$$

where L is the total number of degradable linkages and k is a rate constant (min^{-1}). L can be substituted to $N_0(M/m - 1)$, where N_0 is the total number of polymer chains, M is the average molecular weight, and m is the molecular weight of the repeating unit. Assuming that $M/m \gg 1$, Eq. (4) can be obtained as following:

$$\frac{1}{M_t} = \frac{1}{M_0} + \frac{kt}{m} \quad (4)$$

where M_t and M_0 are the molecular weights of hydrosate at degradation time t and 0, respectively. This linear relationship between the inverse molecular weight and degradation time has been applied to various systems for the study of degradation kinetics (Hien, Phu, Duy, & Lan, 2012). Besides, M_t is related to the intrinsic viscosity through Mark-Houwink equation:

$$M_t = \left(\frac{[\eta]}{K} \right)^{1/\alpha} \quad (5)$$

Finally, the substitution of Eqs. (5) in (6) yields:

$$Kt = m \times K^{1/\alpha} ([\eta]_t^{-1/\alpha} - [\eta]_0^{-1/\alpha}) \quad (6)$$

where $[\eta]_t$ and $[\eta]_0$ are the intrinsic viscosities at time t and zero, respectively, α and K are the constants of Mark-Houwink equation.

Kinetics analysis of KGM at the different concentration of OH^- showed the general heterogeneity of the degradation reaction with time. It presents two kinetically distinguishable polysaccharide fractions with different reactivity. The rate of degradation in two fractions represents the first-order random hydrolysis process for the chain scission of KGM under alkaline condition. The two distinguishable degradation stages with different reactivity were marked by K_1 and K_2 , respectively. Briefly, K_1 is assigned to the first fraction with a higher degraded rate in the first 1 h and K_2 is the second fraction with a stable rate constant in the latter 1 h. The rate constants for the degradation of KGM at different pH and temperature conditions were shown in Fig. 2. Based on kinetics data, the degradation rate constants (K_1 and K_2) became larger with higher pH. At the same incubation temperature, the degradation rate K_2 is always lower than K_1 . When the degradation temperature is 80 °C, K_1 is 0.040, 0.058, 0.088 and K_2 is 0.030, 0.049, 0.055 at pH 7.2, 8.2, and 9.2, respectively. This might be attributed to the fact that the D-glucose is easier to form C2-epimerization than the D-mannose. The similar degradation kinetics during alkali delignification of the principal polysaccharides, such as cellulose, can

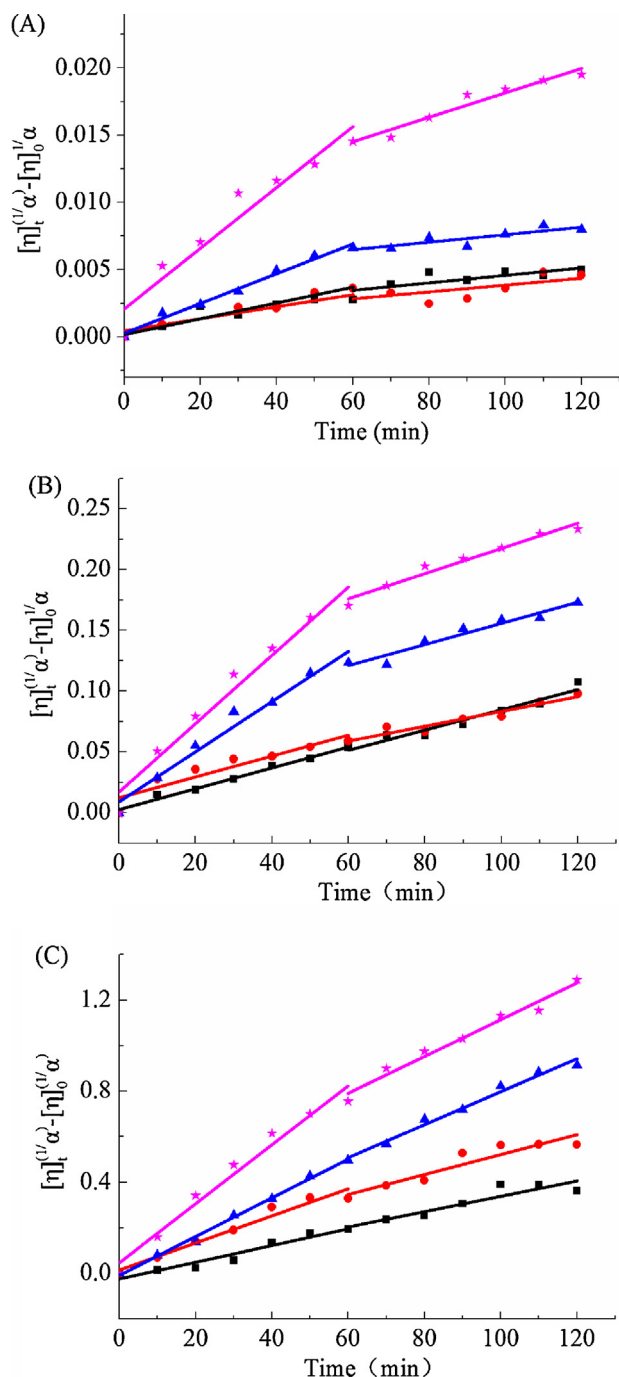


Fig. 2. The relative $(1/[\eta])^{(1/\alpha)}$ changes of KGM solutions with alkali verse time at different temperatures. (A)–(C) are represented the pH 7.2, 8.2, 9.2, respectively. ● : 25 °C; ■ : 50 °C; ▲ : 65 °C; and ★ : 80 °C.

be accurately described in terms of two simultaneous irreversible first-order reactions (Shatalov & Pereira, 2005). Meanwhile, they found the activation energy of cellulose degradation was estimated to be 105.2 and 106.5 kJ/mol in two stages, respectively. Herein, the activation energy of KGM alkaline degradation and the effect of alkalinity were studied either.

3.3. Effect of temperature and alkalinity on degradation rate constants

The hydrolysis rate constants of KGM verse pH and different temperatures are shown in Fig. 3. The temperature dependency

of the alkaline degradation behavior of the KGM was studied by the activation energy. The activation energy (E_a) is the minimum amount of energy required to initiate a reaction in which temperature is a key independent variable, expressed by Eq. (7):

$$\ln k = \ln A - \frac{E_a}{RT} \quad (7)$$

It is the well-known that formula is Arrhenius equation, where A is the Arrhenius constant, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature. Fig. 3a shows a linear relationship in the range of temperature 50–80 °C, which is in a good agreement between the data and the relation expressed in Eq. (7). In the first regime, the activation energy of alkaline degradation decreased from 144.69 to 104.26 kJ/mol with increasing pH. In the second degradation regime, the activation energy was found to be independent on pH, which was 118.70, 126.27 and 121.23 kJ/mol for pH 7.2, 8.2 and 9.2, respectively. That means that the activation energy was influenced by the concentration of OH^- within 1 h incubation. After 1 h, the activation energy could not rely on the OH^- concentration.

The effect of alkalinity on degraded rate constants was recorded in Fig. 3b. The rate constant of alkaline degradation at different temperature (50, 65 and 80 °C) was calculated under the alkaline pH condition. K_1 were 0.45, 0.25 and 0.16 for 80, 65 and 50 °C, respectively. The results indicated that the concentration of OH^- affected the rate constant significantly in the first regime. Oppositely, in the second regime, K_2 was kept almost stable at around 0.12. Therefore, the first 1 h is the critical period of alkaline-thermal degradation.

3.4. Periodate oxidation

Oxidation by periodate ion is a classical method used for determining the structure of complex carbohydrates. Periodate oxidation could select to fracture the specific chemical structure and closely related structures, such as vicinal diols, 1,2-dicarbonyl compounds, α -hydroxyl and α -keto acids (Kim, Kuga, Wada, Okano, & Kondo, 2000). The consumption of periodate and the yield of formic acid are calculated to analyze the degradation products. The periodate oxidation does not only reflect the macromolecular properties, but also provides some details on chain flexibility and extension. Fig. 4a presents the mechanism and main products obtained for (1 → 2)-linked and (1 → 3)-linked. KGM is a linear random polymer of β -1,4-linked D-glucose and D-mannose residues. The C2–C3 bond of the 1,4-glucan units of KGM could be specifically cleaved by periodate oxidation and the vicinal hydroxyl groups of KGM can be oxidized to dialdehyde and its derivatives. The consumption of sodium periodate increased with increasing pH from 5.6 to 8.2 and then decreased at pH 9.2 (Fig. 4b). Fig. 4c reflected the generation of formic acid under different alkalinity at 80 °C. At pH 9.2, the generation of formic acid was lowest, which might be because the periodate oxidation was largely affected by the pH condition which has been reported that the oxidization reaction is catalyzed by the presence of H^+ . On the other hand, pH-sensitive compounds is easily formed during the reaction, such as aldehyde acetal (Li, Wu, Mu, & Lin, 2011). Actually, the amount of generated formic acid is always higher than that by theoretically calculated. This was because pH value acts a vital role in integrity of the internal group as well as the reaction process and production.

3.5. Rheological behavior

3.5.1. Steady shear analysis

The apparent viscosities of hydrolyzed KGM at different shear rates are shown in Fig. 5. The apparent viscosities decreased with

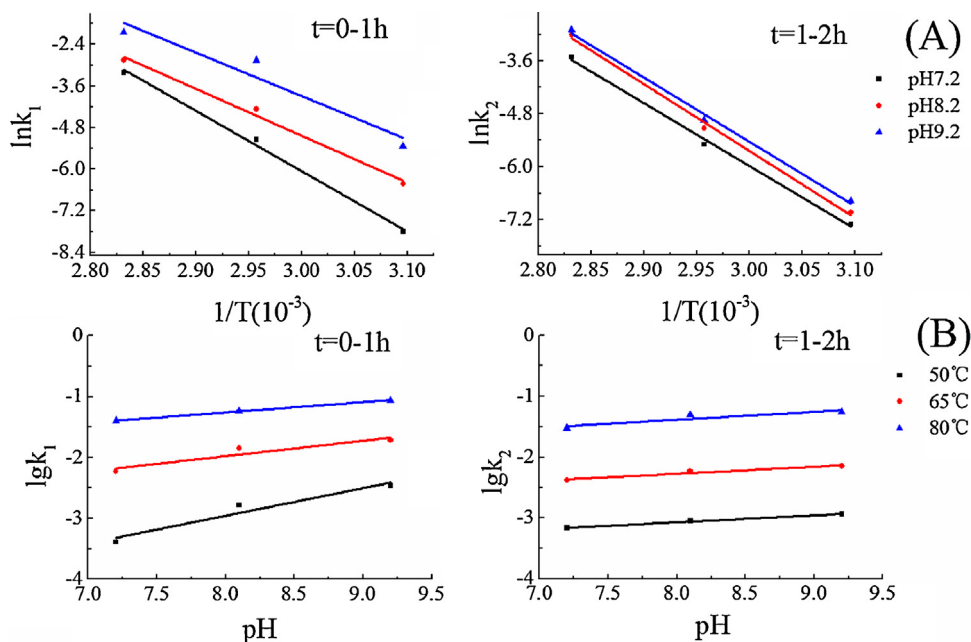


Fig. 3. Correlation between the degradation rate and absolute temperature (A) and alkalinity (B).

the increasing of the shear rate in most samples, indicating they belonged to the non-Newtonian fluids and owned the pseudo plastic characteristics. The shear thinning behavior is similar to each group prepared with the same concentration, irrespective of structural details and measurement conditions. These results are in agreement to the previous study (He, Ng, Toh, & Goh, 2012; Mei et al., 2012; Chua et al., 2012). It may be due to the orientation of rigid molecular chains which disturbs the formation of chain entanglements during the applied shear force. When the polymer with higher molecular weight exists in solutions, the more interactions can be established by entanglements and

hydrogen, electrostatic and hydrophobic bonds. At the lower shear rates, the rate of disruption is fit for creation of new ones, resulting in a constant apparent viscosity. At the higher shear rates, the disruption predominates, leading to the decrease apparent viscosity.

However, an interesting phenomenon of apparent viscosity sudden spurt in the range of lower shear rates ($0.01-0.05 \text{ s}^{-1}$) is observed at pH 9.2 and 25°C (Fig. 5). This is attributed to deacetylation mechanism, which confers KGM solubility to insoluble soft gel in aqueous solution. To study the alkaline degradation of KGM, it is thus essential to take deacetylation into consideration.

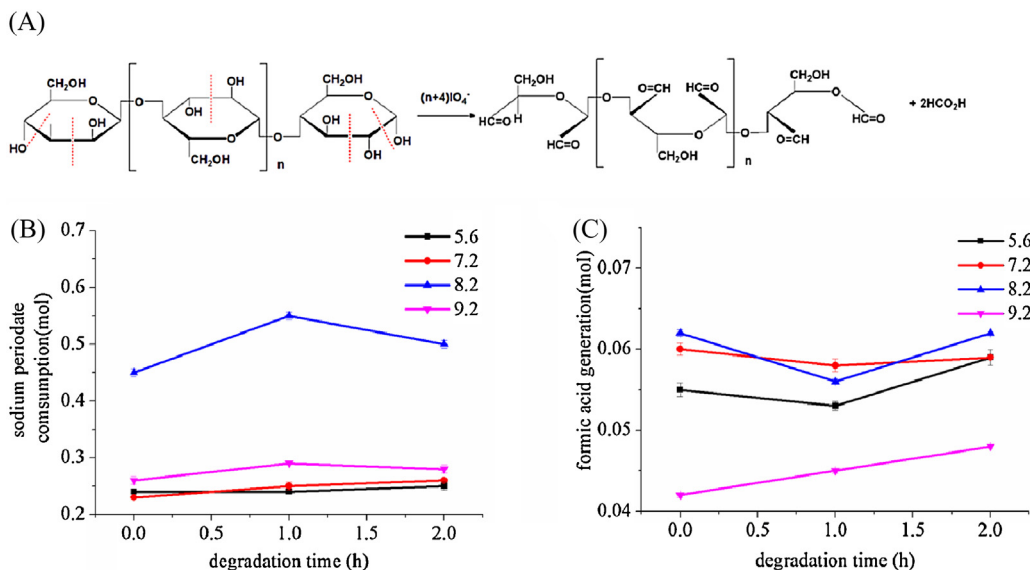


Fig. 4. Periodate oxidation data (A) the mechanism of KGM periodates oxidation; (B) variation of sodium periodates consumption of different hydrolysis KGM; and (C) variation of formic acid generation from different hydrolysis KGM.

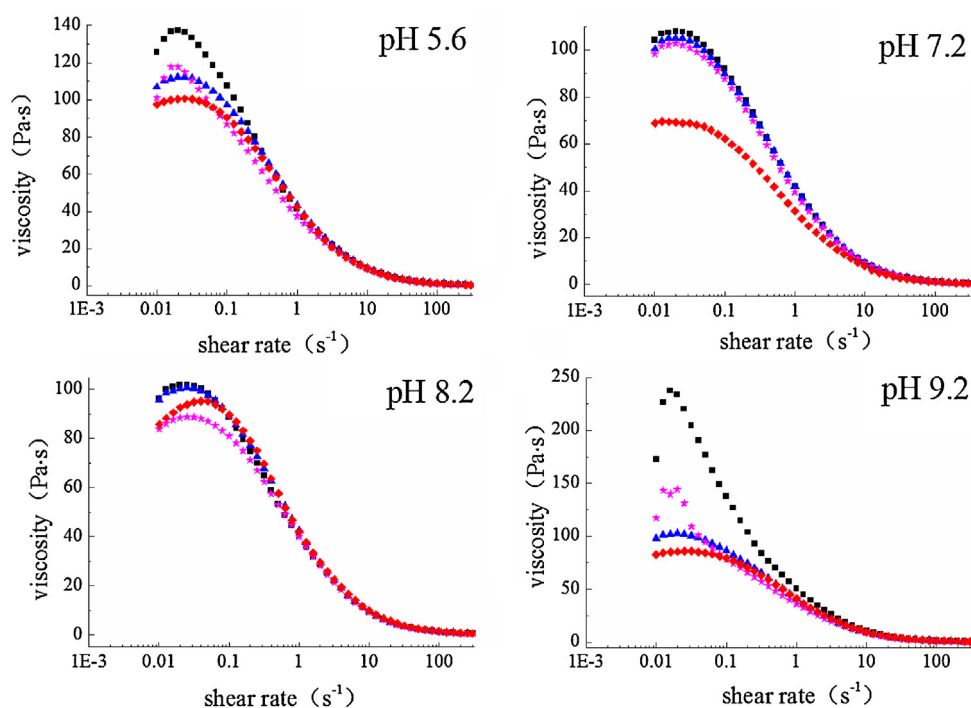


Fig. 5. Shear rate dependence of viscosity for hydrolyzed KGM in different alkaline solutions ■: 25 °C; ▲: 50 °C; ★: 65 °C; and ◆: 80 °C.

Data fitting of shear thinning behavior was obtained by a two-parameter model, namely power law function:

$$\eta = K \cdot \gamma^{n-1} \quad (8)$$

where η is apparent viscosity; K is the consistency index; n is the flow behavior index; γ is the shear rate. Table 1 listed the values of K and n of the hydrolyzed KGM with alkaline-thermal treatment. At lower pH condition (5.6 and 7.2), K decreased and n increased slightly with increasing temperature. The results reflected that the characteristics of pseudo plastic seemed weaker, which meant higher temperature disordered the arrangement of the molecular and weakened the interaction molecular forces. On the other side, when the pH reached 9.2, the value of K sudden increased to 51.99, which is correlative to the change of apparent viscosity, due to deacetylation.

3.5.2. Frequency sweep test

Frequency sweep test was carried out to verify the viscoelastic property and interaction of KGM molecular chains. All samples

displayed typical of an amorphous viscoelastic liquid with flexible macromolecular conformation (Fig. 6). Both the storage modulus (G') and the loss modulus (G'') of the hydrolyzed KGM displayed a growth with the increasing frequency. G' was almost frequency-dependent at all frequencies ranges, while G'' was apparently frequency-independent at higher frequencies. G' value represented the elastic behavior of the sample, while G'' value reflected the viscous behavior. G' was smaller than G'' at low frequency but larger than G'' at high frequency. This tendency revealed that entanglement and disentanglement transformation at the level of macromolecules. The crossover point of the modulus (G' and G'') was recorded to indicate commencement of polymer chain entanglement. When the temperature was lower than 65 °C, the frequency sweep curves of hydrolyzed products changed slightly at pH 5.6, 7.2 and 8.2. The crossover point of sample hydrolyzed at 25 °C under different pH was 1.408, 1.339, 1.207 and 0.621 rad/s for pH 5.6, 7.2, 8.2 and 9.2, respectively. That suggests that the KGM molecular structure was not degraded significantly at pH 7.2 and 8.2. Inversely, deacetylation of KGM at pH 9.2 forms a more compacted molecular entanglement network. The modulus crossover point shifted to low frequencies.

When the temperature rose to 65 °C, the viscosity behavior increased with increasing pH, which might be caused by the speeding molecular motion exposed more active sites, thus the molecular entanglement and the hydrogen bonding was weakened. Therefore, the crossover points shift to higher frequencies. At pH 9.2, the crossover point is 2.056 rad/s.

3.5.3. Temperature sweep test

In order to investigate the effect of temperature on the elastic-viscosity properties of hydrolyzed KGM, dynamic temperature oscillatory tests were performed (Fig. 7). It is observed that the value of G' and G'' remarkably decreased dependent on temperature increasing. This may be attributed to increased activities of molecular chains and decreased hydrogen bonding

Table 1

(a) Parameter K (mPa sⁿ) of power law equation fit by computer and (b) parameter n of power law equation fit by computer.

pH	Temperature (°C)			
	25	50	65	80
(a)				
5.6	44.38	44.46	44.40	42.61
7.2	43.25	43.19	42.13	33.99
8.1	43.42	43.73	42.24	44.85
9.2	51.99	42.53	40.05	43.80
(b)				
5.6	0.236	0.235	0.233	0.237
7.2	0.235	0.237	0.242	0.247
8.1	0.240	0.235	0.240	0.241
9.2	0.231	0.237	0.249	0.245

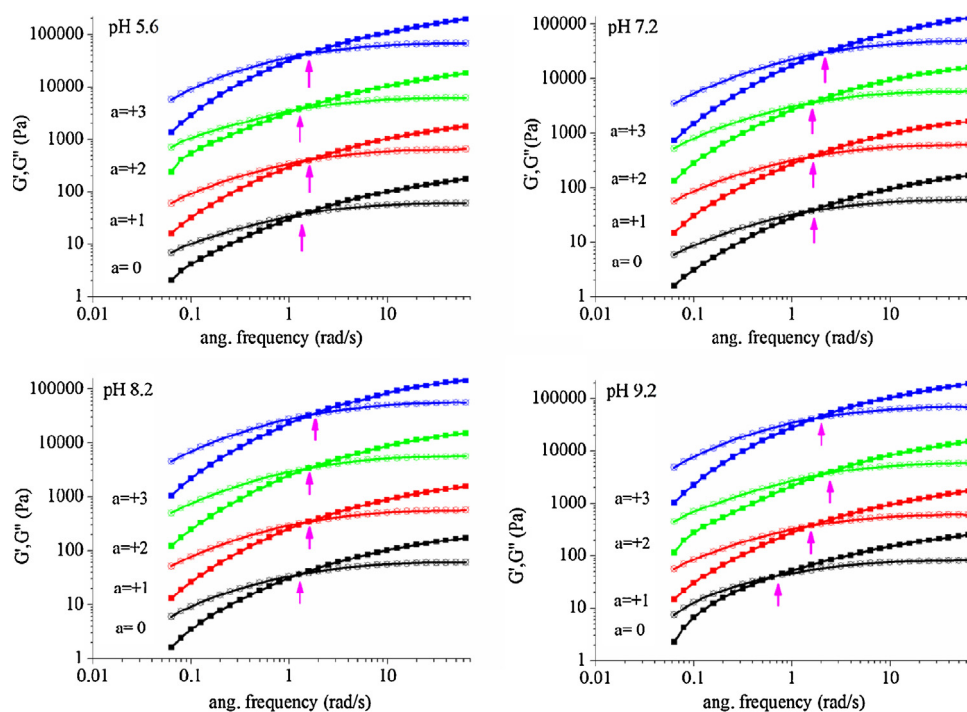


Fig. 6. Frequency dependence of G' and G'' for 1.0% KGM samples hydrolyzed in different condition. G' : $\circ$, G'' : $\bullet$. Dark, red, green and blue lines are represented 25 °C, 50 °C, 65 °C, and 80 °C respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of intermolecular, which promotes the flow capacity of solution. Shear viscosities were sensitive to temperature, indicating that flow characteristic of KGM can be adjusted by regulating the temperature. The modulus (G' , G'') of every hydrolyzed KGM reached a plateau at the end of test temperature (near 90 °C). However, the rates of modulus decrease became fastest when pH reached 9.2.

The sol–gel crossover point determined from the commonly used criterion $G' = G''$ are shown in Fig. 7. Both of hydrolyzed samples have the similar sol–gel crossover points during heating process. The gelling temperature at all pH conditions was around 55 °C. During cooling process, G' was kept higher than G'' at pH 9.2, revealing that a thermo-irreversible gel was formed. This result has also been found in the previous study (Chen et al., 2011).

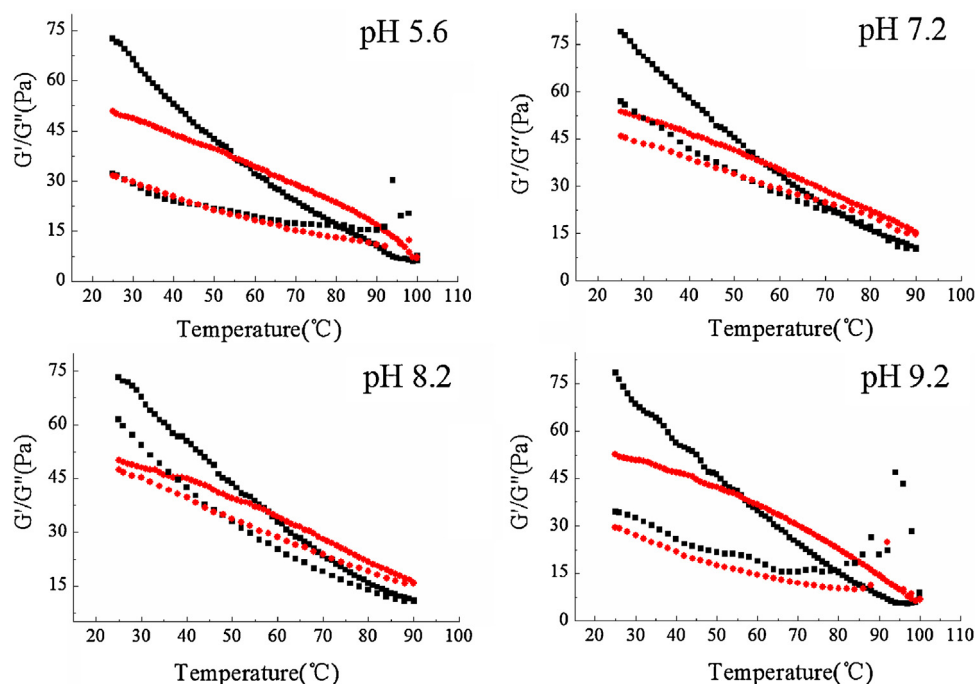


Fig. 7. Temperature sweep of different pH KGM solution (0.1 g/L) at 0.5% strain and frequency of 1 Hz. The dark and red lines are represented G' and G'' , respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

4. Conclusions

Low-viscosity KGM was obtained by alkaline-thermal hydrolysis treatment. The decreasing average-viscosity molecular weight (M_v) was dependent on high alkalinity and temperature. The alkaline hydrolysis process was found to be two stages and the hydrolysis rate in the first stage (within 1 h) was higher than that in the second stage (from 1 to 2 h). Both the hydrolysis rate was accelerated by increasing temperature. Rheological results demonstrate that deacetylation of KGM happened at pH 9.2 and 25 °C. More specific, Figs. 5 and 6 exhibited KGM had formed a weak gel network at pH 9.2 and 25 °C, Fig. 7 revealed KGM at pH 9.2, it had a property of irreversible thermal gel, which G' was kept higher than G'' at the cooling process. Presumably, deacetylation plays a positive role in KGM alkaline hydrolysis. The molecular weight of KGM sharply decreased with the deacetylation extended (Fig. 1). On the other hand, the degradation rate of deacetylated KGM shared the same trend and exhibited higher value than that of samples disposed at 50 °C when pH 9.2 (Fig. 2).

Acknowledgments

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References

- Akbar, J., Iqbal, M. S., Massey, S., & Masih, R. (2012). Kinetics and mechanism of thermal degradation of pentose- and hexose-based carbohydrate polymers. *Carbohydrate Polymers*, 90(3), 1386–1393.
- Al Ghazzewi, F. H., Khanna, S., Tester, R. F., & Piggott, J. (2007). The potential use of hydrolysed konjac glucomannan as a prebiotic. *Journal of the Science of Food and Agriculture*, 87(9), 1758–1766.
- Alonso Sande, M., Teijeiro Osorio, D., Remuñán López, C., & Alonso, M. (2009). Glucomannan, a promising polysaccharide for biopharmaceutical purposes. *European Journal of Pharmaceutics and Biopharmaceutics*, 72(2), 453–462.
- Chen, X., Fu, D., & Ou, Y. (2002). The review of chemical structure and modification of konjac glucomannan. *Natural Product Research and Development*, 14(2), 65–68.
- Chen, J., Li, J., & Li, B. (2011). Identification of molecular driving forces involved in the gelation of konjac glucomannan: Effect of degree of deacetylation on hydrophobic association. *Carbohydrate Polymers*, 86(2), 865–871.
- Chua, M., Baldwin, T. C., Hocking, T. J., & Chan, K. (2010). Traditional uses and potential health benefits of *Amorphophallus konjac* K. Koch ex NE Br. *Journal of Ethnopharmacology*, 128(2), 268–278.
- Chua, M., Chan, K., Hocking, T. J., Williams, P. A., Perry, C. J., & Baldwin, T. C. (2012). Methodologies for the extraction and analysis of konjac glucomannan from corms of *Amorphophallus konjac* K. Koch. *Carbohydrate Polymers*, 87(3), 2202–2210.
- Feng, C., & He, Q. (2008). Optimization of ultrasonic degradation of konjac glucomannan by response surface analysis. *Science and Technology of Food Industry*, 1, 041.
- Funami, T., Fang, Y., Noda, S., Ishihara, S., Nakauma, M., Draget, K. I., et al. (2009). Rheological properties of sodium alginate in an aqueous system during gelation in relation to supermolecular structures and Ca^{2+} binding. *Food Hydrocolloids*, 23(7), 1746–1755.
- Gaaloul, S., Corredig, M., & Turgeon, S. L. (2009). Rheological study of the effect of shearing process and κ -carrageenan concentration on the formation of whey protein microgels at pH 7. *Journal of Food Engineering*, 95(2), 254–263.
- Gao, J., Lou, D., & Liu, K. (2010). The degradation of konjac glucomannan by cellulase. *Journal of Neijiang Normal University*, 8, 014.
- Hansson, J. Å., & Hartler, N. (1970). Alkaline degradation of pine glucomannan. *Holzforchung-International Journal of the Biology, Chemistry, Physics and Technology of Wood*, 24(2), 54–59.
- Haug, A., Larsen, B. R., & Smidsrod, O. (1967). Studies on the sequence of uronic acid residues in alginic acid. *Acta Chemica Scandinavica*, 21, 691–704.
- He, P., Ng, K. S., Toh, S. L., & Goh, J. C. (2012). In vitro ligament-bone interface regeneration using a trilineage coculture system on a hybrid silk scaffold. *Biomacromolecules*, 13(9), 2692–2703.
- Hien, N. Q., Phu, D. V., Duy, N. N., & Lan, N. T. K. (2012). Degradation of chitosan in solution by gamma irradiation in the presence of hydrogen peroxide. *Carbohydrate Polymers*, 87(1), 935–938.
- Jankovic, B. (2013). Thermal characterization and detailed kinetic analysis of Cassava starch thermo-oxidative degradation. *Carbohydrate Polymers*, 95(2), 621–629.
- Jian, W., Sun, Y., Huang, H., Yang, Y., Peng, S., Xiong, B., et al. (2013). Study on preparation and separation of konjac oligosaccharides. *Carbohydrate Polymers*, 92(2), 1218–1224.
- Kim, U. J., Kuga, S., Wada, M., Okano, T., & Kondo, T. (2000). Periodate oxidation of crystalline cellulose. *Biomacromolecules*, 1(3), 488–492.
- Kristiansen, K. A., Potthast, A., & Christensen, B. E. (2010). Periodate oxidation of polysaccharides for modification of chemical and physical properties. *Carbohydrate Research*, 345(10), 1264–1271.
- Li, B., Kennedy, J., Jiang, Q., & Xie, B. (2006). Quick dissolvable, edible and heatsealable blend films based on konjac glucomannan–Gelatin. *Food Research International*, 39(5), 544–549.
- Li, H., Wu, B., Mu, C., & Lin, W. (2011). Concomitant degradation in periodate oxidation of carboxymethyl cellulose. *Carbohydrate Polymers*, 84(3), 881–886.
- Li, B., Xia, J., Wang, Y., & Xie, B. (2005). Grain-size effect on the structure and antiobesity activity of konjac flour. *Journal of Agricultural and Food Chemistry*, 53(19), 7404–7407.
- Li, B., & Xie, B. (2004). Study on molecular chain morphology of konjac glucomannan. *Scientia Agricultura Sinica*, 37(2), 280–284.
- Mei, T., Xu, X., Li, B., Li, J., Cui, B., Zhou, B., et al. (2012). Synergistic interaction of konjac glucomannan and gellan gum investigated by rheology and texture analysis. *Journal of Applied Polymer Science*, 125(2), 1363–1370.
- Nishinari, K. (2000). Konjac glucomannan. *Developments in Food Science*, 41, 309–330.
- Riedo, C., Scalapone, D., & Chiantore, O. (2010). Advances in identification of plant gums in cultural heritage by thermally assisted hydrolysis and methylation. *Analytical and Bioanalytical Chemistry*, 396(4), 1559–1569.
- Shatalov, A. A., & Pereira, H. (2005). Kinetics of polysaccharide degradation during ethanol–alkali delignification of giant reed—part 1. Cellulose and xylan. *Carbohydrate Polymers*, 59(4), 435–442.
- Takigami, S. (2000). Konjac mannan. In G. O. Phillips, & P. A. Williams (Eds.), *Handbook of hydrocolloids* (pp. 413–424). Boca Raton: CRC/Woodhead Publishing.
- Whistler, R. L., & BeMiller, J. (1958). Alkaline degradation of polysaccharides. *Advances in carbohydrate chemistry*, 13, 289–329.
- Xu, Z., Sun, Y., Yang, Y., Ding, J., & Pang, J. (2007). Effect of γ -irradiation on some physiochemical properties of konjac glucomannan. *Carbohydrate Polymers*, 70(4), 444–450.
- Yaseen, E., Herald, T., Aramouni, F., & Alavi, S. (2005). Rheological properties of selected gum solutions. *Food Research International*, 38(2), 111–119.
- Yong chun, H., Qing-ruo, X., Ren, H., & Yan, C. (2005). Study on the degradation of konjac glucomannan with H_2O_2 under the microwave. *Food Science*, 8, 055.
- Zawadzki, J., & Kaczmarek, H. (2010). Thermal treatment of chitosan in various conditions. *Carbohydrate Polymers*, 80(2), 394–400.