



Optimization of adding konjac glucomannan to improve gel properties of low-quality surimi

Jianhua Liu, Xinping Wang, Yuting Ding*

Department of Food Science and Engineering, College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310014, PR China

ARTICLE INFO

Article history:

Received 5 July 2012

Received in revised form 7 August 2012

Accepted 25 August 2012

Available online 1 September 2012

Keywords:

Konjac glucomannan

Response surface methodology

Low-quality surimi

Glycation

Gel properties

ABSTRACT

This paper reports a study of the influence of konjac glucomannan (KGM) on the gel properties of low-quality surimi. Compared with the surimi control, adding KGM significantly improved its gel properties. KGM content, heating temperature and heating time had significant effects on gel properties. Response surface methodology (RSM) was applied to optimize the processing parameters of adding KGM to low-quality surimi for improving the gel properties. The optimal conditions for gel properties were as follows: KGM content 1.50%, heating temperature 32.3 °C and heating time 184.6 min. The predicated gel strength for optimum conditions was 3578 g mm. The predicated results for optimum conditions coincided well with experiment values.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Many species of freshwater fish are of low quality because of their rapid growth and high yield. They can be processed as surimi-based products, which is one of their major processing approaches. Low-temperature frozen storage is a widely used method for long-term storage of surimi products. However, during frozen storage, surimi may lose its functional properties as a result of myofibrillar protein denaturation, such as the decrease of water-holding capacity, solubility and gel-forming ability (Xiong et al., 2009). Therefore, the prevention of protein denaturation is of much importance when surimi is used as foodstuffs.

Glycation is an effective and promising method for improving the functional properties of food proteins (Liu, Ru, & Ding, in press). The Maillard reaction is often used for glycation of proteins as a safe and mild modification method (Saeki, 1997). Different proteins, such as ovalbumin, lysozyme, whey proteins and soy proteins have been used to conjugate with sugar, mainly glucose, dextran, chitosan or galactomannan, with the aim to improve their solubility, foaming properties, emulsifying properties and heat stability (Akhtar & Dickinson, 2007; Aoki, Hiidome, Sugimoto, Ibrahim, & Kato, 2001; Babiker & Kato, 1998; Chevalier, Chobert, Popineau, Nicolas, & Haertlé, 2001; Dickinson & Galazka, 1991; Jiménez-Castaño, Villamiel, & López-Fandiño, 2007; Kato, 2002; Kato, Minaki, & Kobayashi, 1993; Kato, Sasaki, Furuta, & Kobayashi,

1990; Nakamura, Kato, & Kobayashi, 1991; Qi, Liao, Yin, Zhu, & Yang, 2010; Song, Babiker, Usui, Saito, & Kato, 2002). The glycation of myofibrillar protein was first studied to investigate the metabolic change with aging or diabetes (Brown, Keith, & Knull, 1990; Syrový & Hodný, 1992, 1993; Yudkin, Cooper, Gould, & Oughton, 1988). Saeki (1997) has prepared neoglycoprotein from myofibrillar protein for the first time. They made many attempts to prepare neoglycoprotein from fish myofibrillar protein by glycation with monosaccharide, oligosaccharide and polysaccharide for improving its functional properties, such as solubility, heat stability and emulsifying properties (Fujiwara, Oosawa, & Saeki, 1998; Saeki & Inoue, 1997; Sato, Sawabe, Kishimura, Hayashi, & Saeki, 2000). For example, Sato et al. (2000) reported that, at 40 °C and 65% relative humidity, the conjugates of carp myofibrillar and alginate oligosaccharide greatly improved the protein solubility in a low ionic strength medium without significant loss of available lysine. The result indicated that the glycation with alginate oligosaccharide was a superior manner for improving the water solubility of fish myofibrillar in view of its nutritional aspect. Therefore, it was supposed that glycation might be able to prevent the surimi protein denaturation.

Konjac glucomannan (KGM) is the main component of the tuber of *Amorphophallus konjac* C. Koch and forms a thermally stable gel (Konnyaku) upon addition of an alkaline coagulant (Yoshimura, Takaya, & Nishinari, 1996). We expected that the addition of a small amount of KGM to surimi would improve its gel properties. Xiong et al. (2009) investigated the cryoprotective effect of KGM on myofibrillar protein from grass carp (*Ctenopharyngodon idella*) during frozen storage at −18 °C and the influence of five levels

* Corresponding author. Tel.: +86 571 88320237; fax: +86 571 88320237.
E-mail addresses: jhliu@zjut.edu.cn (J. Liu), dingyt@mail.hz.zj.cn (Y. Ding).

of KGM on texture properties of grass carp surimi gels. They first extracted myofibrillar protein from grass carp fish meat, then stored at -18°C for 30 days after mixed with KGM. The results showed KGM at the level of 1% had the same good cryoprotective effect as a conventional cryoprotectant (10% sucrose–sorbitol, 1:1, w/w). As the levels of KGM increased, breaking force and deformation of grass carp surimi gels increased significantly. Iglesias-Otero, Borderias, and Tovar (2010) studied the influence of a konjac glucomannan aqueous dispersion (KAD), at different alkalinity levels, on the viscoelastic properties of low-quality squid surimi gels. They first dispersed KGM in distilled water, then modified the pH to different levels, finally mixed with surimi and analyzed its viscoelastic properties. The results showed gels with KAD at high pH had the best rheological properties. Different from these researches, the object of this study was to add KGM to low-quality surimi, trying to prepare neoglycoprotein from fish myofibrillar protein using the Maillard reaction with KGM, so as to improve its gel properties. Compared with their methods, the present approach was much simple, because it did not need to extract myofibrillar protein or disperse KGM in distilled water. The effects of KGM content, heating temperature and heating time on the gel properties were investigated. In addition, the processing conditions for improving gel properties were optimized by RSM.

2. Materials and methods

2.1. Surimi gel preparation

According to the method of Xiong et al. (2009) with some modifications, the surimi was purchased from Shang Yu Tai Zhi Wei Food Service Limited Company of China and stored at -18°C until use. The frozen surimi was thawed at 4°C fridge for 12 h, then ground for 5 min to obtain homogeneous paste. The paste was added with 2.5% (w/w) NaCl and ground for 5 min, then different levels of KGM were added and the mixture was ground for another 5 min. The raw paste was placed in cylindrical cells, and heated at different temperatures for different time, then the cells were placed in water bath at 90°C for 30 min. Afterwards the cells were placed in a water-ice slurry and finally kept refrigerated at 4°C for 12 h.

2.2. Determination of gel properties

Cylindrical samples ($2\text{ cm} \times 2.5\text{ cm}$) were removed from the cylindrical cells and tempered to about 20°C . Gels were pierced to breaking point using a TA. XT. plus Texture analyzer (SMS, Surrey, UK) with a 5 mm-diameter round-ended metal probe. Crosshead speed was 1 mm/s, and a 2 kg load cell was used. The breaking force and the depth of depression were recorded when the gel sample lost its strength and ruptured. All determinations were carried out at least in quintuplicate. Gel strength was calculated using the following formula:

$$\text{gel strength (g mm)} = \text{breaking force (g)} \times \text{depth of depression (mm)}.$$

2.3. Effects of KGM content, heating temperature and heating time on gel properties

After adding 2.5% NaCl to the paste and grinding for 5 min, (a) 0, 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50% (w/w) KGM were added, respectively, and the mixtures were ground for another 5 min, then the raw paste was placed in cylindrical cells, heated at 30°C for 1 h; (b) 1.50% KGM was added and the mixture was ground for another 5 min, then the raw paste was placed in cylindrical cells, heated at 20, 25, 30, 35, 40, 45 and 50°C , respectively for 1 h; (c) 1.50% KGM was added and the mixture was ground for another 5 min, then

Table 1
Factors and levels of RSM.

Code levels	Variables		
	KGM content, X_1 (%)	Heating temperature, X_2 ($^{\circ}\text{C}$)	Heating time, X_3 (min)
−1	1.00	30	120
0	1.25	35	180
1	1.50	40	240

the raw paste was placed in cylindrical cells, heated at 30°C for 0, 60, 120, 180, 240, 300 and 360 min, respectively. All the cells were placed in water bath at 90°C for 30 min. The forward and after-ward procedures were taken according to the method described in Section 2.2. The surimi without adding KGM was used as the control.

2.4. Experimental design

According to prior experimental findings, the most influential factors on gel properties were KGM content (X_1), heating temperature (X_2) and heating time (X_3). In order to evaluate the effects and interactions of these three factors, RSM was used in designing this experiment. The 'Design Expert' software (version 8.0.6, Stat-Ease, Inc., Minneapolis, USA) was used to generate the Box–Behnken experimental designs. The independent variables were the KGM content (X_1), heating temperature (X_2) and heating time (X_3). Each independent variable had coded levels of −1, 0 and 1. This design was constructed based on a 3^3 factorial design, three replications of the central run, leading to 17 sets of experiments, allowing each experimental response to be optimized. The experimental designs of the coded (X) and actual (KGM content, temperature, time) levels of variables are shown in Table 1. The response (Y) was gel strength. The response function Y was related to the coded variables (X_i , $i = 1, 2, 3$) by a second-degree polynomial equation using the method of least squares:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 \quad (1)$$

where Y is the response calculated by the model; X_1 , X_2 and X_3 are coded variables, corresponding to KGM content, heating temperature and heating time respectively. a_1 , a_2 , a_3 are the linear; a_{11} , a_{22} and a_{33} are the quadratic and a_{12} , a_{13} and a_{23} are the cross-product effects of X_1 , X_2 and X_3 factors on the response.

Analysis of variance (ANOVA) was performed. ANOVA tables were generated and the effects and regression coefficients of individual linear, quadratic and interaction terms were determined. The statistical significance of the regression coefficients was determined by using the F -test and the applicability of the model was checked with significance coefficients of determination (R^2) and the coefficient of variation (CV) values. The optimum processing conditions were obtained by using graphical and numerical analysis based on the criterion of desirability.

3. Results and discussion

3.1. Effects of KGM content, heating temperature and heating time on gel properties

From Fig. 1(a), there were significant increases in gel properties of low-quality surimi after addition with seven levels of KGM. The gel strength of the surimi sample without KGM (control) was 1708 gmm, while that of the gel sample with the highest KGM content (1.50%) was 2829 gmm. As KGM content increased, gel properties of surimi gels increased significantly. The

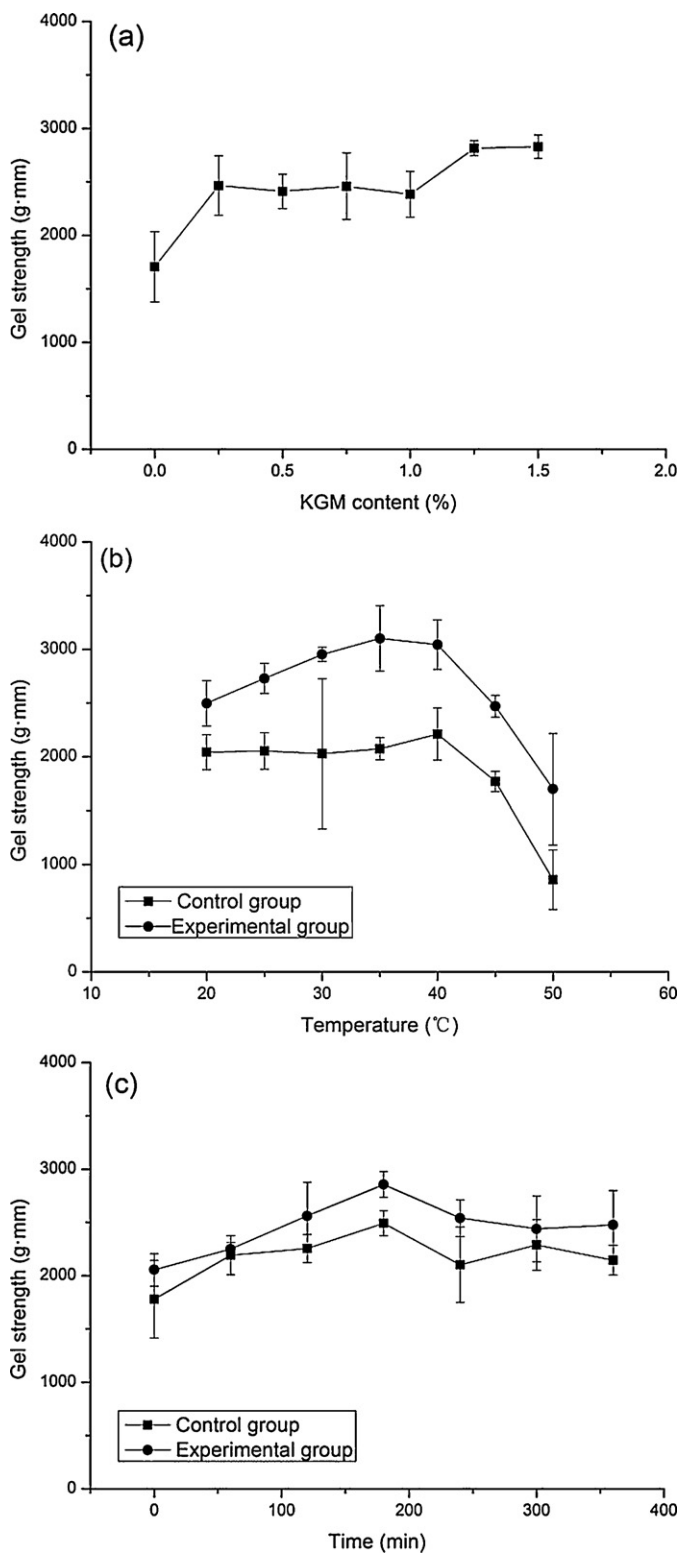


Fig. 1. Effects of KGM content (a), heating temperature (b) and heating time (c) on gel properties of low-quality surimi. Control group: the surimi without adding KGM; experimental group: the surimi with adding KGM.

result suggested that KGM could improve gel properties of surimi gels. We suppose there are two potential reasons: the interaction between KGM and myofibrillar protein to form a viscoelastic three-dimension structure or the conjugation between KGM and myofibrillar protein displaying better gel properties. Xiong et al. (2009) reported the similar result that KGM affected the textural

Table 2

Design program and experimental results of RSM.

Run order	KGM content, X_1 (%)	Heating temperature, X_2 (°C)	Heating time, X_3 (min)	Gel strength (g·mm)
1	1.25	35	180	3147
2	1.50	30	180	3660
3	1.25	35	180	3372
4	1.25	35	180	3014
5	1.00	30	180	3044
6	1.25	40	120	1891
7	1.50	40	180	2006
8	1.00	35	240	1967
9	1.25	35	180	3104
10	1.00	40	180	1443
11	1.25	40	240	1238
12	1.25	30	240	2533
13	1.25	35	180	3007
14	1.50	35	240	2789
15	1.00	35	120	3008
16	1.50	35	120	2971
17	1.25	30	120	2527

properties of surimi gels to increase the gel-forming ability and improve both the gel strength and elasticity of grass carp.

From Fig. 1(b), there were significant increases in gel properties of low-quality surimi heated at seven levels of temperature. The gel properties of surimi sample added with KGM were significantly higher than those of the control group. As the levels of initial heating temperature increased, gel properties of surimi gels increased significantly. When the temperature reached 35 °C, the gel properties decreased as the levels of heating temperature decreased. This might be because the reaction between myofibrillar protein and KGM needed a proper temperature. The high temperature would lead to the protein denaturation. The result suggested that heating temperature could affect gel properties of surimi gels, and there was an optimum temperature for the improvement of gel properties. The results coincided well with the study of Chobert, Gaudin, Dalgalarondo, and Haetle (2006), who reported that the mild heat treatment resulted in Maillard reaction.

As KGM is a high-molecular weight water-soluble non-ionic polysaccharide extracted from tubers of the konjac plant (*Amorphophallus Blume ex Decne* in the family Araceae) (Li, Xie, & Kennedy, 2006), we suppose that the reaction of KGM and surimi would be influenced by heating time. Fig. 1(c) shows the effect of different heating time on gel properties of low-quality surimi. The gel properties of the surimi sample added with KGM and heated for different time were higher than those of the control group. As the levels of initial heating time increased, gel properties of surimi gels increased significantly. When the time reached 180 min, the gel properties decreased as the levels of time decreased. When the protein and KGM were heated at 30 °C for too long time, they would also denature. The result suggested that heating time could affect the gel properties of surimi gels, and there was an optimum heating time for the improvement of gel properties.

3.2. Optimization with RSM

The experiments were carried out in a random order. Values obtained from MR system are given in Table 2, while characteristics of the model for gel properties are shown in Table 3. The ANOVA confirmed adequacy of the statistical model since its Prob > F values were less than 0.05 and statistically significant at 95% confidence level. The model presented high determination coefficients (R^2) and low coefficients of variation (CVs). These values were obtained as follows: $R^2 = 0.951$ and $CV = 8.717$. These results indicated a good precision and reliability for the experiment carried out. The significance of each coefficient was determined by F value and Prob > F value which is listed in Table 3. The smaller the magnitude of the

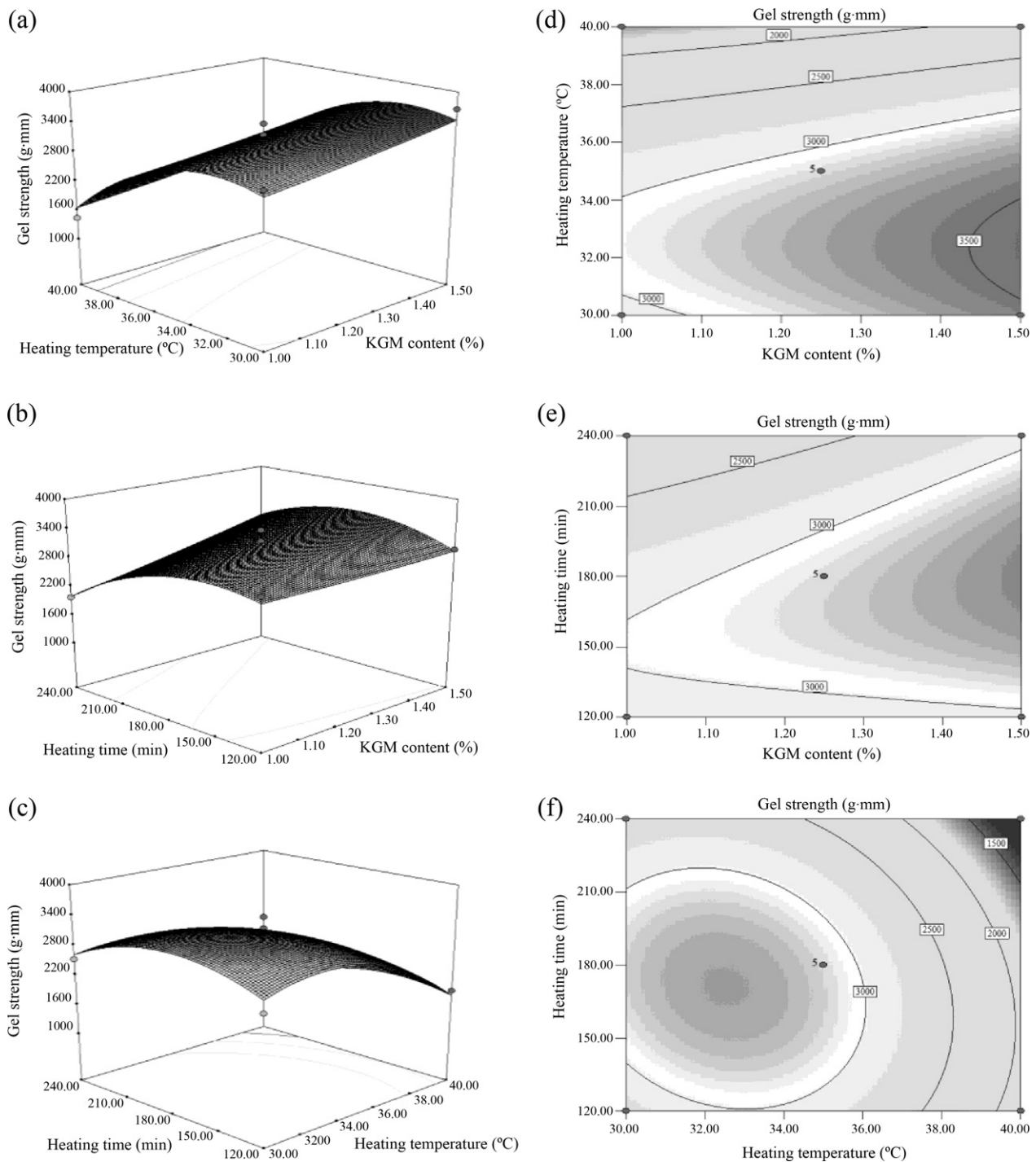


Fig. 2. Three-dimensional figures of interactive effects and contour plot figures of KGM content, heating temperature and heating time on gel properties. (a and d) Interactive effects of KGM content and heating temperature on gel properties. (b and e) Interactive effects of KGM content and heating time on gel properties. (c and f) Interactive effects of heating temperature and heating time on gel properties.

Prob>F value, the more significant was the corresponding coefficient. The fitted model equations were as follows:

$$Y = 3128.82 + 245.41X_1 - 648.08X_2 - 233.77X_3 - 12.97X_1X_2 + 215.59X_1X_3 - 463.03X_2X_3 + 23.22X_1^2 - 612.79X_2^2 - 468.03X_3^2 \quad (2)$$

Fig. 2(a) shows the dependence of gel properties with KGM content and heating temperature at a fixed heating time. It was clear

that at a constant heating time and temperature, gel properties increased with the increase of KGM content. It may also be seen from Fig. 2(a) that gel properties increased quickly at the beginning of the experiment then decreased slightly with increase in heating time at a fixed heating time and KGM content. The variation was curvilinear in nature.

The variation of gel properties with KGM content and heating time at a constant temperature is presented in Fig. 2(b). It is clear that at a constant heating time and temperature, gel properties increased with the increase of KGM content. At a fixed temperature

Table 3
ANOVA for response surface reduced quadratic model.

Variance source	Sum of squares	df	Mean square	F-value	p-Value Prob > F	
Model	7.22×10^6	9	8.02×10^5	15.26	0.0008	Significant
X_1	4.82×10^4	1	4.82×10^5	9.16	0.0192	
X_2	3.36×10^6	1	3.36×10^6	63.89	<0.0001	
X_3	4.37×10^5	1	4.37×10^5	8.31	0.0235	
X_1X_2	673.35	1	673.35	0.01	0.9131	
X_1X_3	1.84×10^5	1	1.84×10^5	3.50	0.1035	
X_2X_3	1.08×10^5	1	1.08×10^5	2.06	0.1942	
X_1^2	2.27×10^3	1	2.27×10^3	0.04	0.8413	
X_2^2	1.59×10^6	1	1.59×10^6	30.16	0.0009	
X_3^2	9.22×10^5	1	9.22×10^5	17.54	0.0041	
Residual	3.68×10^5	7	5.26×10^4			
Lack of Fit	2.80×10^5	3	9.34×10^4	4.25	0.0979	
Pure error	8.79×10^4	4	2.20×10^4			
Cor total	7.59×10^6	16				Not significant

and KGM content, gel properties increased with increased heating time at the beginning but decreased in later stages.

Fig. 2(c) shows the effect of heating temperature and time on gel properties at a fixed KGM content. Gel properties increased in the beginning and decreased afterwards with increased temperature at a constant KGM content and heating time, the same result could be seen for the variable of heating time at a fixed KGM content and temperature.

This signified that the linear effects of KGM content ($p < 0.05$), heating temperature ($p < 0.05$) and heating time ($p < 0.05$) were dominant over the quadratic and interaction terms. The interaction effects between KGM content, heating temperature and time were not significant, but they slightly influenced gel properties. The quadratic effects of heating temperature and time were negative to gel properties. High KGM content was beneficial to the improvement of gel properties, proper heating temperature and time were beneficial to gel properties. Furthermore, proper heating time favored the Maillard reaction (Gu, Abbar, & Zhang, 2009).

The optimum processing parameters were determined to yield surimi gels with high gel properties. Gel properties can be optimized from the contour plot figures (Fig. 2(d)–(f)). The zone of optimization depicted KGM content to be in the range of 1.40–1.50%, temperature and heating time to be in the range of 30–34 °C and 120–210 min, respectively. The model described the optimum conditions for gel properties as: KGM content 1.50%, heating temperature 32.3 °C and heating time 184.6 min.

4. Conclusion

Compared with the surimi control, adding KGM can significantly improve the surimi gel properties at different KGM contents, heating temperatures and heating time. The RSM was a useful tool to investigate the optimum conditions of KGM content, heating time and heating temperature for targeting gel properties in surimi gels. The coefficients of determinations, R^2 values of the all parameters, showed a good fit of the model with the experimental data at 95% confidence level. The different conditions for surimi gels revealed that KGM content had a significant effect on gel properties, while the other two variables had an optimum zone for gel properties. These results and obtained models can be used to the maximum values of the variables.

Acknowledgment

This work was supported financially by the Research Initiation Fund of Zhejiang University of Technology (No. 105007129).

References

- Akhtar, M., & Dickinson, E. (2007). Whey protein–maltodextrin conjugates as emulsifying agents: An alternative to gum Arabic. *Food Hydrocolloids*, 21, 607–616.
- Aoki, T., Hiidome, Y., Sugimoto, Y., Ibrahim, H. R., & Kato, Y. (2001). Modification of ovalbumin with oligogalacturonic acids through the Maillard reaction. *Food Research International*, 34, 127–132.
- Babiker, E. E., & Kato, A. (1998). Improvement of the functional properties of sorghum protein by protein–polysaccharide and protein–protein complexes. *Nahrung/Food*, 42, 286–289.
- Brown, M. R., Keith, T. J., & Knull, H. R. (1990). Decreased actin activated myosin ATPase activity by non-enzymatic glycation. In *The Maillard reaction in food processing human nutrition and physiology* (pp. 487–492). Basel: Birkhäuser Verlag.
- Chevalier, F., Chobert, J. M., Popineau, Y., Nicolas, M. G., & Haertlé, T. (2001). Improvement of functional properties of β -lactoglobulin glycosylated through the Maillard-reaction is related to the nature of the sugar. *International Dairy Journal*, 11, 145–152.
- Chobert, J. M., Gaudin, J. C., Dalgalarondo, M., & Haetle, M. (2006). Impact of Maillard type glycation on properties of β -lactoglobulin. *Biotechnology Advances*, 24, 629–632.
- Dickinson, E., & Galazka, V. B. (1991). Emulsion stabilization by ionic and covalent complexes of β -lactoglobulin with polysaccharides. *Food Hydrocolloids*, 5, 281–296.
- Fujiwara, K., Oosawa, T., & Saeki, H. (1998). Improved thermal stability and emulsifying properties of carp myofibrillar proteins by conjugation with dextran. *Journal of Agricultural and Food Chemistry*, 46, 1257–1261.
- Gu, F. L., Abbar, S., & Zhang, X. M. (2009). Optimization of Maillard reaction products from casein–glucose using response surface methodology. *LWT – Food Science and Technology*, 42, 1374–1379.
- Iglesias-Otero, M. A., Borderias, J., & Tovar, C. A. (2010). Use of konjac glucomannan as additive to reinforce the gels from low-quality squid surimi. *Journal of Food Engineering*, 101, 281–288.
- Jiménez-Castaño, L., Villamiel, M., & López-Fandiño, R. (2007). Glycosylation of individual whey proteins by Maillard reaction using dextran of different molecular mass. *Food Hydrocolloids*, 21, 433–443.
- Kato, A. (2002). Industrial applications of Maillard-type protein–polysaccharide conjugates. *Food Science and Technology Research*, 8, 193–199.
- Kato, A., Minaki, K., & Kobayashi, K. (1993). Improvement of emulsifying properties of egg white proteins by the attachment of polysaccharide through Maillard reaction in a dry state. *Journal of Agricultural and Food Chemistry*, 41, 540–543.
- Kato, A., Sasaki, Y., Furuta, R., & Kobayashi, K. (1990). Functional protein–polysaccharide conjugate prepared by controlled dry-heating of ovalbumin–dextran mixture. *Agricultural and Biology Chemistry*, 54, 107–112.
- Li, B., Xie, B. J., & Kennedy, J. F. (2006). Studies on the molecular chain morphology of konjac glucomannan. *Carbohydrate Polymers*, 64, 510–515.
- Liu, J. H., Ru, Q. M., & Ding, Y. T. Glycation: a promising method for food protein modification: Physicochemical properties and structure, a review. *Food Research International*, in press.
- Nakamura, S., Kato, A., & Kobayashi, K. (1991). New antimicrobial characteristics of lysozyme dextran conjugate. *Journal of Agricultural and Food Chemistry*, 39, 647–650.
- Qi, J. R., Liao, J. S., Yin, S. W., Zhu, J. H., & Yang, X. Q. (2010). Formation of acid-precipitated soy protein–dextran conjugates by Maillard reaction in liquid systems. *International Journal of Food Science and Technology*, 45, 2573–2580.
- Saeki, H. (1997). Preparation of neoglycoprotein from carp myofibrillar protein by Maillard reaction with glucose: Biochemical properties and emulsifying properties. *Journal of Agricultural and Food Chemistry*, 45, 680–684.
- Saeki, H., & Inoue, K. (1997). Improved solubility of carp myofibrillar proteins in low ionic strength medium by glycosylation. *Journal of Agricultural and Food Chemistry*, 45, 3419–3422.

- Sato, R., Sawabe, T., Kishimura, H., Hayashi, K., & Saeki, H. (2000). Preparation of neoglycoprotein from carp myofibrillar protein and alginate oligosaccharide: Improved solubility in low ionic strength medium. *Journal of Agricultural and Food Chemistry*, 48, 17–21.
- Song, Y., Babiker, E. E., Usui, M., Saito, A., & Kato, A. (2002). Emulsifying properties and bactericidal action of chitosan–lysozyme conjugates. *Food Research International*, 35, 459–466.
- Syrový, I., & Hodný, Z. (1992). Non-enzymatic glycosylation of myosin: Effect of diabetes and aging. *General Physiology and Biophysics*, 11, 301–307.
- Syrový, I., & Hodný, Z. (1993). In vitro non-enzymatic glycosylation of myofibrillar proteins. *International Journal of Biochemistry*, 25, 941–946.
- Xiong, G. Q., Cheng, W., Ye, L. X., Du, X., Zhou, M., Lin, R. T., et al. (2009). Effects of konjac glucomannan on physicochemical properties of myofibrillar protein and surimi gels from grass carp (*Ctenopharyngodon idella*). *Food Chemistry*, 116, 413–418.
- Yoshimura, M., Takaya, T., & Nishinari, K. (1996). Effects of konjac-glucomannan on the gelatinization and retrogradation of corn starch as determined by rheology and differential scanning calorimetry. *Journal of Agricultural and Food Chemistry*, 44, 2970–2976.
- Yudkin, J. S., Cooper, M. B., Gould, B. J., & Oughton, J. (1988). Glycosylation and cross-linkage of cardiac myosin in diabetic subjects: A post-mortem study. *Diabetic Medicine*, 5, 338–342.