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# **Development of Texture Model in the Fish Gels Using Eigen-gel Patterns**

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**Abstract:** This study proposes two texture development models for Cod surimi gel. Dimensionality of the training data sets (12 patterns) of surimi gel strength are reduced to four eigen-gel patterns using an unsupervised method, the PCA method. Then we obtain an eigen-gel pattern for each cluster. Two texture models, consecutive and competitive-consecutive first order reactions are developed based on an eigen-gel pattern for each cluster. The correlation coefficient method is introduced to achieve a good identification rate of similarity between the two proposed methods and the eigen-gel pattern for each cluster.

**Key words:** Texture development model, simple consecutive first order reaction, competitive-consecutive first order reaction

## INTRODUCTION

Surimi is a concentrate of the myofibrillar proteins of fish muscle. Surimi-based products are made possible because of gel formation. The mechanisms of gelation comprise two steps: (1) the conversion of minced fish into sol after mixing with salt leading to the dissociation of myofibril structures by protein solubilization; (2) the conversion of sol into gel caused by heat treatment resulting in the partial unfolding of protein structure and the aggregation of unfolded protein via both covalent and noncovalent bonds to form a three-dimensional network (Benjakul et al., 2001; Lanier and Lee, 1992; Stone and Stanley, 1992). Generally, surimigel was obtained from the two heating steps: (1), surimi paste with salt is set at low temperature (50°C) to form a translucent gel; (2), the gel is then cooked at a higher temperature (80°C) to produce an opaque, highly elastic and strengthened gel (Lanier and Lee, 1992).

During the heating period, endogenous enzymes, transglutaminase and proteinase that naturally exist in fish muscle, are activated by temperature. Low-temperature setting is associated with transglutaminase activity. Transglutaminase catalyzes acyl-transfer reactions in which the carboxamide group of peptide-bound glutaminyl residue is the acyl donor. When the amino group of peptide-bound lysine acts as the accepter, the  $\varepsilon$ -( $\gamma$ -glutamyl)lysine bond is formed between the protein, resulting in their crosslinking and possible enhancement of surimi gelling properties (An *et al.*, 1996; Lee *et al.*,

1997; Seguro *et al.*, 1995). On the other hand, gel deformation is induced by endogenous proteinase. The proteinase activity causes the rapid and severe degradation of myofibrillar proteins, particularly myosin, effecting surimi quality and substantially decreasing gel strength (An *et al.*, 1996; Morrissey *et al.*, 1993).

The qualities of surimi gel, notably gel strength, can be affected by heating temperature and heating period during setting step. In order to get a better understanding of the mechanisms by which the gel is developed during setting and cooking, the kinetic model describing the changes in gel strength of cod surimi gel through both gel forming and degradation processes at various setting temperatures and times was developed. Two mathematical models, simple consecutive first order reaction and competitive-consecutive first order reaction, were chosen to describe the change of gel strength. In addition, the similarity method is carried out to test the accuracy of the models.

### MATERIALS AND METHODS

The experiments were conducted in Reading, UK during 2003 to 2004. Then, the texture development models were developed and verified in Thailand, in 2005. All details are expressed as follow.

Materials: Cod (Gadus morhua) fillets were purchased from Frosts Fish LTD, Reading, UK. The fillets were skinned, rinsed with clean water, blended in a Lab

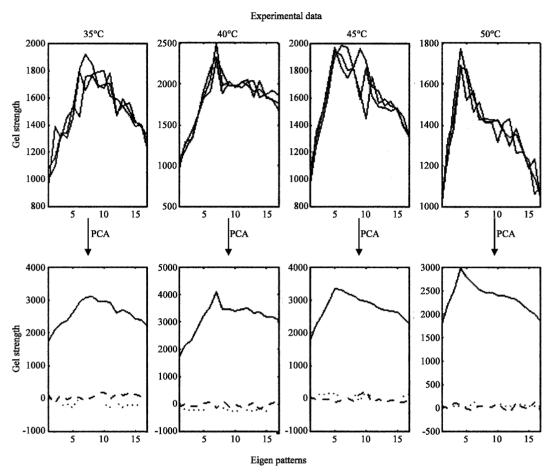


Fig. 1: Surimi gel strengths and their principal directions. Upper row is surimi gel strengths from four experiments. Lower row is the principal direction which the thicked-line is a principal direction and dotted-line and dashed-line are minor directions

Micronizer (Waring Commercial), washed by the ratio of water: minced fish at 3:1 (v/w). Then, the minced fish was dewatered by a basket centrifuge, then mixed with 6% sugar and 0.2% tetrasodium pyrophosphate and stored in a freezer at  $-18^{\circ}$ C as a frozen surimi sample.

**Gel preparation:** The frozen surimi was thawed at 4°C until the temperature of surimi reached 0°C and then, mixed with 2.5% salt by using a Lab Micronizer (Waring Commercial). The sol obtained was stuffed into stainless-steel cylinders of 2.5 cm inner diameter and 2.5 cm length. Surimi gels were prepared by heat setting at 35, 40, 45 and 50°C for 0 to 300 min in a water bath (Grant Y28, type VFP). Then, the gels were cooked at 90°C for 20 min and cooled in ice water. The obtained surimi gels were stored at 4°C for 24 h before analysed.

**Gel strength analysis:** The gel strengths of surimi gels were tested by using a TA-XT2 Texture Analyser (Stable Micro Systems Ltd., Surrey, UK.). All the cooked gels

were compressed to 15 mm at the speed of 1.1 mm sec<sup>-1</sup> using a cylindrical shaped probe of 2.5 cm in diameter. Then, the changes in applied force were recorded. The gel strength was obtained from the peak force multiplied by the compression distance at the peak.

**Proposed methods:** A proposed system is consisting of three main parts, the constructing of principal surimi gel strength, two mathematical models and the similarity analysis. Firstly, Principal Component Analysis, PCA in short, or Karhunen-Loeve transform in data communication (Duda *et al.*, 2001) is used for searching an eigen-gel pattern or principal direction. The PCA returns the principal direction for each class of surimi gel quality as illustrated in Fig. 1. Herein, four fixed setting temperature at 35, 40, 45 and 50°C were experimented. Each experiment was 3 replications. After surimi gel strength in each experiment was passed through the PCA, one principal direction and two minor directions were collected as in Fig. 1 (Chinnasarn *et al.*, 2005). Secondly,

$$\begin{bmatrix} M_{1,1} & M_{1,2} & \cdots & M_{1,17} \\ M_{2,1} & M_{2,2} & \cdots & M_{2,17} \\ M_{3,1} & M_{3,2} & \cdots & M_{3,17} \end{bmatrix}$$

Fig. 2: Matrix contains surimi gel strengths for each heating period

two mathematical models--Kinetic model I: Simple Consecutive First Order Reaction and Kinetic model II: Competitive-Consecutive First Order Reaction-- are developed based on an eigen-gel pattern for each cluster. Finally, correlation coefficient method is used for measurement the similarity between two proposed models.

Construction of principal direction of surimi gel strength: Input data for modeling the principal surimi gel strength are surimi gel strength from 3 replications, controlled by fixed setting temperature at 35, 40, 45 and 50°C, respectively and then fixed cooking temperature at 90°C. During the setting step, we vary setting times for 17 intervals which are 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 120, 180, 240 and 300 min, respectively. In the cooking step, an operating time was fixed at 20 min. From the previous conditions, it can be found that at each setting temperature has 3 input vectors (3 replications). Then a matrix is formed by column that contain 3 input vectors of surimi gel strength. Figure 2 shows example of matrix that contain surimi gel strength.

Now the Principal Component Analysis can be carried out. The calculation of the principal surimi gel strength is given by the solution to the following step:

- Compute the mean for each row mean;
- Generate the zero-mean matrix Mz for each row i,  $Mz_{(i,j)} = M_{(i,j)}$ -mean<sub>i</sub>
- Compute the covariance matrix Cov for Mz
- Compute an eigenvalue, d and eigenvector, v, for the covariance matrix Cov
- Compute an principal direction P = v<sup>T</sup>M, where v<sup>T</sup> is a transpose matrix of v

# Kinetic model i: Simple consecutive first order reaction:

Transglutaminase is an enzymatic catalyst to induce the reaction of gel formation which enhance the crosslink between uncoiled myofibrillar protein during setting stage. On the other hand, the proteinase is the enzymatic catalyst involving in the reaction which decreasing the crosslink of myofibrillar network. Thus, the change of gel strength during texture development can be occurred in two ways, the increase of gel strength from the effect of transglutaminase enzyme and the decrease of gel strength



Fig. 3: Simple consecutive first order reaction

from the effect of proteinase enzyme. Therefore, the gel formation during the setting process can be considered to be a reaction network as shown in Fig. 3.

Where stage

A = Starting paste (effective protein which be able changed to be gel texture)

B = Gel texture

C = Disrupted gel (proteolytic breakdown)

k<sub>1</sub> = Rate constant (min<sup>-1</sup>) of the gel forming process by transglutaminase activity

k<sub>2</sub> = Rate constant (min<sup>-1</sup>) of the gel breakdown by proteinase activity

By assumption above, all reactions occurred in this consecutive reaction are first order reaction, the reaction rate of decreasing of the effective protein which be able changed to be gel texture can be expressed as Eq. (1). And the rate of gel texture formation can be written as Eq. (2). Therefore, the changes of texture development with setting time can be derived as Eq. (3).

$$\frac{\partial A}{\partial t} = -k_1 A \tag{1}$$

and

$$\frac{\partial \mathbf{B}}{\partial t} = \mathbf{k}_1 \mathbf{A} + \mathbf{k}_2 \mathbf{B} \tag{2}$$

For initial conditions  $B(0) = B_0$  and  $A(0) = A_0$ , the change in gel texture (B(t)) can be represented as follows:

$$B(t) = \frac{k_1 A_0}{k_2 - k_1} \left( e^{-k_1 t} - e^{-k_2 t} \right) + B_0 e^{-k_2 t}$$
 (3)

where

A<sub>0</sub> = Initial changeable protein

t = Setting time (min)

Kinetic model ii: Competitive-consecutive first order reaction: Proteinase enzyme involves in the reaction which decreasing the crosslink of myofibrillar network for both of initial protein (A) and transglutaminase-induced gel protein (B). For this reason, the gel formation during the setting process can be considered to be a competitive-consecutive reaction network as shown in Fig. 4.

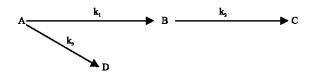


Fig. 4: Competitive-consecutive first order reaction

Where stage

A = Starting paste (effective protein which be able changed to be gel texture)

B = Gel texture

C = Disrupted gel (proteolytic breakdown)

D = Disrupted fish protein (proteolytic breakdown)

k<sub>1</sub> = Rate constant (min<sup>-1</sup>) of the gel forming process by transglutaminase activity

k<sub>2</sub> = Rate constant (min<sup>-1</sup>) of the gel breakdown by proteinase activity

k<sub>3</sub> = Rate constant (min<sup>-1</sup>) of the fish protein breakdown by proteinase activity

By the assumption above, texture development can be also considered as a competitive-consecutive first order reaction of two process; gel forming (A to B) and gel breakdown through proteolysis (B to C and A to D) as the Eq. following

$$\frac{\partial A}{\partial t} = -\left(k_1 + k_3\right)A\tag{4}$$

and

$$\frac{\partial \mathbf{B}}{\partial \mathbf{t}} = \mathbf{k}_1 \mathbf{A} + \mathbf{k}_2 \mathbf{B} \tag{5}$$

For initial conditions  $B(0) = B_0$  and  $A(0) = A_0$ , the change in gel texture B(t) can be represented as follows:

$$B(t) = \frac{k_1 A_0}{k_2 - k_1 - k_3} \left( e^{-(k_1 + k_3)t} - e^{-k_2 t} \right) + B_0 e^{-k_2 t}$$
 (6)

where

A<sub>0</sub> = Initial changeable protein

t = Setting time (min)

Similarity measure: Similarity measure is used for evaluating the difference of the waveforms between an interested vector and its corresponding kinetic model vector. The correlation coefficient analysis,  $\rho$  between the interested vector produced by the principal component analysis and the kinetic model vector I and II recovered signal y is used. Correlation coefficient  $\rho$  between two random variable x and y can be desscribed as:

$$\rho(x,y) = \frac{\text{cov}(x,y)}{\sqrt{\text{var}(x)\text{var}(y)}}$$
(7)

where cov(x,y) is the covariance between two random variables and var(.) is the variance of a random variable. Correlation coefficient values are within [-1,...,1]. If x and y are completely correlated or similar,  $\rho(x,y)$  is 1 or -1. If they are absolutely uncorrelated,  $\rho(x,y)$  is 0. In this study, the principal surimi gel strengths obtained from the experiment during the setting times were compared to the calculated ones solved in Eq. 3 and 6.

#### RESULTS AND DISSCUSSION

**Kinetic model develoments:** After each principal suriming elstrength was fitted to Eq. 3 and 6, then the initial parameters for predicting were obtained as shown in Table 1a and b, respectively.

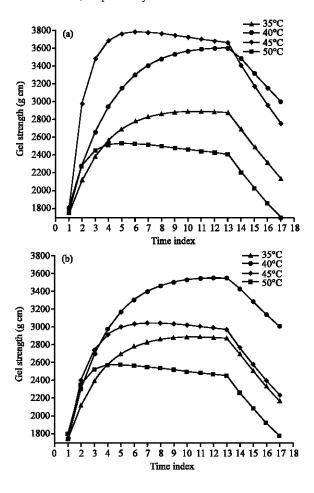


Fig. 5: (a) Kinetic model I: Consecutive first order reaction and (b) Kinetic model II: Competitive-consecutive first order reaction at 35, 40, 45 and 50°C

Table 1: (a) Initial parameters for Eq. 3 and b Initial parameters for Eq. 6

Setting					Setting						
temperature					temperature						
(T)	$A_0$	$B_0$	$\mathbf{k}_1$	$k_2$	(T)	$A_0$	$B_0$	$\mathbf{k}_1$	$\mathbf{k}_2$	k <sub>3</sub>	
35	1364	1732.6	0.068	$1.236e^{-3}$	35	1399	1732.6	0.068	1.193e <sup>-3</sup>	$2.588e^{-3}$	
40	2061	1749.9	0.060	$8.262e^{-4}$	40	2097	1749.9	0.063	$7.412e^{-4}$	$3.942e^{-3}$	
45	2149	1755.3	0.170	$1.181e^{-3}$	45	1437	1755.3	0.124	$1.187e^{-3}$	$1.688e^{-3}$	
50	817.03	1800.6	0.182	$1.437e^{-3}$	50	1188	1800.6	0.158	$1.331e^{-3}$	$6.300e^{-2}$	
(a)						(b)					

Table 2: Correlation Coefficient similarity measure (ρ) between (a) principal and consecutive first order reaction surimi gel strength and (b) principal and competitive-consecutive first order reaction surimi gel strength

Eigen-gel pattem	Kinetic mo	odel I (°C)	•	•	Eigen-gel pattem at setting	Kinetic model II (°C)			
at setting									
temperature (°C)	35	40	45	50	temperature (°C)	35	40	45	50
35	0.9224	0.8546	0.8400	0.6813	35	0.9234	0.8615	0.8759	0.6746
40	0.8434	0.9173	0.7326	0.4262	40	0.8510	0.9209	0.7499	0.4255
45	0.8512	0.7114	0.9082	0.8041	45	0.8546	0.7343	0.9164	0.8049
50	0.6127	0.3384	0.7964	0.8903	50	0.6111	0.3684	0.7894	0.8953
(a)						(b)			

Substitute Eq. 3 by the initial parameters in Table 1a, we obtain the prediction of the consecutive first order reaction as shown in Fig. 5a. Similarly, Eq. 6 is substituted by the initial parameters in Table 1b. Then, the prediction of the competitive-consecutive first order reaction is released and shown in Fig. 5b.

Similarity measures: Table 2a and b display degree of similarity using correlation coefficient method between principal and theoritical surimi gel strength which are consecutive first order reaction, Eq. 3 and competitive-consecutive first order reaction, Eq. 6, respectively. It can be seen that our proposed Eq. 3 and 6 predict the optimal solutions for each principal surimi gel strength or for each setting temperature. And the correlation coefficient similarity method can classify group of principal surimi gel strengths. Furthermore case by case, similarity method shows that the competitive-consecutive first order reaction more fitted to the principal surimi gel strength than the consecutive first order reaction.

#### CONCLUSIONS

Two kinetic model for texture formation of Cod surimi gel were developed using the consecutive and competitive-consecutive first order reaction based on the principal direction of each experimental data or each setting temperature. Eigen-gel pattern or principal surimi gel strength obtained from the PCA method gives better fitted with the competitive-consecutive first order reaction than the consecutive first order reaction.

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