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ORIGINAL PAPER

Kinetics of Quality Changes of Shrimp (*Litopenaeus setiferus*) During Pasteurization

Jungang Wang[1] · Juming Tang[1] · Barbara Rasco[2] · Shyam S. Sablani[1] · Mahmoudreza Ovissipour[1] · Zhi Qu[1]

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Abstract

Effect of cooking between 1 and 80 min at 60 to 100 °C on several quality attributes of whole peeled shrimp (*Litopenaeus setiferus*) (80–90 counts/kg) was studied using an isothermal heating method. Cook loss, area shrinkage, and hardness of shrimp increased with increasing heating time and temperature, following a fractional first-order kinetic model with activation energies (E_a) of 71.0, 53.3, and 29.9 kJ/mol, respectively. Cook loss, area shrinkage, and hardness were positively correlated. The toughness of shrimp muscle increased in the initial period of heating, then decreased in the later period during the treatments. The overall color change (ΔE) increased with increasing treatment time and temperature, and followed a zero kinetic model with an E_a of 37.2 kJ/mol. The kinetic parameters obtained from this study can be applied toward understanding and predicting shrimp-quality changes during pasteurization treatments, and further provides insight into the pasteurization conditions required to achieve safe and high-quality shrimp products and potentially other crustacean shellfish and seafood products.

Keywords Shrimp quality · Thermal pasteurization · Kinetics model · Protein denaturation

Introduction

According to the United Nations Food and Agricultural Organization (FAO), fishery products reached 167 million tons and contributed US $148 billion of trade value worldwide in 2014, making them an important resource of nutritious human food (FAO 2016). Shrimp is one of the most popular seafood products, contributing about 16% of the export value worldwide for seafood products (Gillett 2008), greater than cod, mollusks, tuna, and salmon (FAO 2016; Paquotte and Lem 2008). Shrimp is also the largest import of seafood into the USA (Allshouse et al. 2003; National Marine Fisheries Service 2016). Shrimp meat is considered an excellent source of highly nutritious proteins, fatty acids, and various minerals. In the USA, shrimp is the most often consumed seafood, and exceeded 24% of per-capita seafood consumption in recent years surpassing tuna (USNFI 2017).

Seafood can pose risks for foodborne illnesses. Illness can occur in importing countries if the food is not properly handled or cooked (Crerar et al. 2002; Olsen et al. 2000). Thus, shrimp has been placed in the category of high-risk food due to the historical issues with pathogen contamination (Allshouse et al. 2003, 2004; Wallace et al. 1999). Pathogen control in the supply chain from harvest through consumer use is critical for product safety. Thermal processing is proven to be an efficient and reliable method for extending shelf life of food products (Thorne 1986). But quality deterioration of food products accompanies severe thermal processing, resulting in reduction of sensory, and nutritional value. Changes to the quality attributes of shrimp under various thermal processing conditions have been studied. For example, Ma et al. (1983) reported that the flavor of shrimp develops in the relatively early phase of cooking, but no significant change occurs after the initial cook stage. Texture changes dramatically in the temperature range between 115 and 140 °C, as a result of protein denaturation and aggregation. The accompanying shrinkage and muscle toughness, measured by shear force, had a high negative correlation to the sensory score. Erdogdu and Balaban (2000) reported that the tenderness, juiciness, rubberiness,

✉ Juming Tang
Jtang@wsu.edu

[1] Department of Biological Systems Engineering, Washington State University, PO Box 646120, 1935 E. Grimes Way, Pullman, WA 99164-6120, USA

[2] School of Food Science, Washington State University, Food Science and Human Nutrition Building, Room 106, 100 Dairy Road, Pullman, WA 99164-6376, USA

and overall acceptability of shrimp were significantly influenced by the processing temperature, and that there was a high correlation between textural properties and sensory attributes. Additional adverse effects on shrimp-quality attributes in terms of moisture loss, shrinkage, water holding capacity, and thermal conductivity were also observed during thermal processing (Benjakul et al. 2008; Erdogdu et al. 1999, 2001; Murakami 1994; Niamnuy et al. 2007, 2008). In general, the higher the thermal processing temperature and longer heating time, the greater the quality loss. Thus, thermal processing needs to be carefully controlled to achieve safe while maintaining high-quality food products.

Pasteurization is widely used to ensure safety and extend the shelf life of food products. The Food and Drug Administration (FDA) of the USA recommends a minimum 6-log reduction of *Listeria monocytogenes* or *nonproteolytic Clostridium botulinum types E* by equivalent thermal treatment of 70 °C for 2 min or 90 °C for 10 min, respectively (FDA 2011). Compared to food thermal sterilization, in which foods are heated to temperatures higher than 115 °C (Lopez 1987), pasteurization uses relatively low processing temperatures (less than 100 °C) (Downing 1996). Haefner (2005) reported that a kinetic study can contribute to the understanding, prediction, and control of chemical and physical changes in foods during thermal processing. Determining the kinetics of thermal quality changes (Ovissipour et al. 2013; Kong et al. 2007a, b) associated with thermal processing of seafood products provides the basis for selecting thermal processing conditions to maximize product quality while maintaining safety.

To our best knowledge, there has been no systematic research on the kinetics of quality changes in shrimp for thermal pasteurization. The objective of this study was to investigate the kinetics of cook loss, shrinkage, texture, and color changes of pasteurized shrimp. Correlations between cook loss, shrinkage, and texture were also determined.

Materials and Methods

Materials

Wild white shrimps (*Litopenaeus setiferus*) were purchased from Anna Marie Shrimp, LLC in Montegut, LA, USA. Shrimps were harvested from the northern port of the Gulf of Mexico and immediately sacrificed by immersing in ice. Frozen shrimps with a size range of 80–90 counts/kg were delivered in insulated box with dry ice to Washington State University (WSU), Pullman, WA, USA, and stored in a freezer at − 30 °C. The shrimps were thawed on ice, heads removed, and shells peeled before thermal treatment. All shrimps were used in experiments within 2 weeks of arrival at WSU.

DSC Measurement

Thermal transitions of shrimp meat were obtained using a differential scanning calorimeter (DSC) (MDSC, Q2000, TA Instruments, Waters LLC., New Castle, DE). Ten to fifteen milligrams of samples was placed and sealed in the aluminum pans, and an empty sealed pan was used as a reference. Both sample and reference were heated over the range from 20 to 100 °C with heating rate of 1 °C/min. Higher transition temperature (T_{max}) was recorded, and the residual denaturation enthalpy (ΔH) (J/g) was evaluated by measuring the area of the denaturation peak. The tests were conducted in triplicates. Mean transition temperature and denaturation enthalpy were reported.

Thermal Treatments

Shrimps were equilibrated at room temperature (23 °C) for 120 min. Each peeled shrimp was sealed in a custom-built aluminum thermal kinetic testing (TKT) cell filled with tap water as the heating transmission medium. The TKT aluminum test cell was designed at WSU with a 50-mm inner diameter, 8-mm inner height, and 3-mm cell thickness (Fig. 1a, b). The high thermal conductivity of the aluminum minimized the come-up-time (CUT) defined as the time needed for the sample to reach 1 °C below the treatment temperature. The CUT was measured using 0.1-mm diameter thermal sensor made of copper-constantan thermocouple (Type-T) installed in the middle of the TKT cell lid, and with 3 mm into the cell (Fig. 1c). The temperature was read through an exterior thermocouple thermometer (Type-T thermocouple thermometer, Eutech Instruments, Vernon Hills, IL, USA). This design minimizes the heat conduction from the temperature probe to sample, and the endpoint of the sensor was inserted into the middle of the sample (4 mm from the top) providing a more precise temperature measurement. The CUT of each treatment temperature is shown in Table 1.

The thermal treatments were designed (Table 1) to cover a wide range of processing conditions for control of norovirus, *Listeria monocytogenes*, and *Clostridium botulinum type E* inactivation during thermal pasteurization (Bozkurt et al. 2014; Buckow et al. 2008; Gaze et al. 2006; Gibson and Schwab 2011; Peng et al. 2017). After heating in a water bath (Model HAAKE DC 30, Thermo Electron Corp., Waltham, MA, USA), the TKT cells were cooled immediately by immersing in a water/ice bath for 5 min, and the shrimps were removed for the following tests.

Cook Loss Measurement

The weight of single shrimp was measured before each treatment. After heating, shrimp was gently dabbed

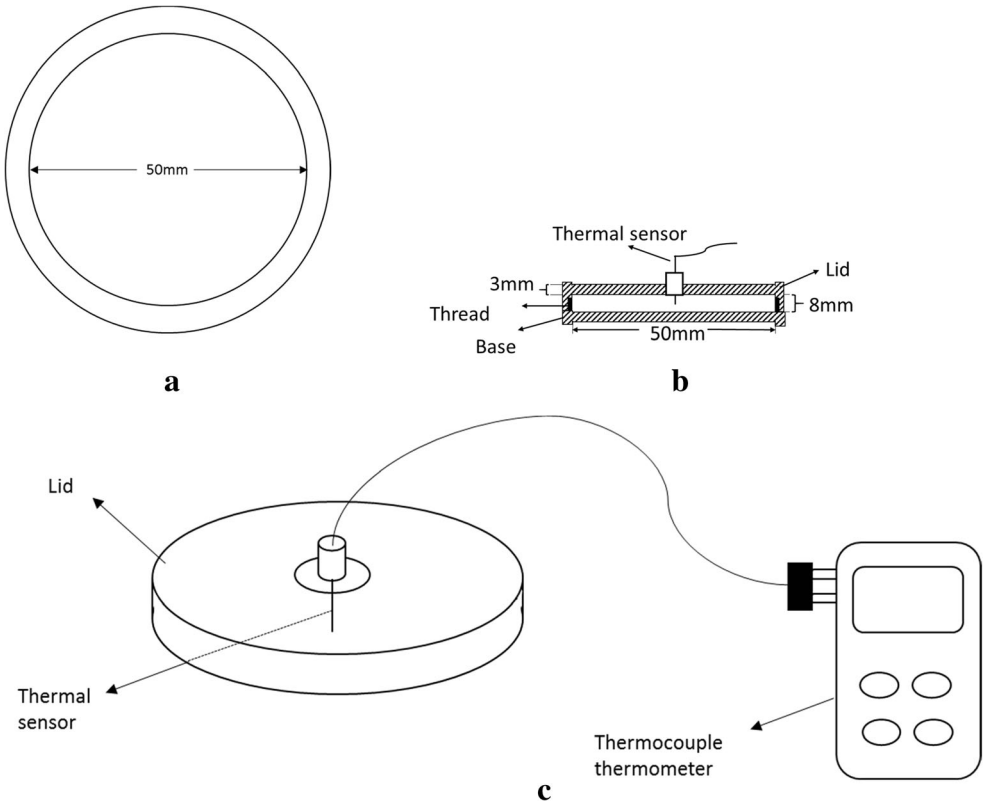

Fig. 1 Custom-built aluminum thermal kinetics test (TKT) cell (**a**, **b**) and TKT cell lid with thermal sensor (**c**)

against a piece of filter paper to remove the surface water, then weighed again. Cook loss was calculated as follows:

$$\text{Cook loss}\% = \left(\frac{C_0 - C_s}{C_0}\right) \times 100 \quad (1)$$

where C_0 is the weight of the raw sample and Cs is the weight of the processed sample.

Area Shrinkage Measurement

Image processing program ImageJ (National Institute of Health, Bethesda, MD, USA) was used for area shrinkage measurement. The testing procedures followed the area measurement feature of the software. The shrinkage ratio was calculated as follows:

$$\text{Area shrinkage}\% = \left(\frac{A_0 - A_s}{A_0}\right) \times 100 \quad (2)$$

where A_0 is the area of the raw sample and As is the area of the processed sample.

Table 1 Thermal treatments for shrimp

Temp (°C)	Heating time (min)								CUT (min)
60	1	7	15	24	35	50	65	80	2:22
70	1	5	7	11	19	27	35	43	2:30
80	1	3	5	8	12	16	20	26	2:44
90	1	2	3	5	7	10	15	20	3:16
100	1	2	3	4	6	9	12	15	3:55

Texture Measurement

Two batch shrimp samples were heat treated. One batch was used for hardness measurement and the other batch for toughness measurement. A texture analyzer, TA-XT2 (Stable Micro Systems Ltd., Surrey, UK) with a 5-kg load cell was used in the tests. Both raw and heat-treated shrimp samples were placed at 22 °C for 30 min before each measurement. The measurement of hardness was performed as described in Niamnuy et al. (2008). Briefly, the second segment as described in Nunak and Schleining (2011), which is considered the thickest segment (Erdogdu and Balaban 2000) of the shrimp, was cut into an $8 \times 8\text{-mm}^2$ square, and the thickness of each sample was measured before testing. A flat-end cylindrical probe ø 50 mm (Stable Micro Systems, TA-25) was used for the compression test. The testing speed was 0.5 mm/s to a depth of 60%

deformation (press the shrimp from the side with skin), and the maximum compressive forces were recorded by the Texture Expert software (version 1.15, Stable Micro Systems Ltd). The compressive stresses were calculated as shown in Eq. (3) to indicate the hardness of the shrimp. The toughness of the shrimp was measured with a Warner-Bratzler knife probe with guillotine block (Stable Micro Systems, TA-7). The thickness and width of the second segment of the shrimp samples were measured before the test. The cross-sectional area of each shrimp was calculated as shown in Eq. (5) (shrimp samples were considered to have an elliptical shape). The maximum shear force was obtained by using the knife probe to cut the shrimp samples from the second segment with a testing speed of 0.5 mm/s. The maximum shear stress used to indicate the toughness of shrimp was calculated as shown in Eqs. (4) and (5). Six shrimp samples were tested from each treatment ($n = 6$), and the average values are reported.

$$\text{Compressive stress} = \frac{\text{Compressive force}}{\text{Contact area}} \tag{3}$$

$$\text{Shear stress} = \frac{\text{Shear force}}{\text{Cross-sectional area}} \tag{4}$$

$$\text{Cross-sectional area} = \pi \times \frac{\text{Thickness} \times \text{Width}}{4} \tag{5}$$

Color Measurement

Whole shrimp was selected for color measurement. The color parameter values L, a, and b of the whole shrimp before and after treatments were measured by using a Computer Vision System (CVS) and CS6 Photoshop Software (Adobe system, Inc., San Jose, CA). The CVS is as described by Kong et al. (2007a). The L, a, and b values obtained from PhotoShop are on a different color scale than the standardized CIE LAB color scale. In the CIE LAB color scale, L^* ranges from 0 to 100 and a^* and b^* typically range from −128 to 128 (Schanda 2007). In the Photoshop color model, the L, a, and b values range from 0 to 255. The L^*, a^*, and b^* were calculated as described in Yam and Papadakis (2004). The total color difference (ΔE) was calculated as follows:

$$\Delta E = \sqrt{\left(L^* - L_0^*\right)^2 + \left(a^* - a_0^*\right)^2 + \left(b^* - b_0^*\right)^2} \tag{6}$$

where L_0^*, a_0^*, and b_0^* are the color parameters of the unprocessed shrimp, and L^*, a^*, and b^* are the color parameters of the processed shrimp.

Data Analysis

Based on Wang et al. (2004), the quality degradation under isothermal conditions was calculated as follows:

$$\frac{dC}{dt} = -k(C)^n \tag{7}$$

where k is the rate constant, C is the quantitative indicator of quality at time t, and n is the order of reaction. The zero-, first-, and second-order kinetic models for quality changes can be represented by the following:

$$\text{Zero order}: \quad C_t = C_0 - kt \tag{8}$$

$$\text{First order}: \quad \ln\frac{C_t}{C_0} = C_0 - kt \tag{9}$$

$$\text{Second order}: \text{kt} = \frac{1}{C_t} - \frac{1}{C_0} \tag{10}$$

where C_0 is the quality value before treatment (time zero), C_t is the quality value at time t, and k is the reaction rate constant. The fractional conversion model is a widely used kinetic model, which measures the extent of a reaction to evaluate the corresponding changes. Quality index f was used in the fractional conversion model which is defined as (Rizvi and Tong 1997) follows:

$$f = \frac{C_0 - C_t}{C_0 - C_\infty} \tag{11}$$

For a first-order reaction, the natural log of $(1 - f)$ versus reaction time followed a linear relationship

$$\ln(1-f) = \ln\left(\frac{C_t - C_\infty}{C_0 - C_\infty}\right) = -kt \tag{12}$$

where f is the color change index, C_0 is the initial color value, C_t is the color value at time t, and C_∞ is the color value after prolonged heating time. The Arrhenius equation is usually used to describe temperature dependence of reaction rate constant k

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \tag{13}$$

where E_a is the activation energy of the reaction (kJ/mol), R is the universal gas constant (8.3145 J/mol/K), T is absolute temperature (K), and k_0 is frequency factor (per min). If the Arrhenius equation applies to a reaction, a plot of the rate constant on a semi-logarithmic scale as a function of the reciprocal absolute temperature ($1/T$) should yield a straight line, and the E_a can be calculated as the slope of the line multiplied by the gas constant R.

In the current study, unless otherwise stated, the kinetic study of data was initiated after the CUT (around 2.5–

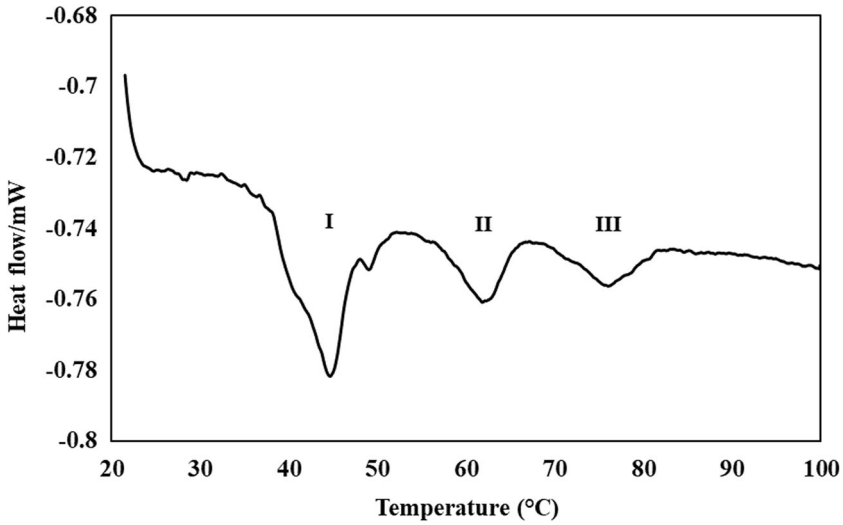

Fig. 2 DSC curves for shrimp muscle over the range from 20 to 100 °C ($N = 3$)

4 min). That is, the end of the CUT was considered as the zero-time, and the corresponding quality data was considered as the initial quality value of the isothermal condition. Statistical analyses were conducted by using SAS (SAS Institute Inc., Cary, NC, USA) and the significance level P was set at a 0.05 probability level.

Results and Discussion

DSC Analysis

Representative DSC thermogram of shrimp meat is shown in Fig. 2. Three peaks (I, II, III) were obtained over the range from 20 to 100 °C with T_{max} values of 43.4 ± 0.6 °C, 62.8 ± 0.8 °C, and 74.7 ± 0.9 °C and denaturation enthalpy (ΔH) of 1.23 ± 0.06 J/g, 0.27 ± 0.12 J/g, and 0.23 ± 0.06 J/g (means from three replicates), respectively. Each peak represents the denaturation of certain proteins (Hastings et al., 1985). Peaks I, II, and III are associated with denaturation of myosin or myosin heavy chain, sarcoplasmic proteins and connective tissue proteins (mainly collagen), and actin, respectively (Schubring, 2009; Skipnes et al., 2008). Previous studies indicated that the denaturation temperatures of myosin, collagen, and actin could range from 38 to 60 °C (Kemp et al., 2009; Schubring, 2009; Sriket et al., 2007), 60–70 °C (Schmidt, 1988), and 58–78 °C (Schubring, 2009; Sriket et al., 2007; Wright et al., 1977) of different meats, respectively. In this study, the T_{max} values of shrimp meat agreed with the denaturation temperature range of previous research results.

Cook Loss

Cook loss is considered as an important factor to evaluate the quality of seafood (Bell et al. 2001; Erdogdu et al. 2001). The cook loss significantly increased with increasing treatment severity (Fig. 3). The fractional first order described well (R^2

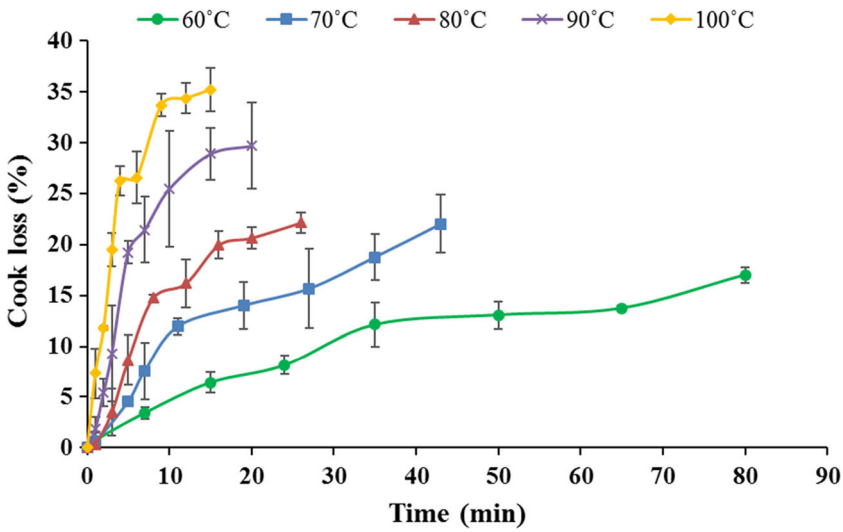

Fig. 3 The changes of cook loss of shrimp with different treatment temperatures and times, $N = 3$

Table 2 Fractional first-order parameters for cook loss of shrimp after heat treatment at different temperatures

Temp (°C)	k (min^{-1})	R^2	E_a (kJ/mol)	k_0 (min^{-1})	R^2
60	−0.014	0.95	71.0	8545	0.94
70	−0.039	0.95			
80	−0.044	0.92			
90	−0.091	0.96			
100	−0.289	0.96			

from 0.92 to 0.96) the changes of cook loss with time. The cook loss was high at the initial stage of a thermal treatment, followed by a shallower slope at the later stage. The temperature dependence of the rate constant (Eq. (13)), E_a and k_0 values, and coefficient of correlation are shown in Table 2. The activation energy was 71.0 kJ/mol for shrimp, which is close to the E_a of other muscle foods: e.g., 54.9 kJ/mol for beef (Bertola et al. 1994) and 55.6 kJ/mol for whole mussel (Ovissipour et al. 2013).

The cook loss represents separation of water, lipids, and solids (collagen or gelatin, muscle fragments, and coagulated sarcoplasmic proteins) from a shrimp sample during the heat treatment (Bell et al. 2001; Erdogdu et al. 2001; Skipnes et al. 2011). More than 85% of the cook loss was water. The water content in raw shrimp is around 80% on a wet basis, with most of the water in the muscle being trapped within the muscle by capillary forces (Trout 1988) within myofibrils, the space between the thick filaments (myosin) and thin filaments (actin), and in connective tissue (stroma) (Bertola et al. 1994; Niamnuy et al. 2008). Heat induces the denaturation of proteins in shrimp muscle, which changes the three-dimensional structure and results in a reduction or loss of the water holding ability (Ofstad et al. 1993). Meanwhile, the protein denaturation and aggregation in thermal treatment results in shrinkage of the shrimp muscle, which leads to a denser protein structure (Fennema 1996; Straadt et al. 2007). The newly formed protein structure creates internal pressure and expels the free water out of the shrimp muscle. Here, the cook loss increased quickly at all treatment temperatures, more than 50% of the cook loss occurred within the first 10 min at temperatures higher than 70 °C. At 60 °C, however, samples had a relatively lower cook loss; around 60% cook loss occurred in the first 30 min, and 40% cook loss took place in the rest of the 50 min. Similar results were observed by Skipnes et al. (2007) for cod and Ovissipour et al. (2013) for whole mussel thermal treatment where not much change in cook loss occurred between temperatures from 40 to 60 °C, but significantly increased from 70 to 100 °C.

The overall cook losses ranged between 17 and 36% for treatment temperatures from 60 to 100 °C with treatment times from 1 to 80 min. Similar results were reported by Erdogdu (1996) that around 1 to 40% cook loss of tiger shrimp (*Penaeus monodon*) were observed with treatment temperatures from 55 to 95 °C. The highest cook loss was around 36%, which is higher than the cook loss observed for salmon (Kong et al. 2007b) and cod (Skipnes et al. 2007).

Area Shrinkage

The changes of area shrinkage are presented in Fig. 4. The obtained data followed well fractional first-order model (R^2 from 0.93 to 0.98). The E_a, k_0 values, and coefficient of correlation are shown in Table 3. The activation energy was 53.3 kJ/mol for shrinkage. Lower treatment temperatures with longer treatment times resulted in relatively small changes, and higher treatment temperatures led to higher and faster shrinkage.

Sarcoplasmic protein, myofibrils, and collagen are denatured during thermal processing (Niamnuy et al. 2007; Ofstad et al. 1993) leading to loss of moisture and tissue

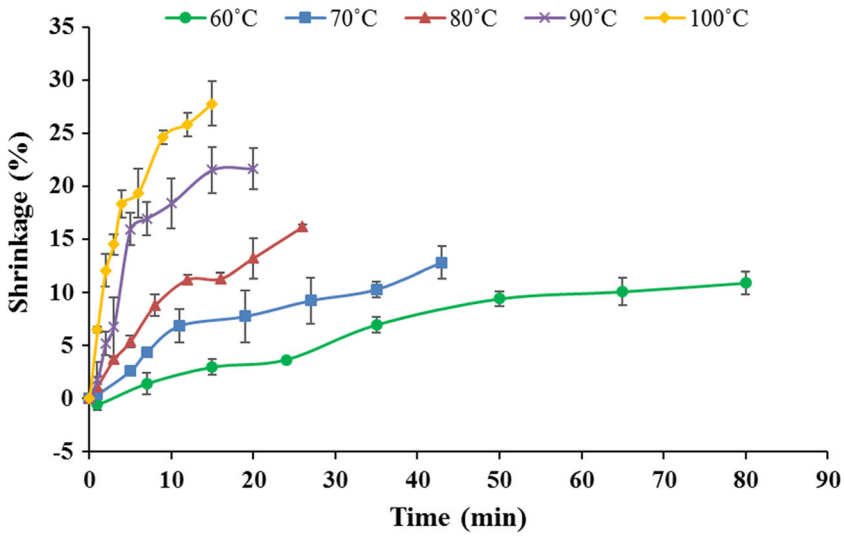

Fig. 4 The changes of shrinkage of shrimp with different treatment temperatures and times, $N = 3$

Table 3 Fractional first-order parameters for area shrinkage of shrimp after heat treatment at different temperatures

Temp (°C)	k (min^{-1})	R^2	E_a (kJ/mol)	k_0 (min^{-1})	R^2
60	− 0.026	0.98	53.3	6414	0.82
70	− 0.023	0.95			
80	− 0.037	0.97			
90	− 0.067	0.93			
100	− 0.209	0.96			

Table 4 Fractional first-order parameters for hardness of shrimp after heat treatment at different temperatures

Temp (°C)	k (min^{-1})	R^2	E_a (kJ/mol)	k_0 (min^{-1})	R^2
60	− 0.025	0.96	29.9	3598	0.82
70	− 0.031	0.88			
80	− 0.056	0.99			
90	− 0.083	0.90			
100	− 0.064	0.82			

shrinkage (Erdogdu et al. 2004; Kong et al. 2007b). Niamnuy et al. (2008) observed a reduction of collagen in shrimp during thermal treatment.

In the current study, a 10% shrinkage was observed after 60 °C treatment for 80 min, with the same degree of shrinkage observed after 10 min at 80 °C. Shrinkage reached around 30% after heating at 100 °C for 15 min. Murakami (1994) studied shrinkage of shrimp following commercial sterilization ($F_{121°C}$ = 3.5 min) in a can with cream of potato soup. He reported less than 30% shrinkage after heat treatment, possibly due to the protective effect of components in the soup matrix that could have had a protective effect in addition to limiting moisture diffusion. Erdogdu (1996) studied shrimp qualities at temperatures from 55 to 95 °C, and found up to 40% shrinkage. One possible factor that could have influenced the shrinkage was the shrimp size. However, the effect of size was not considered in this study.

Texture

The maximum compression forces of 60% deformation were measured to evaluate the hardness of the processed shrimp. As shown in Fig. 5, the hardness of shrimp muscle increased with increasing treatment time and temperature. Similar to the changes of cook loss and area shrinkage, hardness had a high rate of increase at the initial stage of heating and then had a relatively low rate of increase at the later stage of a thermal treatment. The fractional first order described well (R^2 from 0.82 to 0.99) the changes of hardness versus time. The E_a, k_0 values, and coefficient of correlation are shown in Table 4. The activation energy was 29.9 kJ/mol for the changes of hardness of shrimp.

The hardness of shrimp was highly related to the treatment temperature. In the current study where the treatment temperature started from 60 °C, myofibrillar proteins (primarily actomyosin) were denatured at the beginning of the treatment (Fennema 1996). This denaturation led to the aggregation of the myofibrillar proteins, which resulted in shrinkage of the muscle fibers and tightness of the shrimp muscle (Ma et al. 1983). Collagen and actin were next to be denatured with the increased treatment time and temperature, which changed the structure of the proteins, and led to coagulation of proteins and segregation of surrounding cells. Such changes further enhanced the tightness and stiffness of the processed shrimp, and resulted in an increase of the hardness (Aberle 2001; Erdogdu et al. 2004; Ma et al. 1983; Mizuta et al. 1999). As indicated in Fig. 5 that for any given treatment time, the higher the treatment temperature, the higher the hardness. Similar

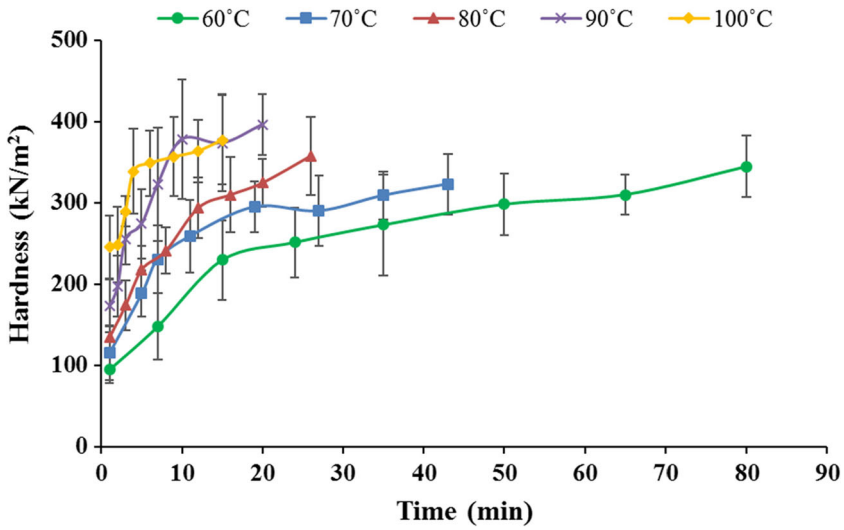

Fig. 5 The changes of hardness of shrimp with different treatment temperatures and times, $N = 6$

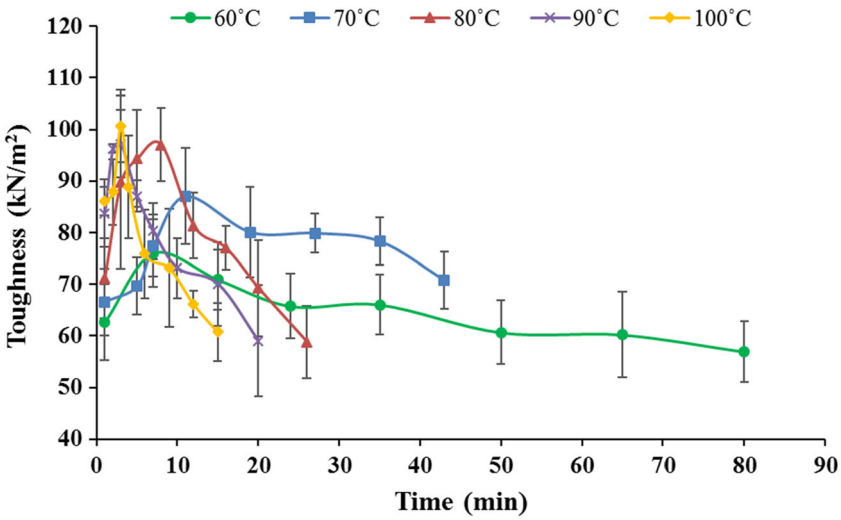

Fig. 6 The changes of toughness of shrimp with different treatment temperatures and times, $N = 6$

changing trends of hardness (compression force) were also found in whole blue mussel (Ovissipour et al. 2013) and beef (Tornberg 2005).

Toughness is considered to be a critical factor in meat and seafood products, which measures the total energy required to penetrate through the sample (Sajeev et al. 2004). As shown in Fig. 6, toughness increased during the initial period of heat treatment and then decreased during the later period of thermal treatment. Martens et al. (1982) reported that the connective tissue and the myofibril proteins are the two main protein systems responsible for toughness. During the initial period of thermal treatment, denaturation of myofibril proteins (primarily actomyosin) occurred, which induced a shortening of the sarcomere length, which resulted in an increase in toughness, evidenced by an increase in the required shear force to cut the muscle (Ma and Harwalkar 1991). Moreover, the denaturation of connective tissue proteins (primarily collagens) led to muscle contraction, and this forced water out and increased the toughness of shrimp muscle (Fennema 1996). In the later period of thermal treatment, the extended processing time changed the collagen to gelatin, which lowered the collagen content and led to a decrease of toughness. In addition, degradation of myofibrillar proteins also occurred with prolonged thermal processing time, which reduced the toughness of shrimp muscle correspondingly (Fennema 1996).

The change of the toughness of shrimp muscle occurred faster at higher processing temperatures compared to lower processing temperatures. Specifically, it required 3 min to reach the maximum toughness at 100 and 90 °C, but 8, 11, and 7 min for the temperatures of 80, 70, and 60 °C. The influence of thermal treatment on the toughness of shrimp muscle is a complicated phenomenon. Toughness increases as a result of the denaturation of myofibrils and connective tissue proteins, but toughness tends to decrease through the degradation of myofibrillar proteins and conversion of collagens to gelatin (Fennema 1996). The higher the treatment temperature, the higher the maximum toughness of shrimp indicating that the higher temperature process first led to greater protein denaturation and also did not allow for collagen breakdown. At a lower processing temperature (60 °C), the denaturation of myofibrillar proteins (mainly actomyosin, see Fig. 2) is the primary reason for the changes of the toughness of shrimp muscle due to its relatively low thermostability properties (Martens and Vold 1976). The T_{max} of shrimp collagen in the current study is 62 °C as shown in Fig. 2; thus, both the changes of myofibrillar proteins and collagen engendered the changes in the toughness for temperatures higher than 70 °C (Fennema 1996), as evidenced by higher maximum toughness and changing rate of the toughness of shrimp muscle.

Correlation of Cook Loss, Shrinkage, and Texture (Hardness)

Cook loss, area shrinkage, and hardness of shrimp were highly correlated (Fig. 7). The correlation coefficient between cook loss and shrinkage was 97.8%, between cook loss and hardness was 92.3%, and between shrinkage and hardness was 88.4%. Similar high correlations between cook loss, area shrinkage, and texture were also found in salmon and chicken muscles (Kong et al. 2008) and whole mussel (Ovissipour et al. 2013) during thermal processing. A main reason for this high correlation is the denaturation of proteins. The structure of proteins changed after denaturation that reduced water holding ability, and led to an increase in cook loss. As a part of the cook loss, drip loss occurred during thermal processing. This produced voids between shrimp muscle fibers, increasing overall density (related to texture) and reducing volume (as reflected by shrinkage) after thermal treatments (Chau and Snyder 1988; Erdogdu et al. 2004). The denaturation of myofibrillar proteins and shrinkage of collagen led to the shrinkage

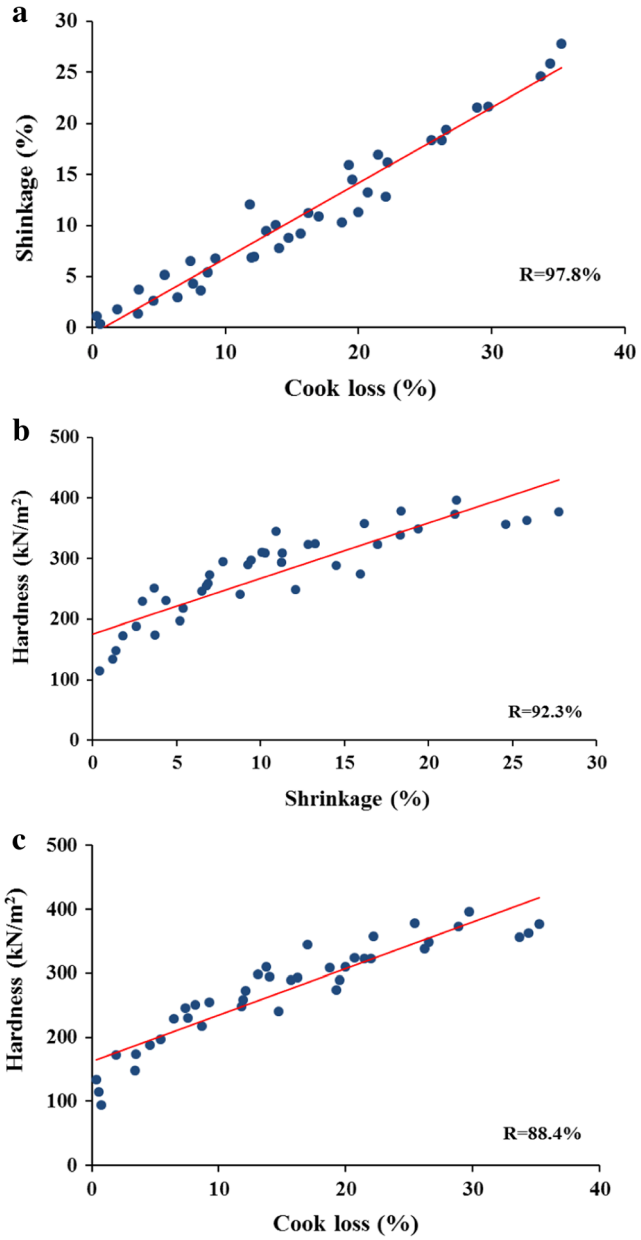

Fig. 7 The correlation of quality attributes of processed shrimp. **a** Cook loss and shrinkage. **b** Shrinkage and hardness. **c** Cook loss and hardness

of shrimp muscle and tighter tissues (Ma et al. 1983). Meanwhile, increasing internal pressure from connective tissue shrinkage forced the water out of the shrimp muscle, and led to an increase of cook loss (Erdogdu et al. 2004).

Color

The treatment conditions greatly influenced the color of shrimp. An increase in ΔL^* is anticipated with cooking at 60 and 70 °C during the early stage. Oxidation and browning resulted in a decrease during the later stage for temperatures higher than 80 °C (Fig. 8a). Limbo and Piergiovanni (2006) introduced a color scale for evaluating the difference between two colors and reported that $6 < \Delta E < 12$ indicated a strong difference of the color; $\Delta E > 12$ indicated two different colors. In this study, the ΔE was higher than 6 after 1 min at 60 °C. After 7 min at 60 °C, the ΔE was higher than 12. All the ΔE were higher than 12 after 1-min treatments at temperatures higher than 70 °C. Zero-order kinetic model better described (R^2 from 0.69 to 0.88) the changes of ΔE versus time (Table 5). The same reaction order was also founded in the color changes of salmon during the thermal process (Kong et al. 2007b). The E_a, k_0 values, and coefficient of correlation are shown in Table 5. The activation energy was 37.2 kJ/mol for the changes of ΔE of shrimp.

The pink/red color of shrimp is due to the presence of the carotenoid astaxanthin, obtained from ingestion of carotenoid-containing marine plants (Muriana et al. 1993). Some carotenoids are bound to proteins (Belitz et al. 2004; Fennema 1996). In raw shrimp, the astaxanthin pigment is blue color and heat induces the denaturation of the astaxanthin-protein complex, and alters visual properties of the pigment, with a change of color from blue to red (Fennema 1996; Muriana et al. 1993). The a^* and b^* increased with increasing treatment time and temperature (Fig. 8b, c), indicating a relative increase in red color. ΔL^* represents the change of lightness of shrimp muscle. For processing temperatures higher than 70 °C, two phases were observed: a whitening phase (L^* increased) at the early stage, followed by a browning phase in the late phase (L^* decreased). The highest lightness was obtained after 4, 7, and 20 min treatment at 100, 90, and 80 °C, respectively. Thus, the higher the temperature, the shorter the time needed to switch from the whitening phase to the browning phase. Haard (1992) reported that the denaturation of heme proteins (hemoglobin and myoglobin) are the main reason for whitening of certain muscles, such as salmon (Kong et al. 2007b) and cod (Franklin et al. 1994). Shrimp contains hemocyanin which performs a similar oxygen transport function as heme proteins. Hemocyanin is blue color in the oxygenated status and colorless/white in the deoxygenated status. The following browning phase is mainly due to the Maillard reaction, in which glycogen and proteins react to produce a brown color (Haard 1992). Higher processing temperature and longer treating time resulted in a more pronounced brown color (Whisler and Daniel 1985), which presented as the decreased L^* (Fig. 8a) and increased b^* (Fig. 8c). The ΔE represents the overall changes of L^*, a^*, and b^* and in this study, increased with increasing treatment time and temperature. Besides the denaturation of protein and astaxanthin, the area shrinkage resulting from the cook loss and shrinkage of myofibrils and collagens led to a smaller area, which increased color density of shrimp (Niamnuy et al. 2007).

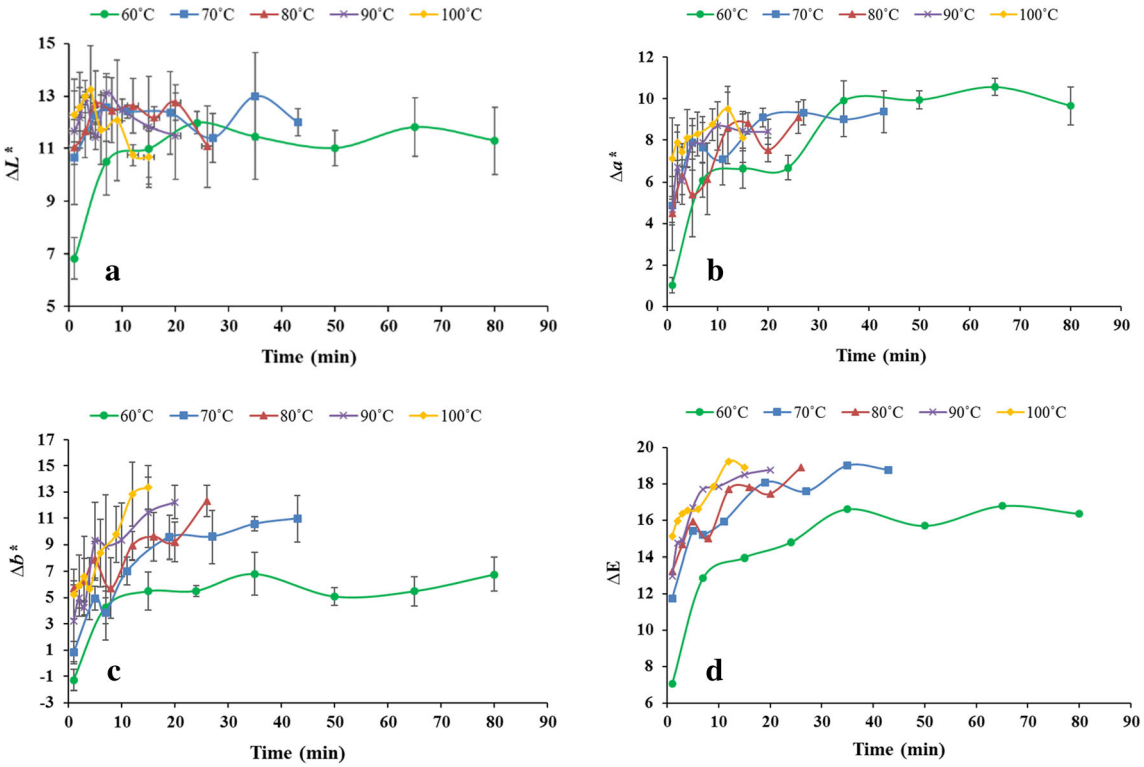

Fig. 8 The changes of color of shrimp with different treatment temperatures and times. **a** ΔL^*. **b** Δa^*. **c** Δb^*. **d** ΔE, $N = 3$

Conclusions

The effects of different pasteurization times and temperatures on quality attributes of shrimp (*Litopenaeus setiferus*) (80–90 counts/kg) were studied. The denaturation of proteins induced by the thermal treatment led to different quality changes in of the test shrimp samples. The cook loss, area shrinkage, and hardness of shrimp increased with increasing pasteurization time and temperature, and followed fractional first-order kinetic model. The toughness of shrimp muscle increased during the initial stage and decreased at the later stage during the pasteurization treatment. The overall color change (ΔE) increased with increasing pasteurization time and temperature, following a zero-order kinetic model. The kinetic data provide useful insight into the mechanisms of shrimp-quality changes during pasteurization, and could be applied toward designing the optimal thermal processing conditions. This research only considered shrimp size of 80–90 counts/kg to simply the experimental design. Future studies should consider more shrimp sizes for more comprehensive understanding of kinetic parameters determining shrimp-quality changes in thermal processing.

Table 5 Zero-order parameters for ΔE of shrimp after heat treatment at different temperatures

Temp (°C)	k (min^{-1})	R^2	E_a (kJ/mol)	k_0 (min^{-1})	R^2
60	0.046	0.69	37.2	4472	0.75
70	0.102	0.86			
80	0.172	0.81			
90	0.109	0.80			
100	0.266	0.88			

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