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Investigation on Powder Content Ratio in Shaving Process of *Katsuobushi* with Various Moisture Content by Considering Glass Transition Phenomena

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   Katsuobushi is one of the most famous Japanese traditional foods and it has been empirically known that giving moisture was effective to realize good shaving with yielding less powder. In this article, in the aim of finding scientific elucidation for this presumption, shaving experiments were carried out with varying moisture content of the *Katsuobushi* under the almost constant temperature as 25℃. For the experimental consistency, the moisture content of the sample was controlled by using saturated salt solutions and the commercial shaving equipment was introduced. As a result, it was found that most of the shaved product was obtained as powder if the moisture content was less than 0.5% d.b. With gradual increasing of moisture content of *Katsuobushi*, the powder content gradually decreased, and at the condition moisture content reached about 14% d.b., the powder content drastically decreased. By referring existing data, the glass transition temperature of *Katsuobushi* of 14.4% d.b. in moisture content was appeared to be about 25℃, that coincided with the sample temperature at the shaving. From the result, it would be elucidated that moistured *Katsuobushi* could be shaved with less powder content because the glass transition temperature of the *Katsuobushi* went down below the actual temperature at the shaving and the *Katsuobushi* turned into rubbery state.

Keywords: *Katsuobushi*, shaving, powder, moisture content, glass transition

1. Introduction

   Katsuobushi, boiled and highly dried bonito meat, is well known traditional Japanese food which is an essential every day product commonly used by Japanese. In traditional way, *Katsuobushi* is stored as a large chunk and thin bits called *Kezuribushi* are shaved off the chunk just before they are used. Currently, most of *Katsuobushi* have come to be industrially processed into *Kezuribushi* and packed in small plastic bags. The *Kezuribushi* product includes *Hana*, thinly sliced sheet form bits, and undesired powder. The mass fraction of powder in whole shaved off product is defined as powder content ratio. If the powder content ratio is too high, it can make cooking quality worse. In fact, Japanese Agricultural Standards (JAS) has determined upper limit for the powder content ratio to qualify the commercial *Kezuribushi* products [1]. Therefore, a lot of efforts have been made to find optimum shaving conditions that could reduce the powder

content. It has been well−known that the powder content can be reduced by letting the *Katsuobushi* moist before shaving, but it is only empirically known to be true and there has been no scientific explanation yet.

   On the other hand, it has been revealed that *Katsuobushi* is in a glassy state when it is adequately dried and kept at ambient temperature [2]. Several properties of *Katsuobushi* such as high storage stability, glass−like appearance, and the state change according with its temperature or moisture content have been found to have strong relation with the glassy state [2]. Glassy state is one typical state of amorphous materials generally realized in low temperature and/or low water content condition, which present very solid, plastic, rigid and brittle in physicochemical properties. It has been reported that foods can be very stable at the glassy state, because the compounds involved in deterioration reactions take many months or even years to diffuse over molecular distances and approach each other to react [3]. The temperature under which the amorphous materials turn into glassy state is called as glass transition temperature, T_g. The hypothesis has recently been stated

that this transition greatly influences food stability, as the water in the concentrate phase becomes kinetically immobilized and, therefore, does not assist or participate in reactions. Formation of a glassy state results in significant arrest of transitional molecular motion, and chemical reactions become very slow [4]. There is a detailed review on applications of glass transition on stability of foods and processing [5]. Glass transition is a second-order time–temperature–moisture–dependent transition, which is generally characterized by a discontinuity in physical, mechanical, electrical, thermal, and other properties of a material.

At high temperatures and/or high water contents, the amorphous materials turn into soft, visco–plastic state, that is called as rubbery state. In a molecular scale, glass transition corresponds to a change in energy that allows the components to pass from high amplitude motions involving the main macromolecular chains (i.e., the rubbery state) to local molecular motions of low amplitude (i.e., the glassy state) [6]. This glass–rubber transition is used to describe the structure property relationships, to control the textural properties and to understand the physicochemical properties changes in food materials [7–9]. The phase transitions of foods are important in characterizing their quality and designing efficient processing systems, and to determine the physical state during processing, storage, and consumption [5, 10]. In various food and biological materials the solids can be in an amorphous metastable state which is very sensitive to changes in temperature and moisture content. This amorphous matrix, which consists of food polymers or other food components such as sugars, can exist either as a very viscous glass or as a more liquid–like rubber.

In fact, in case of *Katsuobushi*, it has been revealed that the energy needed for shaving could be reduced by increasing the temperature above T_g because the *Katsuobushi* turned into rubbery state [11]. It has been also found if *Katsuobushi* was shaved under the temperature lower than T_g, shaved off product included a lot of powder and yield rate was deteriorated. By taking into account the fact that T_g of most hydrophilic systems is mainly affected by the water content, it would be presumed the shaving characteristics is improved by controlling water content so that the *Katsuobushi* turns into rubbery state; that coincides with the empirical knowledge that the yield rate of *Kezuribushi* is improved by letting the *Katsuobushi* moist before shaving.

In this article, quantitative investigation was made on the effect of moisture content on the powder content ratio in the shaving process of *Katsuobushi* and the optimum shaving condition that reduced the powder content ratio was disclosed in relation with the glass transition phenomena. In addition, thickness of *Kezuribushi* product was also measured for several different moisture content of *Katsuobushi*.

2. Materials and methods

2.1 Shaving equipment

Since many experimental run were made with various moisture contents of *Katsuobushi*, particular shaving equipment was needed to ensure the repeatability of shaving condition. In present study, OKAKA No.7 (AIKOGYO Co., Ltd) was used with some modification. Figure 1–(a) is a picture of the equipment taken from the top. By turning around the handle, a saucer installed in the equipment was rotated. The saucer had three sharp
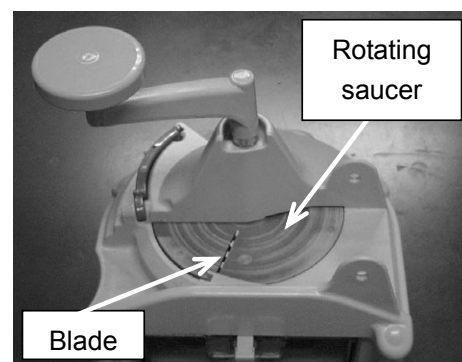
(a) Top view of the equipment
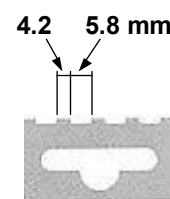
(b) Blade
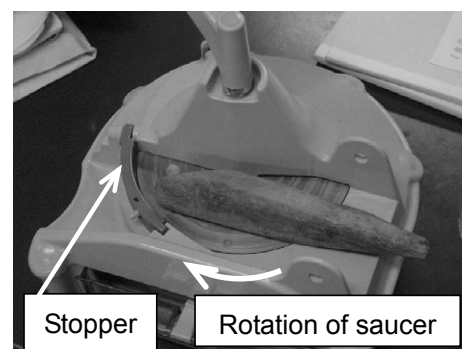
(c) Setting of *Katsuobushi* to be shaved

Fig. 1 Experimental equipment.

blades radially attached every 120 degrees as shown in Fig. 1−(a) and each blade had five keen shares as wide as 4.2 mm as shown in Fig. 1−(b). Moisture controlled *Katsuobushi* sample was put on the saucer as shown in Fig. 1−(c), and then adequate weight was put on the sample to apply constant pressing force as 10 kgf. Subsequently, the saucer was rotated clockwise in 60 rpm for 30 seconds. Shaved off product was accommodated in a container put beneath the saucer and then separated by stainless testing sieve with 850 μm aperture which coincided with the value that JAS of *Kezuribushi* adopted. [1] The experimental room temperature and humidity was about 25℃ and 70%RH, respectively. Powder content ratio of shaved off product was calculated as the mass of powder divided by total mass of whole *Kezuribushi* product.

2.2 Sample preparation

Katsuobushi manufactured by Iseoto Co., Tokyo Japan, was purchased at a market in Tokyo. All of the *Katsuobushi* was so−called *Honkarebushi* type, which was *Katsuobushi* treated by mold fungus to add flavor and improve stability by reducing moisture. Experimental samples were prepared as follows: Large chunk of *Katsuobushi* was sliced into pieces of 5 mm in thickness to minimize distribution of temperature and moisture content in each sample. To control moisture content of the samples, the sliced samples were placed in hermetic chambers containing saturated salt solutions with different relative humidity. They had been placed in the chambers for several days or even weeks until they reached the equilibrium condition. Temperature was kept at 25℃ by using low temperature incubator (ELEYA, LTI−6000SD). As saturated salt solutions, CH₃COOK, NaBr, NaCl, KCl that gave relative humidity of 23, 33, 58, 75.5%RH, respectively, were used [12]. The sample weights were controlled until the constant value (within ± 0.0005 g) was attained, where the equilibrium was assumed to be achieved [13]. The lowest moisture content (0−1% d.b.) samples were obtained by dehydrating in vacuum desiccators over P_2O_5. The initial and final moisture content of samples were measured by oven method which placed the samples in a drying oven at 105℃ until it reached constant mass. The controlled water content of samples is presented by dry basis moisture content which is determined by the mass fraction of water against the dry matter.

3. Results and discussions

3.1 Glass transition temperature of *Katsuobushi*

Hashimoto *et al.* [2] have made detailed measurements of the glass transition temperature (T_g) of *Katsuobushi* of several moisture content (% dry basis) by using differential scanning calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). The DSC measurements were made for two different *Katsuobushi* manufactured by two different companies to confirm the glass transition behavior was a general characteristic of *Katsuobushi*. Gordon−Taylor equation has been known as an empirical equation that could be generally applied to predict the glass transition temperature (T_g) of mixtures comprising amorphous synthetic polymer and water [14] , presented as Eq. (1):

$$T_g = \frac{x_s T_{g,s} + k x_w T_{g,w}}{x_s + k x_w} \qquad (1)$$

where T_g, $T_{g,s}$ and $T_{g,w}$ are the glass transition temperatures (℃) of the mixture, solid and water, respectively, x_s and x_w are the mass fraction of solid and water, respectively, and k is a constant which can be given theoretically by the ratio of Eq. (2), where $\Delta c_{p,s}$ and $\Delta c_{p,w}$ are the heat capacity difference due to glass transition for solid and water, respectively.

$$k = \frac{\Delta c_{p,w}}{\Delta c_{p,s}} \qquad (2)$$

In order to correlate the *Katsuobushi* data, the glass transition temperature and the difference in heat capacity of solid were determined as $T_{g,s}$=163.3℃ and $\Delta c_{p,s}$=0.28 J/(g K), respectively [2]. And the glass transition temperature and the difference in heat capacity of pure water were taken as $T_{g,w}$=−135℃ and $\Delta c_{p,w}$=1.36 J/(g K). Notice that constant k=6.0 is applied here for better approximation than k=4.86 derived by Eq. (2). This approximation curve is used as T_g hereafter.

3.2 Measurement of powder content ratio

Pictures of typical appearance of *Kezuribushi* product are shown in Fig. 2. Significant difference is seen between the successfully shaved off product which is called *Hana* and the undesired powder, shown in Fig. (a) and (b), respectively. The relationship between powder content ratio in *Kezuribushi* product and the moisture content of *Katsuobushi* during shaving is shown in Fig. 3. The data clearly indicate the moisture content has significant effect on the powder content ratio. When the moisture content is very low as 0.5% d.b., almost all the prod-

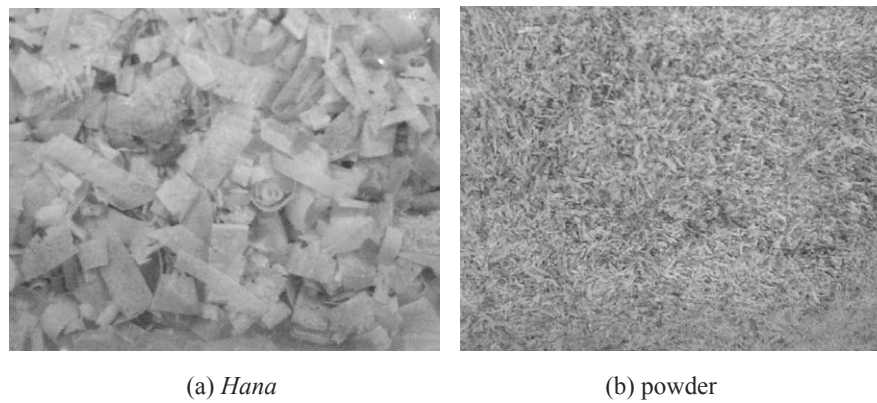(a) *Hana*   (b) powder

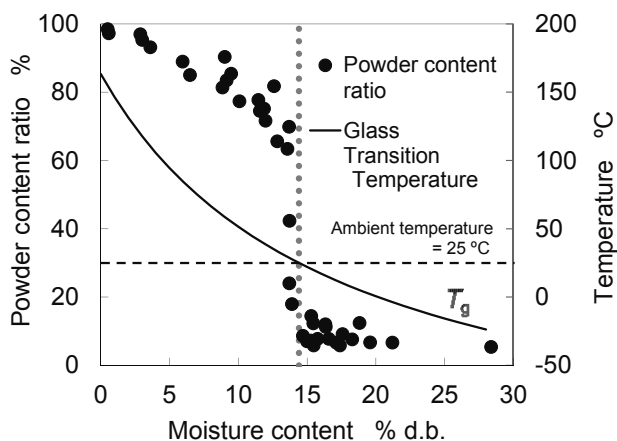Fig. 2   Typical appearances of *Kezuribushi* product.

Fig. 3   The relationship between powder content ratio and moisture content under the condition of 25℃ in ambient temperature.

uct becomes powder. Then the powder content ratio gradually decreases with increasing moisture content. When the moisture content has reached about 14% d.b., the powder content ratio drastically decreases and at the region where the moisture content excesses 14.4% d.b., indicated by dotted vertical line, the powder content ratio becomes sufficiently low even though it slightly decreases with increasing moisture content. Since the solid line shown in Fig. 3 gives the relationship between glass transition temperature T_g of *Katsuobushi* and the moisture content which was obtained in 3.1 and broken horizontal line indicates 25℃ in temperature, dotted vertical line specifies the critical moisture content of glass–rubber transition of *Katsuobushi* under the condition of 25℃ in sample temperature.

From the viewpoint of glass transition, the obtained data trend can be explained as follows: At the region where the moisture content is lower than 14% d.b., the glass transition temperature of *Katsuobushi* is much higher than actual sample temperature and the sample is in the glassy state. Therefore, the sample is very hard

and difficult to be shaved so that the shaved off product is very thin or even becomes powder. When the moisture content reaches about 14% d.b., the glass transition temperature reduces to approach the actual sample temperature and glass–to–rubber phase transition begins. Glass–to–rubber phase transition drastically proceeds with increasing moisture content. When the moisture content excesses about 14.4% d.b., *Katsuobushi* is sufficiently in the rubbery state so that it is soft and easy to be shaved. Consequently, powder content ratio becomes very small. It can be concluded that this study would give scientific explanation to the traditional and empirical knowledge that *Katsuobushi* should be shaved in moist condition to make good *Kezuribushi* product of less powder content. Further, it will be useful that we can quantitatively predict the critical water content of *Katsuobushi* desired for given temperature condition by using Fig. 3.

3.3 Measurement of thickness of *Hana*

Figure 4 shows the relationship between average thickness of *Hana* and the moisture content during shav-
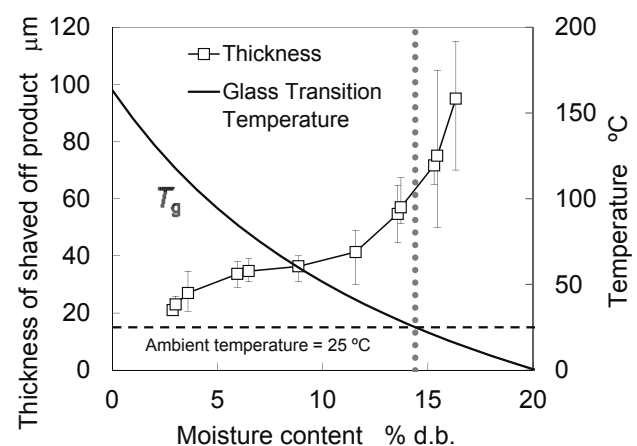

Fig. 4   The relationship between thickness of *Hana* and moisture content.

ing. The thickness is obtained by averaging triplicate measurements. There was no measured data at about 0.5% d.b. because almost all products were powder. In such low moisture content condition, *Katusobushi* would be so very hard that the operation could be scraping rather than shaving and the whole products becomes powder. At the range of moisture content approximately from 3% d.b. to 12% d.b., the thickness of *Hana* gradually increases with increasing moisture content. Once the moisture content excesses about 12% d.b., the thickness comes to show drastic increase and reaches to 0.1 mm at about 16% d.b. It is clearly seen the thickness of *Hana* is affected by the moisture content during shaving although the change is not so drastic compared to the change of powder content ratio. Since *Hana* is generally desired to be thin, it would be concluded that letting water content of *Katsuobushi* a little higher than the critical moisture content for glass to rubber phase transition is the optimum shaving condition.

4. Conclusions

It has been empirically known that giving moisture was effective to shave *Katsuobushi* with less powder content. In this article, a lot of shaving experiments were carried out with varying moisture content of the *Katsuobushi* and it was found the powder content in shaved off products drastically decreased when the moisture content of the *Katsuobushi* exceeded 14.4% d.b. under the condition of 25℃ in sample temperature. By referring existing data, the glass transition temperature of *Katsuobushi* whose moisture content was 14.4% d.b. was appeared to be about 25℃ that coincided with the actual sample temperature. Namely, under the condition of 25℃ in sample temperature, the *Katsuobushi* with lower moisture content than 14% d.b. is in glassy state so that it is hard and the shaved of product tend to contain a lot of powder while the *Katsuobushi* with higher moisture content than 14.4% d.b. is in rubbery state so that it is soft enough for preferable shaving with less powder content. This result gives clear scientific elucidation to the empirical knowledge that *Katsuobushi* can be shaved well with less powder content by letting the *Katsuobushi* moist before shaving.

NOMENCLATURE

Δc_p : heat capacity change at the T_g, $J\cdot g^{-1}\cdot K^{-1}$
T_g : glass transition temperature, ℃

x : mass fraction, %

Subscripts

s : solid
w : water

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