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◇◇◇ **Original Paper** ◇◇◇

Study on the Enthalpy Relaxation of Katsuobushi (Dried Glassy Fish Meat) by Differential Scanning Calorimetry and Effect of Physical Aging upon Its Water Sorption Ability

Tomoko HASHIMOTO, Tomoaki HAGIWARA†, Toru SUZUKI and Rikuo TAKAI

Department of Food Science and Technology, Tokyo University of Marine Science and Technology,

Enthalpy relaxation behavior of Katsuobushi (dried glassy bonito meat) during several storage conditions below its T_g was studied by differential scanning calorimetry (DSC). The magnitude of the relaxed enthalpy (ΔH) became larger with the increase in aging time, and the relaxation speed became faster with the increase in aging temperature. This tendency was quite similar to other amorphous materials. The process of the ΔH change during aging could be fitted successfully to the Kohlrausch–Williams–Watts (KWW) equation, which was often used to describe the kinetic process of enthalpy relaxation for many amorphous polymers. The mean relaxation time constant that was calculated through the fitting process suggested that the glassy state of Katsuobushi was easy to relax as compared with sucrose and starch. Furthermore, it was observed that aging process reduce the water sorption ability of Katsuobushi. This suggested that physical properties of food could be changed even if it is stored in the glassy state.

Key words: enthalpy relaxation, physical aging, Katsuobushi, KWW equation, water sorption ability

1. Introduction

The enthalpy relaxation phenomenon is one of important characteristic for many amorphous materials. In the glassy state, long-range cooperative molecular motions are strictly prohibited. However, lower amplitude molecular motions takes place even when it is kept in the glassy state. Since the glassy materials are far from the thermodynamic equilibrium, molecular re-arrangement takes place, leading to lower state of enthalpy during long-term storage. This process is generally called 'enthalpy relaxation' or 'physical aging'. Fig. 1 shows schematic representation of the change in enthalpy and heat capacity of a glassy material as a function of temperature. When a molten state material (f) is cooled very quickly, it reaches to a glassy state (a) through a glass transition at its glass transition temperature (T_g). When a glassy material stored under the T_g (this process is called 'aging'), microstructural evolution may take place with some extra loss in enthalpy (a→b). When a stored material (b) is then heated, relaxed enthalpy is recovered rapidly to the equilibrium state (e) at the vicinity of the T_g. This enthalpy recovery process can be detected from the endothermic overshoot in DSC curves (d). This physical aging process affects a number of physical properties of amorphous materials, such as density, modulus, enthalpy and volume. In the case of synthetic polymer, enthalpy relaxation behavior is recognized as very important factor to predict the physical changes during long-term storage because

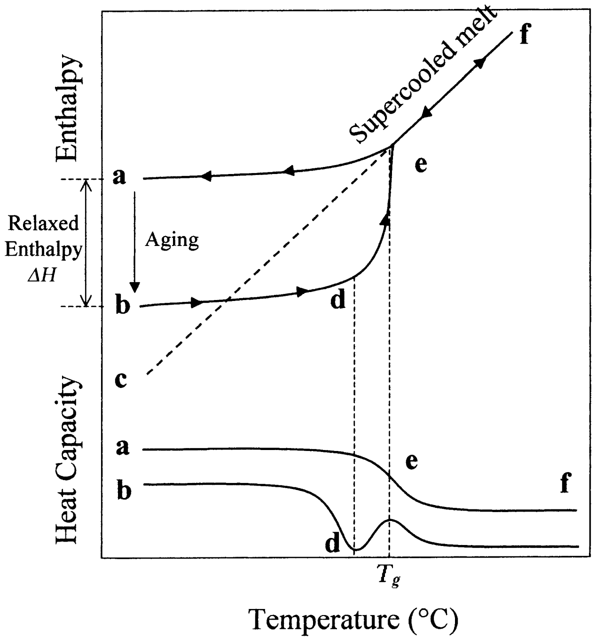

Fig. 1 Schematic representation of the change in enthalpy and heat capacity of glassy materials as a function of temperature.

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† Tel: 81-3-5463-0402, Fax: 81-3-5463-0585, E-mail: tomoaki@s.kaiyodai.ac.jp

enthalpy relaxation rate is useful indicator of molecular motion below its T_g [1]. Also in the field of food science, the importance of enthalpy relaxation has been recognized recently from the relevance of this process to some food technology applications [2,3]. However, the enthalpy relaxation study is relatively scarce for food products or food ingredients. These researches are mainly about sugars [4–8] and polysaccharides [9–16].

In our previous study [17], we have performed DSC and DMA analysis of Katsuobushi (boiled and smoke-dried bonito meat product) and proved it was a glassy material. Furthermore, stored Katsuobushi showed a large endothermic peak lapped over step-wise heat capacity change in DSC curve. Since enthalpy relaxation can be detected as an endothermic peak in DSC thermograms, it can be considered that the endothermic peak observed in Katsuobushi may be caused by its enthalpy relaxation. Similar behaviors were also reported for several proteins and protein-rich product [18–21]. However, more intimate information focused on the enthalpy relaxation behavior has not been obtained. In this study, we attempted to examine the enthalpy relaxation behavior of Katsuobushi under the several aging conditions using DSC. Additionally, quantitative analysis was carried out to follow the kinetic aspect of it using the Kohlrausch-Williams-Watts (KWW) equation, which has been often used to describe the process of enthalpy relaxation [22]. Furthermore, the effect of the physical aging process on some physical properties of Katsuobushi was also examined. In this study, the water absorption ability was chosen as one of physical properties because it is very important factor for long-time storage of dried food materials. It has been already reported the relation between the enthalpy relaxation and water sorption ability for amorphous potato starch [10]. Therefore, it was expected that the water absorption ability was affected by aging process also for Katsuobushi.

2. Materials and Methods

2. 1 Sample Preparation

Katsuobushi manufactured by Ninben Co., Ltd. was used as a sample. It was sliced by a power band saw and selected the parts of red meat region, which has a shiny red-color glass-like appearance, was selected for analysis after removal of dark muscle and surface moldy region because such removal parts were unsuitable to detect the clear glass transition phenomenon in DSC data. It was crashed into powder using hammer and sifted using strainer to adjust the particle size. Sample powder was equilibrated by CH_3COOK saturated salt solution (relative humidity was 23%) for 1 week to adjust the moisture content.

2. 2 Enthalpy relaxation measurement

Shimadzu DSC-50 differential scanning calorimeter fitted with a LTC-50 cooling system was used in this study. The temperature calibration was performed with indium (melting point, 156.6°C; ΔH_m, $28.5 Jg^{-1}$) and distilled water (melting point, 0.0°C; ΔH_m, $333 Jg^{-1}$). α-Alumina powder was used as a reference. N_2 at a flow rate of 20 ml min^{-1} was used as carrier gas. About 20mg sample was weighed and hermetically sealed into aluminum pans by using a sealer. Liquid nitrogen was used as a cooling medium to cool the sample below the room temperature. The Tg value of the sample was determined as follows. In the first heating, the sample was heated to 150°C at 5K/min to eliminate the previous thermal history and then cooled to −50°C at 5K/min using liquid nitrogen. In the second heating, the sample was re-heated to 150°C at 5K/min and the onset, midpoint and endpoint Tg values and the change in heat capacity at Tg (ΔC_p) were determined.

Aging was carried out according to the method described by Hancock [4]. Prior to aging, the sample was heated to 30°C above T_g at 5K/min, and then cooled to 100°C below Tg at 5K/min to standardized thermal history. It was heated again to the aging temperature Ta (25, 42, 60°C). The samples were held isothermally for 0-120 hours, cooled to 100°C below Tg, and subsequently heated through Tg to 150°C. During the final heating scan the pronounced endothermic recovery peak located at the end of the glass transition region, reflecting enthalpy relaxation, was analyzed. The area of the endothermic peak (ΔH) was determined using following equation:

$$\Delta H = \int Cp_{aging}(T)\,dT - \int Cp_{not\text{-}aging}(T)\,dt \qquad (1)$$

where Cp_{aging} and $Cp_{not\text{-}aging}$ are the heat capacity of aged glass and non-aged glass, respectively. These thermal analyses were performed using the analysis software TA-60WS (Shimadzu CO., LTD.). To determine the moisture content of the sample, the top cover of DSC pan was pierced by drill and dried at 110°C until it reached constant weight after DSC measurement.

2. 3 Fitting to the KWW equation

In general, the enthalpy relaxation cannot be often described by a normal single exponential relaxation function. To describe the non-exponentially, the KWW equation approach assumes the concept of distribution of relaxation time. The KWW equation is given by:

$$\Phi(t) = \exp[-(t/\tau)^{\beta}] \qquad (2)$$

where $\Phi(t)$ is the relaxation function and t is aging time and τ is the mean relaxation time constant and β is a relaxation time distribution parameter with a value of between 0 and 1. A value of unity for β indicates a single relaxation time. The β value is generally lower (broader distribution of relaxation times) for polymers than for low molecular weight materials [3]. The KWW equation can be applicable for many glassy materials, such as synthetic polymers [23–25], sugars [4,5,6,8], and starches [16] and also for proteins [26]. However, this type analysis has not been performed for natural food systems like dried fish.

The relaxation function $\Phi(t)$ in Eq. 2 can be also described as following equation [4,5,16]:

$$\Phi(t) = 1 - (\Delta H/\Delta H_{\infty}) \qquad (3)$$

where ΔH is the measured enthalpy recovery under those conditions calculated from Eq.1. ΔH_{∞} is the maximum enthalpy recovery at any given temperature and it can be described as following equation:

$$\Delta H_{\infty} = \Delta Cp\ (T_g - T_a) \qquad (4)$$

where T_g is the glass transition temperature of the sample and T_a is the aging temperature and ΔC_p is the change in heat capacity at T_g. Combining equation 1, 3 and 4, the experimental data were fitting to the KWW equation (Eq. 2) by using τ and β as fitting parameters. The fitting was done with the help of the mathematical software named Kaleida Graph for Windows (Version 3.08, Synergy Software, U.S.A.) and the initial parameters provided were $\tau = 100$, $\beta = 0.5$ for all samples.

2. 4 Water sorption experiment

2. 4. 1 Aging process

Prior to aging, hermetically sealed Katsuobushi powder was stored at 120°C for 1 hour to eliminate sample history. The sample was aged at 40°C for 1, 2, 3 weeks in thermostatic chambers to examine the effect of aging time. At the same time, another sample was aged at several aging temperatures (20, 30, 40, 60°C) for 1 week to examine the effect of aging temperature.

2. 4. 2 Water sorption isotherm experiment

Aged Katsuobushi powders with different moisture content were prepared by equilibrating them in separate chambers with different RH (relative humidity) for 1 week at 25°C. Saturated salt solutions of LiBr, LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, KI, NaCl, KCl giving RH of 6.6, 11.3, 23, 33, 44, 58, 70, 75.5, 84.5%, respectively, were used in this study. It took about 3–4 days until the weight change of the sample was stopped. Moisture contents of equilibrated samples were determined by placing the samples in a drying oven at 110°C for 24 hours.

3. Results and Discussion

3. 1 Characterization of the glass transition for Katsuobushi

Fig. 2 shows typical DSC curve of Katsuobushi. The moisture content of this sample was 8.3%. A clear step-wise change in heat capacity that was an indicator of the glass transition was observed as same as our previous report [17]. From this DSC result, the glass transition temperature and the heat capacity change at T_g (ΔC_p) of Katsuobushi could be calculated. The values of onset, midpoint and endpoint T_g were 43.1, 76.0 and 108.9, respectively. The width of the glass transition region of Katsuobushi was a relatively broader than other glassy synthetic polymers [27]. This phenomenon was probably attributed to the fact that Katsuobushi is a multicomponent system constituted of many substances including water, several types of protein, lipids, sugars and minerals. The value of ΔC_p was 0.26 J/g.

3. 2 Enthalpy changes for Katsuobushi aged at different temperature

The DSC curves of Katsuobushi aged at different temperatures (25, 42, 60°C) for different times (0 to 70 hours) were shown in Fig. 3. Each samples showed clear endothermic peaks lapped over the step-wise heat capacity changes and these peaks were dependent on aging temperature and aging time. For the sample aged at 60°C, the time dependence behavior of relaxation peak magnitude was also obvious nevertheless this aging temperature was higher than onset T_g value of the sample. Since such tendency is a general characteristic of amorphous material,

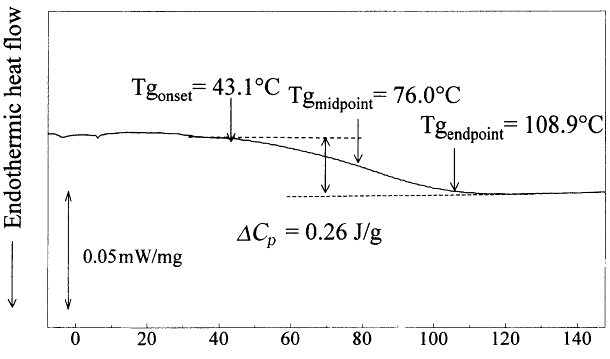

Fig. 2 Typical differential scanning calorimetry thermograms of Katsuobushi at moisture content 8.3%.

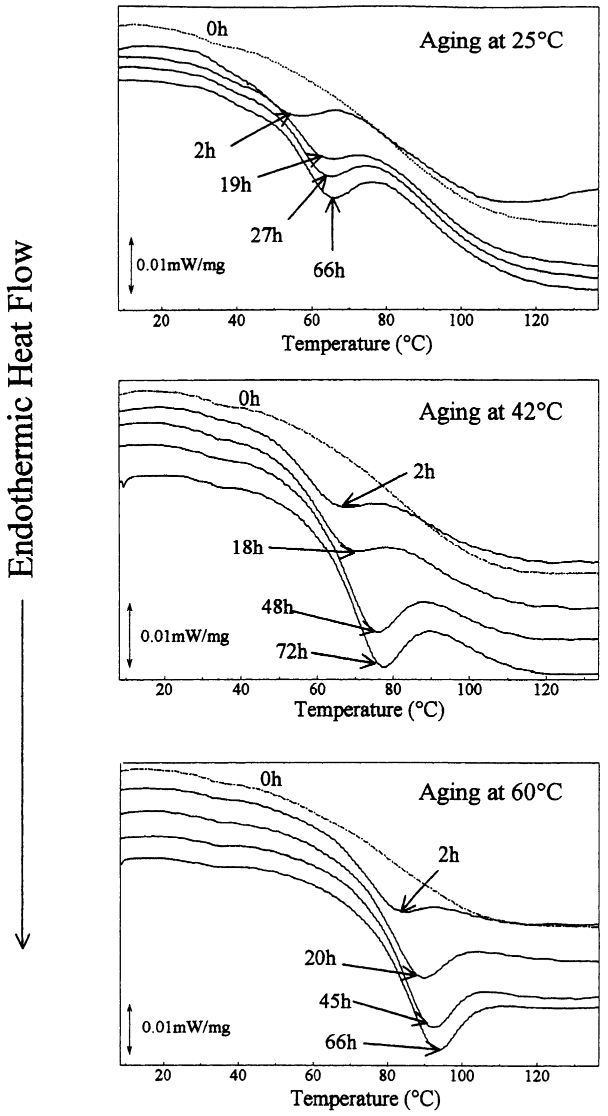

Fig. 3 Typical differential scanning calorimetry thermogram thermograms of Katsuobushi aged at different temperatures (25, 42, 60°C) and different aging times (0 to 72h).

it could be considered that these peaks indicated the enthalpy relaxation of Katsuobushi. The magnitude of these endothermic peaks (ΔH) calculated from DSC results using Eq. 1 is shown in Fig.4. The values of ΔH for all samples were increased with aging time. The amorphous polymers generally relax easier as aging temperature is closer to their glass transition temperature. The same phenomenon was also observed for Katsuobushi. The sample aged at 60°C that was the highest aging temperature showed the highest ΔH value. This was caused by the fact that the sample stored at higher temperature has higher segmental mobility of the polymer chains and higher mobility produced the higher speed to molecular re-arrangement. From these results, it became clear that the characteristics of enthalpy relaxation behavior of Katsuobushi, such as aging time and aging temperature dependence, were quite similar to other amorphous materials.

3. 3 Physical aging kinetics

Physical aging kinetics of Katsuobushi was examined using the KWW equation. The values of Φ (t) as a function of aging time calculated from Eqs. 3 and 4 are shown in Fig. 5. Dotted line in the figure is the best fitting line to Eq. 2. From the fact that correlation coefficient was over 0.99 for each samples, it could be considered that this fitting was done successfully. Obtained values of β and τ were listed in Table 1. The experimental results obtained in this study were relatively short-term data (storage times were 0-120 hours) compared to practical shelf life. However, this data make it possible to predict the enthalpy relaxation behavior during longer-term storage. The corresponding β values of Katsuobushi were 0.25-0.35

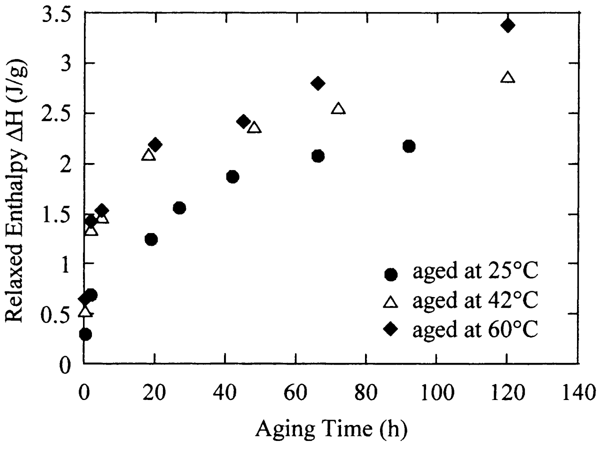

Fig. 4 The dependence of the magnitude of enthalpy relaxation on aging time measured after isothermal aging at various aging temperatures (25, 42 and 60°C) below the glass transition temperatures of Katsuobushi.

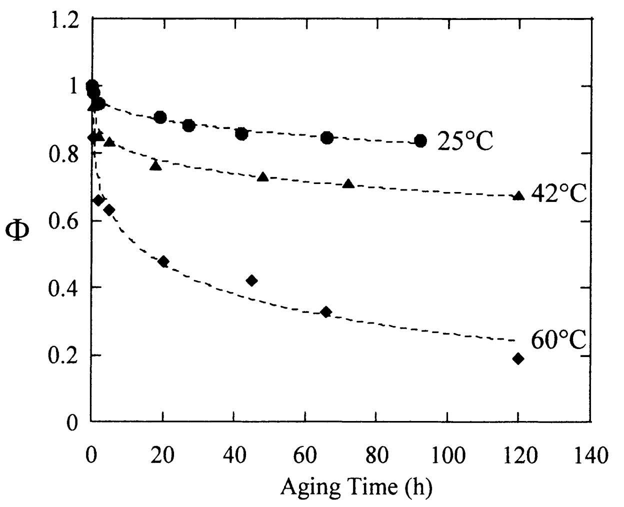

Fig. 5 Plot of the relaxation function (Φ) of glassy Katsuobushi aged at 25, 42 and 60°C.

Table 1 The fitting parameters β and τ of KWW equation for ΔH change in *Katsuobushi.*

Aging Temp. Ta (°C)	β (–)	τ (h)
25	0.35	1.05E + 04
42	0.25	4.65E + 02
60	0.35	0.44E + 02

and these were significantly different from 1 for all aging temperatures. This result indicated a distribution of the relaxation time rather than a single relaxation time. The β value is generally 0.5 for glassy polymer [28] and this value was relatively higher than that of Katsuobushi. This smaller β value of Katsuobushi was attributed to the fact that multicomponent system often shows a broad distribution of relaxation time because of its structural complexity [3].

The variation of the relaxation parameter τ of Katsuobushi with scaled temperature T_g-T_a is shown in Fig. 6. The τ value can be considered as an indicator of stability under the glass transition temperature. The higher τ value indicates its lower enthalpy relaxation rate [24]. The τ value of Katsuobushi decreased with the increase in aging temperature similar to other glassy materials. This result indicated that the relaxation speed became faster with aging temperature increased. We could not compare the τ value of Katsuobushi with similar materials because this type analysis has not been performed for proteins or protein–based products. Therefore, the reported τ values for sucrose [4] and starch [16] obtained in similar way experiments were also plotted in the figure for comparing. The τ values of Katsuobushi for all aging temperatures were relatively smaller than that of sucrose and starch. This result suggested that the glassy state of Katsuobushi is relatively unstable and easy to relax than sucrose and starch in the same reduced temperature range. Kim and others suggested that the larger τ value of starch than sucrose was attributed to its higher molecular weight and structure complexity such as blanching of polymer chain [16]. On the contrary, the τ value of Katsuobushi was lower than that of sucrose though Katsuobushi is protein –rich product and has high molecular weight and very complex structure consist of tangled polymer chain. Probably, this lower stability is related to the fact that Katsuobushi is a multicomponent system. It has been reported that the addition of anti–plasticizer increases the relaxation time of sucrose–additive mixture system [6]. This result suggests that the presence of plasticizer also affects the enthalpy relaxation rate of mixture system. Since Katsuobushi contains several low–molecular weight materials (sugars, salts, minerals, nucleotides) that have plasticizing effect, there is a possibility that the lower τ value of Katsuobushi is caused by the presence of these plasticizing components in bonito muscle. From this assumption, it is expected that the enthalpy relaxation behavior of multicomponent system would be affected strongly by the difference in its component composition. At the present stage, it is not clear how each constituted components affect the relaxation process of whole system. For further discussion, more research about a large variety of foods and food ingredients must be examined.

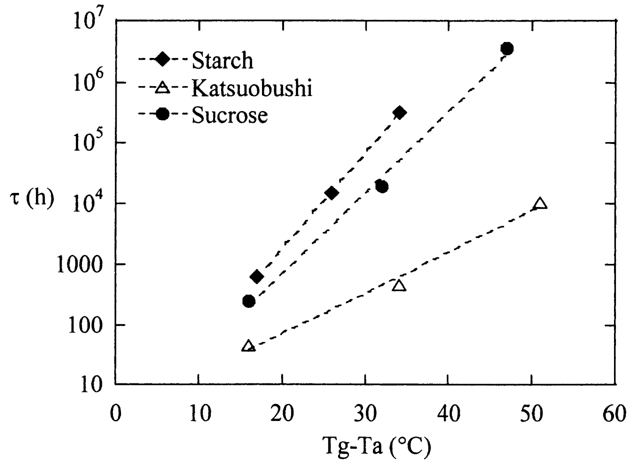

Fig. 6 Semi logarithmic plot of mean relaxation time τ as a function of the scaled temperature T_g-T_a. ◆: starch △: Katsuobushi ●: sucrose.

In the case of Katsuobushi, the other possible explanation of this instability could be considered, that is the complicacy of production method of Katsuobushi. Several operations, such as boiling, gradual drying and molding, are added to Katsuobushi during production process. It is expected that these processing condition may produce the gradual decomposition of some part of protein in bonito meat into amino acid. This decrease in molecular weight of fish muscle protein may affect the stability of glassy state of Katsuobushi.

In order to examine the reactivity of the enthalpy relaxation process of Katsuobushi to the to the aging temperature change in the range of 25–60°C used in this study, we calculated the apparent Arrhenius activation energy (E_a). Fig.7 shows Arrhenius plot of τ values as a function of aging temperature. The E_a value calculated from this plot was 129 kJ/mol. The reported E_a values for sucrose and potato starch obtained in a similar way are 360 and 284 kJ/mol, respectively [4,16]. The fact that the E_a value of Katsuobushi was relatively smaller than these amorphous materials suggested that aging temperature change does not so effective on enthalpy relaxation process of

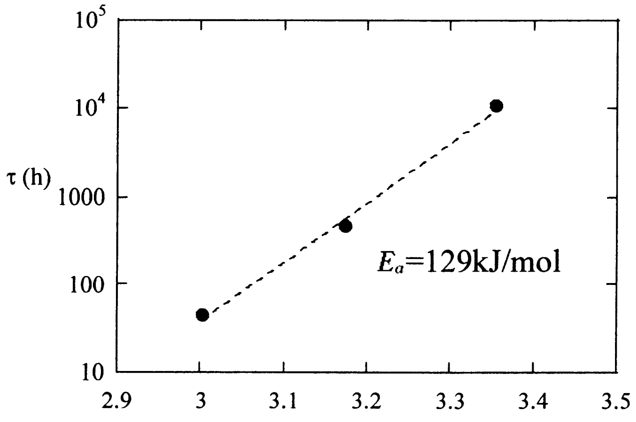

Fig. 7 The Arrhenius plot of the molecular relaxation time τ of Katsuobushi as a function of aging temperature.

Katsuobushi in the same scaled temperature range. This was probably attributed to the complexity of the component composition of Katsuobushi. Katsuobushi is composed of several materials and it is expected that these materials have their own different T_g values. The T_g value of Katsuobushi obtained from a DSC curve is considered as an average value of the T_g of constituted materials. The broader glass transition temperature region of Katsuobushi suggested this fact. Therefore, it can be considered that the value of relaxed enthalpy calculated in this study is the sum of several enthalpy relaxations due to its constituted materials. Even at the lowest aging temperature, some components having lower T_g values were relaxed easily and this produced the increase in the total ΔH value. While, at the highest aging temperature, some parts of these low T_g components may become already rubbery state and the total ΔH value become lower than expected because these components does not contribute to the enthalpy relaxation of whole system. Due to such variation in the relaxation behavior of several components under several aging temperatures, the aging temperature dependence of relaxation time of Katsuobushi may not become so obvious compared to the simple component system like sucrose or starch.

Our experimental results suggested that Katsuobushi was a relatively unstable material over relatively broad temperature range below its T_g compared to sucrose and starch. Therefore, to keep Katsuobushi completely in stable state for long-term storage, the storage temperature must be lower enough from its T_g.

3. 4 The change in water sorption ability of Katsuobushi by physical aging

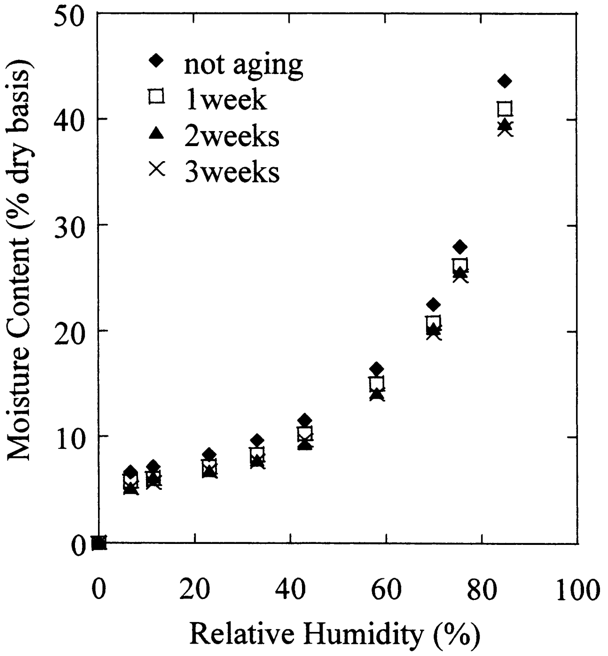

Fig. 8 Water sorption isotherms at 25°C for Katsuobushi after aged at 40°C for 1, 2, 3 weeks.

Fig. 8 shows the water sorption isotherms of non-aged and aged Katsuobushi at the same temperature (40°C) for different times (1, 2, 3 weeks). All water sorption isotherms of these samples showed typical sigmoidal curves. The moisture content of the sample before aging was about 8.99% and the glass transition temperature measured by DSC was about 70°C. Therefore, all samples were remained in the glassy state during aging process. From this sorption isotherm, it became clear that the water sorption ability of Katsuobushi was affected by

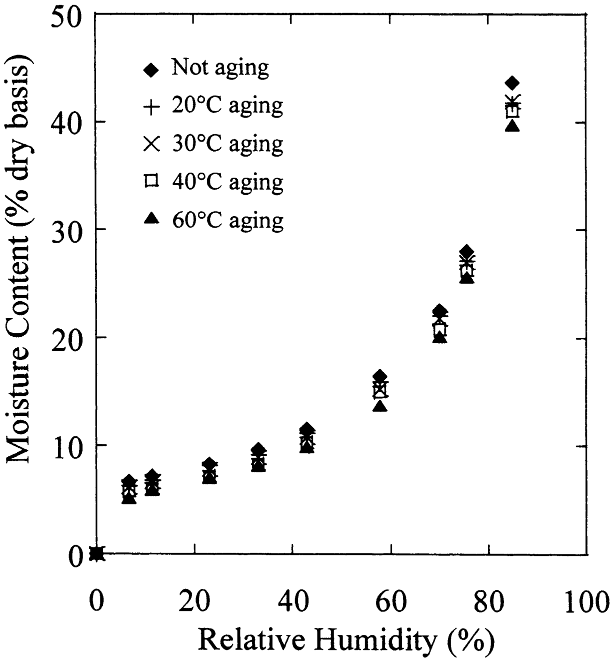

Fig. 9 Water sorption isotherms at 25°C for Katsuobushi after aged at various aging temperatures (20, 30, 40 and 60°C) for 1 week.

aging process strongly. As aging time increased, the amount of absorbed water was decreased. The difference in the sorption ability of the samples aged for 2 weeks and 3 weeks were not so clear. This was probably attributed to the fact that these samples were already reached to the relaxation equilibrium at 2 weeks. The effect of aging temperature on the water sorption ability was also examined. Fig.9 shows the water absorption isotherm of non-aged and aged Katsuobushi at different aging temperatures (20, 30, 40, 60°C) for 1 week. The difference in aging temperature also affected to the water sorption ability of Katsuobushi. As aging temperature increased, the water sorption ability decreased. The difference in equilibrium moisture content between the non-aged sample and the sample aged at 60°C was over 4% when relative humidity was highest (RH = 85%). These results suggested that aging process depressed the water absorption ability of Katsuobushi. The reduction of water sorption ability with the proceeding of the enthalpy relaxation has been already reported for potato starch [10] and also for similar experiments. For water vapor permeability (WVP) experiments, it has been reported that the WVP tended to decrease as aging time increased for several synthetic polymers [29-33] and potato starch [16]. In the research for potato starch, the mechanism of such reduction of the water permeability with aging time was explained using the 'free volume' concept. The free volume is defined as a vacant space not occupied by the microstructure of the polymer molecule [34] and the reduction of the water permeability during aging is caused by the decrease in free volume with the relaxation proceeding. It can be considered that this prospect may be applicable the reduction of water absorption ability of Katsuobushi observed in this study.

It became clear that water absorption ability that is one of important physical characteristic of food material could be changed even it is stored below the glass transition temperature and this change is affected by storage temperature and storage time. Similar tendency may be observed for other glassy food materials. Additionally, it is expected that other physical properties such as several transport properties and density and mechanical strength may be changed during aging. In the field of food science, the glass transition temperature is considered as very important factor to control the storage stability. Because the several deterioration reactions accompanied by the diffusion of molecular are significantly reduced when it is in the glassy state. However, our experimental results suggested several physical properties would be changed during storage even it is in the glassy state. Even for short-term storage, the change of physical property was so obvious. This result suggests that the effect of the relaxation process on the physical properties is not negligible considering the practical storage term. Therefore, it can be concluded that not only glass transition concept but also enthalpy relaxation phenomenon must be paid attention strongly to control the stability of dried food materials during long-term storage.

In recent years, the information about the molecular mobility of glassy material below the T_g has been attracted attention in the field of food science because it affects several physical properties of glassy materials for long time storage. However, there are few researches about the enthalpy relaxation behavior for food materials. In this study, we could obtained the information about the enthalpy relaxation for natural food system like dried fish glass using DSC and this results indicated that the experimental method using DSC was so effective and easy to examine the enthalpy relaxation process of food materials. Furthermore, it should be noted that the KWW equation could be applicable to natural food system in spite of its complicate component composition and obtained fitting parameters could provide the useful information about the stability of its glassy state. Therefore, we could conclude that the study about the enthalpy relaxation was so effective for deep understanding of its glassy state. The sample used in this study was not so commonly used and specialized food material. However, our experimental methods and results can be beneficial for many dried protein-rich products. It is expected that similar research about the enthalpy relaxation behavior below the Tg for food materials will be increased in the future.

4. Conclusion

The enthalpy relaxation behavior of Katsuobushi was studied using differential scanning calorimetry. From the DSC results, it became clear that Katsuobushi showed clear enthalpy relaxation by aging and its magnitude of relaxed enthalpy (ΔH) was dependent on aging temperature and aging time. This tendency was general characteristic of many glassy materials. This enthalpy relaxation behavior of Katsuobushi could be successfully described by the KWW equation and this result suggested that the long-term relaxation process could be predicted using the short-term experimental data. The two fitting parameters τ and β, which is the mean relaxation time constant and relaxation time distribution parameter, were obtained.

The β values are 0.25–0.35 for several aging temperatures and these were relatively smaller than reported values for other glassy polymers. The τ values at several aging temperatures were 1.05E + 04, 4.65E + 02, 0.44E + 02 (h), respectively. These τ values were considerably smaller than reported values of sucrose and starch obtained by the same method. This result suggested that the glassy state of Katsuobushi was easy to relax compared to sucrose and starch. The water absorption ability of Katsuobushi was affected by aging below T_g and this result suggested that some physical properties could be changed even when it is kept in the glassy state.

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◇◇◇ 和文要約 ◇◇◇

カツオ節のエンタルピー緩和現象と物理的エージングがその水分吸着能に及ぼす影響

橋本朋子，萩原知明†，鈴木　徹，高井陸雄

東京海洋大学海洋食品科学科

エンタルピー緩和現象は，アモルファス物質における重要な基本的特性の一つである．高分子化学の分野においては，緩和の進行と巨視的な力学的特性が関連していることから，その現象がアモルファス物質の安定性に深く関与している重要な因子であることが認識されている．一方，食品科学の分野においても，糖やデンプンなどのエンタルピー緩和に関する研究が進められており，近年その重要性が認識されつつある．しかしながら，食品のエンタルピー緩和に関する研究例は未だ少なく，とくに実際の食品系に対しての検討例は今のところ存在しない．既往の研究において，我々はガラス状食品であるカツオ節が，DSC曲線においてエンタルピー緩和に起因すると思われる吸熱ピークを示すことを明らかにした．そこで本実験では，カツオ節のエンタルピー緩和挙動に関するより詳細な情報を得るため，保存条件（温度・時間）の違いが及ぼす影響についての検討を行った．同時に，既往の理論式を用いて緩和過程の解析を試みた．さらに，緩和の進行が巨視的物性に及ぼす影響を調べるため，本実験では水分吸着特性に着目し，保存条件がカツオ節の水分吸着能に及ぼす効果についての検討を行った．

試料にはにんべん製のカツオ本枯れ節を用いた．あらかじめ昇温速度5 K/minで150℃まで加熱して試料の熱履歴を消去した後，冷却速度5 K/minで−50 ℃まで冷却し，再度5 K/minで所定の保存温度（25，42，60℃）まで昇温して，そのままDSC内で一定時間（0−120h）放置することによりエージング処理を行った．エージング終了後，再度冷却・昇温測定を行い，最終的に得られたDSC曲線における吸熱ピークの大きさ，すなわちエンタルピー緩和量（ΔH）を算出した．また，異なる保存時間・保存温度で処理したカツオ節を，各種飽和塩を用いて湿度調整したデシケータ内に放置して水分吸着させ，最終的な平衡水分含量から水分吸着能について調べた．

エージング処理を施したすべての試料において，DSC曲線上にエンタルピー緩和に起因する吸熱ピークが観察された（Fig. 3）．算出された緩和量ΔHの値は明らかなエージング時間依存性を示し，その挙動は他のアモルファス物質と一致していた（Fig. 4）．さらなる詳細な情報を得るため，アモルファス物質の緩和過程を記述するのにしばしば用いられるKWW式により，カツオ節エンタルピー緩和過程の解析を行った．KWW式は以下のように記述される．

$$\Phi(t) = \exp[-(t/\tau)^{\beta}]$$

ここで$\Phi(t)$は緩和関数，τは緩和時間，βは緩和時間分布・非指数関数パラメーターである．τの値が大きいほど，ガラス状態下における安定性が高いことを意味している．式(3)および式(4)を組み合わせることにより，実験値のKWW式へのフィッティングを行った（Fig. 5）．本実験により，カツオ節のエンタルピー緩和過程がKWW式により良好に記述可能であることが明らかとなり，短時間保存のデータを用いて，長期間保存した場合の緩和過程を予測することが可能となった．フィッティングによって得られた緩和時間τの値を換算温度に対してプロットし，同手法で得られたデンプンおよびスクロースの値との比較を行った結果，カツオ節のτの値は両物質と比べると明らかに低く，カツオ節のガラス状態が比較的緩和しやすいものであることが示された（Fig. 6）．このような低い安定性が食品系において一般的なものであるのか，またはカツオ節に特有のものであるのかは現段階では明らかでない．食品のガラス状態の安定性に関与する因子を明らかにするためには，今後より多くの食品に対するエンタルピー緩和研究を進めていく必要がある．

また，カツオ節の水分吸着能は保存時間および保存温度に依存し，緩和の進行と共に水分吸着能が低下した（Fig. 8, 9）．同様の結果はデンプンにおいてすでに報告されており，吸着能の低下と緩和に伴う自由体積減少の関連性が指摘されている．カツオ節においても，同様の機構で吸着量低下が生じたものと思われる．すなわち，緩和の進行に伴う自由体積の減少が水分吸着のための空間を減少させ，結果として水分吸着量の減少が生じたものと推察される．最大3週間という保存期間でも，緩和の影響は明らかであった．したがって，実際の食品の保存期間を考慮すれば，緩和がその食品の物性に及ぼす影響というのは決して無視できないものであると考えられる．

〒108-8477　東京都港区港南4-5-7

† Fax: 03-5463-0585, E-mail: tomoaki@tokyo-u-fish.ac.jp

以上，カツオ節がエージング処理によってエンタルピー緩和現象を示すことが明らかとなり，その挙動が他のアモルファス物質と一致していることが示された．また，KWW式を用いた解析により，カツオ節のガラス状態が比較的緩和しやすい状態にあることが示された．さらに，緩和の進行が水分吸着能という低水分食品にとって非常に重要なパラメーターに影響を及ぼすことが明らかとなった．緩和現象は水分吸着能だけでなく，その他の様々な巨視的物性に影響を及ぼすことが予想される．以上の結果から，食品の品質安定性を議論していくうえで，今後はガラス転移現象だけではなく，ガラス状態下における緩和現象にも着目していく必要性が示された．今回はカツオ節という比較的特殊な食品を試料として用いたが，同様の傾向はその他の様々なガラス状物質において観察されるものと予想される．本実験で用いた実験方法および実験結果が，今後の食品のエンタルピー緩和研究において有用な情報となることが期待される．