Drying and Rehydration Kinetics of Pasta

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GENERAL INTRODUCTION

An industrial food-making process is often designed and operated based on a great deal of experience. The phenomena occurring during the process have not been fully understood. Drying is one of the most common processes for improving the shelf life of food and is applied to the manufacturing of various foodstuffs. The primary objective of food drying is to ensure longer quality preservation by decreasing the moisture content of the food to a level that minimizes microbial spoilage. Dried foods are usually sorbed or rehydrated prior to their use or consumption to improve the taste and digestibility, i.e., the water molecules in food are removed and added during the drying and rehydration processes, respectively. The quality of dried and rehydrated foods is largely affected by the water migration behavior during the processes. Therefore, better understanding of the water migration kinetics would help to efficiently manufacture dry food of good quality and cook it to a good texture, taste, and digestibility. However, the key mechanism controlling the water migration inside food remains unclear.

Pasta consists of the major components of food, such as starch and protein, and is a porous material; therefore, the knowledge obtained from pasta can be applied to the design of other food-making processes. Moreover, pasta has the advantage of being easy to measure and analyze its properties because it can be regarded as a macroscopically homogeneous material.

I-1. Pasta

The word “pasta” is Italian for “dough” and is generally used to describe products fitting the “Italian” style of extruded foods such as spaghetti or lasagna. Pasta is a healthy food that is relatively low in fat, high in carbohydrates, and has a good composition of protein. The main ingredients for making pasta are principally durum wheat semolina and water. Durum wheat (Triticum durum) is the hardest wheat and durum milling produces a coarse particle called semolina, which is the ideal for making pasta because of its hardness, intense yellow color, and nutty taste [1].
I-2. Pasta processing

A proportion of 18-25% of water is added to dry raw durum semolina at 35-40°C and the mixture is kneaded for 10-20 min to produce fresh dough of an average moisture content of 30-32% [1]. Then, the stiff durum semolina dough is extruded through a die using a vacuum extruder to produce pasta [1, 2]. Die made of bronze has traditionally been used. However, die made of Teflon has recently been used due to the following reasons [3-5]: elongation of the lifetime of the die by reducing wear, a smoother surface of pasta, and improvement of general appearance of dried pasta.

Pastas prepared using the dies made of Teflon and bronze have smooth and rough surfaces, respectively. It has been reported that pasta prepared using the bronze die has higher porosity, lower density, lower rupture strength, and larger effective diffusion coefficient of water during drying than that prepared using the Teflon die [6, 7].

I-3. Drying of pasta

In many countries, including Japan, pasta is usually distributed in the dry state in order to improve its storage stability and transportation efficiency. The moisture content of fresh pasta is reduced to ca. 11% on a wet basis, which is suitable for preservation, by drying it.

I-3.1. Moisture sorption isotherm

A moisture sorption isotherm has been used to describe the relationship between moisture content and equilibrium relative humidity, and knowledge on it is useful for understanding the phenomena occurring during the drying or rehydration process of food [8]. The equilibrium moisture content allows us to optimize drying times and energy utilization. Moreover, the knowledge can be useful to evaluate the storage stability of food products. The microbial growth, enzymatic reactions, non-enzymatic browning, and lipid oxidation are some of the deteriorative mechanisms that are known to be related to the moisture content [9, 10]. In this context, the moisture sorption isotherms of many food products, for example, starchy foods (e.g., corn, potato, wheat flour, and rice), high protein foods (e.g., chicken, egg, milk, and cheese), fruits (e.g., banana, apple, apricot, and raisin), and vegetables (e.g., green
pepper, lentil, tomato, onion, sugar beet root, carrot, and celery) have been experimentally
determined as reviewed by Al-Huhtaseb et al. [11].

A number of models have been proposed in the literatures for the dependence of the
equilibrium moisture content on the relative humidity. In 1981, van den Berg and Bruin
classified the models into 77 types. These models can be further categorized into several
groups: kinetic models based on the monolayer sorption theory (e.g., Langmuir model),
kinetic models based on the multilayer sorption theory (e.g., BET and GAB models), and
empirical and semi-empirical models (e.g., Peleg and Oswin models) [12].

I-3.2. Drying conditions of pasta

Pasta is dried under various conditions, where both temperature and humidity are
changed with time, and the product is distributed in a dry form. Because the process takes
several days at a drying temperature of 30°C, dried pasta is presently prepared on an industrial
production scale at temperatures above 30°C. The production processes can be classified into
low-temperature (LT), high-temperature (HT), and very-high-temperature (VHT) ones
depending on the maximum temperature during processing. The maximum temperatures of
LT, HT, and VHT processes are ca. 50, 70, and 85°C, respectively, and drying times are ca.
20, 13, and 6 h, respectively. Among the processes, the VHT process is most commonly
adopted by manufacturers because of the short production time, although pasta has
traditionally been dried by the LT process. Recently, an ultrahigh temperature process has
been demonstrated at a drying temperature of 95°C.

I-3.3. Drying characteristic of pasta

A typical drying curve for pasta, which reflects the transient change in moisture content,
is concave, i.e., the moisture content rapidly decreases during the early stage of drying, and
gradually decelerates to become very low at the later stage [13].

The drying characteristic curve, which is the relationship between the moisture content
and the drying rate, is usually divided into three periods; i.e., the pre-heating, constant
drying-rate, and decreasing drying-rate periods. The heat received from the air is consumed
for evaporation of free water on sample surface at a constant temperature during the constant
drying-rate period. The decreasing drying-rate period starts when the supply of free water from the inside to the surface is not able to catch up with its evaporation on the surface.

I-3.4. Quality of dried pasta

The drying conditions include the temperature, humidity, and duration that largely affect the pasta quality, such as texture and appearance. However, the conditions are usually determined based on the significant experience in practical processes. Therefore, the relationship between the drying conditions and pasta properties has been extensively investigated to reasonably determine the optimal conditions which are needed to produce pasta of fine quality with a high efficiency. The drying temperature affects the cooked pasta quality [14], and drying in the temperature range from 60 to 80°C is reported to produce high quality pasta [15-18]. The effect of temperature on the progress of the Maillard reaction, which affects the red-color development of pasta, was also studied [19, 20].

I-4. Rehydration of pasta

Rehydration by cooking is an important process for recovering the properties of dried pasta. Therefore, it is important to fully understand the phenomena occurring during the rehydration of dried pasta. However, the rehydration is a complicated mass transport process and is governed by several imbibition-mechanisms of water in pores [21].

I-4.1. Rehydration characteristic of pasta

Typically, equations to describe the rehydration kinetics can be characterized by two approaches: theoretical and empirical [22]. The theoretical equations are based on the Fick's first and second laws of diffusion, where the difference in the moisture content of pasta is considered to be a driving force for water migration [22-26]. Theoretical equations provide insights into the mechanistic relevance of an observed phenomenon [21]. However, they are not convenient for practical purposes due to their complexity [27, 28]: in addition to water diffusion, starch crystalline domains melting, macromolecular matrix relaxation, and “residual deformation” release also occur during rehydration [29]. On the other hand, the development
of empirical equations requires considerably less effort. Therefore, empirical equations can be useful tools for prediction and optimization of the rehydration kinetics [30]. Empirical or semi-empirical equations of 6 types are often utilized to describe the rehydration kinetics [27]. These include the exponential equation [31], Peleg's model [32], first order kinetics [33], Becker's model [34], Weibull distribution function [35], and normalized Weibull distribution function [36]. In the empirical equations, the rehydration process is treated as a ‘black box’, varying specific input setup parameters, measuring output quantities, and deriving the adequate correlations. Therefore, it is necessary to determine the coefficients of the equation by varying the specific input setup parameters in detail.

I-4.2. Quality of rehydrated pasta

Dried pasta is eaten after rehydration by cooking. Drying conditions affect the properties of cooked pasta. In particular, the maximum temperature during drying plays the most important role on properties of cooked pasta. Petitot et al. [37] reported based on texture measurements that pasta dried under high-temperature conditions had better quality after cooking than that dried under low-temperature conditions. The dependence of the properties of cooked pasta on drying conditions is due to changes in the inner structure of pasta during drying [38, 39]. The major components of pasta are starch and protein, and the drying conditions affect their states. Guler et al. [14] examined the characteristics of starch gelatinization in pasta dried under high- and very-high-temperature conditions using a rapid viscoanalyzer, a differential scanning calorimeter, an X-ray diffractometer, and a polarization microscope. Baiano et al. [40] measured the leakage of amylose from the pasta dried under low-, high-, and very-high-temperature conditions during their cooking processes and showed that more amylose leaked from the pasta dried at lower temperature. Drying under high-temperature conditions enhanced the denaturation of protein and suppressed the swelling and collapse of starch granules [38].
II. Objectives and outline of the thesis

This study focused on the drying and rehydration kinetics of pasta in part 1 and part 2, respectively.

II-1. Drying kinetics of pasta (part 1)

In chapter 1, the equilibrium moisture content, which is required to reasonably determine the optimal drying conditions of pasta, is predicted. In chapter 2, the partial molar volume of water sorbed to durum wheat flour is analyzed by dilatometric measurement. In chapter 3, the averaged moisture content of pasta during drying is predicted based on the thermogravimetric analysis of durum semolina dough. In chapter 4, the effects of the glass transition of durum semolina dough on the drying rate and the activation energy are extensively studied. In chapter 5, the effects of anisotropic shrinkage behavior and the surface area of pasta on the mechanical strength during drying are studied.

II-2. Rehydration kinetics of pasta (part 2)

In chapter 6, a novel method of estimating the gelatinization temperature of starch-containing foods, without pulverization of a sample from a rehydration curve under temperature-programmed heating conditions, is developed. In chapter 7, the averaged moisture content of pasta during rehydration by cooking at various temperatures is predicted. In chapter 8, the effects of salt in rehydration solution on the rehydration rate and the equilibrium moisture content are studied. In chapter 9, the effects of drying conditions on the rehydration and leakage behaviors of pasta are examined. In chapter 10, the effect of surface roughness on the rehydration kinetics is studied. In chapter 11, a novel method to measure the moisture distribution inside pasta during rehydration using a digital camera is developed by focusing on the color change of pasta. In chapter 12, the effect of gluten network on the rehydration kinetics of pasta surface is studied.
PART 1

Drying kinetics of pasta
CHAPTER 1

Moisture sorption isotherm of durum wheat flour

1.1. Introduction

A moisture sorption isotherm, which represents the relationship between the water activity and the moisture content at a specific temperature, reflects the interaction [41-43]. The temperature dependence of moisture sorption behavior provides information on the thermodynamic properties. The Clausius-Clapeyron equation is applicable to the determination of the isosteric heat from the moisture sorption isotherms. Knowledge of the differential heat of sorption is useful for designing equipment to be utilized in drying processes [44, 45].

Drying is a combined heat and mass transfer process, in which the product temperature rises from room temperature to the drying air temperature. Although the drying air temperature is 30-40°C in a traditional process for drying pasta, the maximum drying temperature in industrial production of dry pasta is 80-90°C in order to shorten the drying time. Therefore, the moisture sorption isotherm of durum semolina over a wide range of temperature is necessary in order to design the industrial pasta drying process.

The objectives of this study are to experimentally obtain the moisture sorption isotherms of durum semolina in the temperature range of 30-80°C and the relative humidity range of 11-97% by the static gravimetric method using saturated salt solutions and to calculate the heat of water sorption on the durum semolina. The isotherms of starch and gluten were also measured in order to examine their contribution to the isotherm of durum semolina or pasta.

1.2. Materials and Methods

1.2.1. Materials

Durum wheat flour was supplied by Nisshin Foods, Inc., Tokyo, Japan. The supplier
analyzed the flour to contain 14.8% water, 12.8% protein, 2.1% lipid, 69.6% carbohydrate, and 0.73% ash on a weight basis. *Ma·Ma* (Nisshin Foods, Inc.) was purchased from a local supermarket, and its diameter was 1.6 mm (spaghetti).

1.2.2. Extraction of starch and gluten

Wheat starch and gluten were extracted as follows: Durum semolina (800 g) and distilled water (540 g) were kneaded using a mixer (Kitchen-aid KSM5; FMI, Osaka, Japan) for 15 min. The mixture was washed with 1 L of water to recover gluten. The gluten was repeatedly washed with water until the wash liquid became transparent. The wash liquids were combined and then centrifuged at 7,000 rpm for 15 min to obtain starch as a precipitate. The recovered starch and gluten were separately freeze-dried for 2 days with an FDU-1200 freeze-drier (Tokyo Rikakiki, Tokyo, Japan). The dried starch or gluten was pulverized using a mill of rotation edge type (CM60-S; Matsuki Corp., Maebashi, Japan) and then sieved into powders smaller than 0.65 mm.

1.2.3. Moisture sorption isotherm

About 2 g of durum wheat flour, starch, gluten, and pasta was accurately weighed into a glass vial (15 mm I.D. × 50 mm). Pasta was broken about 4-cm long without pulverization. The vial was placed in a container made of polypropylene, the water activity or relative humidity of which was regulated at a specific value using a saturated salt solution, and the container was placed in a temperature-controlled oven (DN440; Yamato Scientific, Tokyo, Japan) at a temperature from 30 to 80°C. The sample was occasionally weighed until the weight reached a constant value. It took a few days to 3 weeks depending on the temperature and relative humidity until sorption equilibrium was achieved. When the weight change of the sample was less than 1 mg/day, the equilibrium was regarded as being established. The amount of sorbed water, \( m \), was calculated by the following equation:

\[
m = \frac{w_e - w_d}{w_d}
\]  

where \( w_e \) is the sample weight at equilibrium, and \( w_d \) is the weight of the dry sample, which was dehydrated at 105°C for 4 days. The \( m \) value was measured at various water activities.
using saturated salt solutions: LiCl (0.113), CH₃COOK (0.216), MgCl₂ (0.324), K₂CO₃ (0.432), Mg(NO₃)₂ (0.514), NaBr (0.560), NaNO₃ (0.73), NaCl (0.751), and KCl (0.836). The values in the parentheses are water activities at 30°C. Because the water activity depends on temperature [46], the values at different temperatures are different from those in the parentheses. When the water activity at a specific temperature was not available from the literature, it was measured using a Hygrolog hygrothermograph (Rotronic, Bassersdorf, Switzerland).

The sample for sorption experiments was dehydrated to a moisture content of 3 g-H₂O/100 g-d.m. or lower using a vacuum pump. For measurement of the desorption isotherm of water, the sample had been dampened to a moisture content of 30 g-H₂O/100 g-d.m. or higher.

The amount of water sorbed onto or desorbed from the wheat flour, starch, gluten, or pasta was measured in triplicate and averaged. The sorption and desorption isotherms onto durum semolina were measured from 30 to 80°C at 10°C intervals. The sorption isotherms onto starch and gluten were measured at 30°C, and the sorption isotherm onto pasta was measured at 60°C.

1.3. Results and Discussion

1.3.1. Sorption and desorption isotherms onto durum wheat flour

Figure 1-1 shows the moisture sorption and desorption isotherms for durum semolina at various temperatures. Isotherms that were sigmoidal at any temperature and were categorized as type II according to Brunauer et al. [42]. These results were similar to those reported by other researchers [8, 43, 47]. The amount of sorbed water was smaller at higher temperature, indicating that the sorption of water onto the flour was exothermic. A slight hysteresis was observed between sorption and desorption at low temperatures.

Both the sorption and desorption isotherms could be separately expressed by the Guggenheim-Anderson-de Boer equation (abbreviated GAB equation):

$$ m = \frac{abca_w}{(1 - ca_w)(1 - ca_w + bca_w)} $$

(1-2)
where $a_w$ is the water activity and $a$, $b$, and $c$ are constants. The constant $a$ corresponds to the amount of water for monolayer coverage, $b$ is a measure of the interaction between adsorbate (water) and solid material (flour), and $c$ is a correction coefficient. The constants, $a$, $b$, and $c$, were determined to best-fit the observed $m$ values to the calculated ones using the Solver of Microsoft Excel®.
Figure 1-2 shows the temperature dependencies of the constants, $a$, $b$, and $c$, for both the sorption and desorption processes. The $a$ and $b$ values became smaller at higher temperature, while $c$ scarcely depended on the temperature. Because the temperature dependencies of the parameters were obtained, the equilibrium moisture content of durum semolina can be evaluated under any conditions of temperature and relative humidity.

![Figure 1-2](image-url)

**Fig. 1-2.** Temperature dependencies of the constants, $a$ (○, ●), $b$ (△, ▲), and $c$ (□, ■), of GAB equation for sorption (open symbols) and desorption (closed symbols) processes.

### 1.3.2. Isosteric heat for sorption or desorption

Isosteric heat, $q$, is an indication of the interaction force between a water molecule and a sorption site on the durum semolina. The $q$ value at a specific amount of sorbed water, $m$, can be estimated based on the following Clausius-Clapeyron equation [48]:

$$q = -R \left[ \frac{d \ln a_w}{d(1/T)} \right]_m$$  \hspace{1cm} (1-3)

where $a_w$ is the water activity or relative humidity at the amount of sorbed water $m$, $R$ is the gas constant, and $T$ is the absolute temperature. Figure 1-3 shows the plots for estimation of the $q$ values at some $m$ values from both the sorption and desorption isotherms. The plots were linear in all cases, indicating that Eq. (1-3) is applicable to estimating the $q$ value.
Fig. 1-3. Estimation of isosteric heats $q$ for sorption (open symbols) and desorption (closed symbols) at moisture contents of 5 (○, ●), 10 (□, ■), 15 (△, ▲), and 20 (◇) g-H$_2$O/100 g-d.m. according to the Clausius-Clapeyron equation.

Figure 1-4 shows the dependencies of the $q$ values for the sorption and desorption processes on the moisture contents of durum semolina. The larger $q$ values at the lower moisture content indicate that water molecules interact more strongly with durum semolina at lower moisture contents. The plots for the desorption process lie over those for the sorption process. This fact indicates that the desorption of a water molecule sorbed onto the durum semolina consumes more energy than the liberation of energy during water sorption.

Equation (1-4) has also been used for cereals to express the relationship among the amount of sorbed water $m$, temperature $T$, and water activity $a_w$ [49, 50].

$$\frac{\ln a_w}{1/T_\beta - 1/T} = K_1 K_2^m$$

where $T_\beta$, $K_1$, and $K_2$ are parameters. The equation was applied to the amounts of sorbed water shown in Fig. 1-1 for both the sorption and desorption processes. The $T_\beta$, $K_1$, and $K_2$ values for the sorption process were evaluated to best-fit the $m$ values at various temperatures and water activities using the Solver of the Microsoft Excel® and were 448 K, $6.37 \times 10^3$ K, and 0.814, respectively. The $T_\beta$, $K_1$, and $K_2$ values for the desorption processes were also
determined to be 400 K, $9.55 \times 10^3$ K, and 0.821, respectively. The $m$ values calculated by using the estimated $T_β$, $K_1$, and $K_2$ values are plotted against the observed $m$ values in Fig. 1-5. The plots for both sorption and desorption processes lie on the line having a slope of unity, indicating that the equation is applicable to the moisture sorption onto durum semolina. As shown in Fig. 1-4, the isosteric heat for the sorption and desorption processes calculated from Eq. (1-4) coincided with those for the processes calculated from Eq. (1-3). This fact indicated that Eq. (1-4) was also useful to calculate the moisture-content dependences of the isosteric heats as well as Eq. (1-3).

![Fig. 1-4. Dependencies of isosteric heat on moisture contents for sorption (---○---) and desorption (—●—) processes. Symbols and lines were calculated from Eqs. (1-3) and (1-4), respectively.](image)
Fig. 1-5. Applicability of Eq. (1-4) to the moisture contents observed at 30°C (○, ●), 40°C (□, ■), 50°C (▽, ▼), 60°C (◇, ◆), 70°C (▶, ◢), and 80°C (△, ▲) for sorption (open symbols) and desorption (closed symbols) processes.

1.3.3. Sorption isotherms onto starch and gluten

Moisture sorption isotherms on starch and gluten, which were isolated from durum wheat flour, were measured at 30°C (Fig. 1-6). The isotherm onto the original durum semolina is also shown in the figure. All the isotherms were categorized as the sigmoidal type II according to Brunauer et al. [42] and could be expressed by the GAB equation. The $a$, $b$, and $c$ values were 8.76 g-H$_2$O/100 g-d.m., 45.6, and 0.715 for starch and 7.63 g-H$_2$O/100 g-d.m., 37.0, and 0.728 for gluten.

Roman-Gutierrez et al. [51] reported that the equilibrium moisture content could be expressed by summing the products of the fractions of constituent components and their moisture contents for weak flour. The carbohydrate and protein contents of durum semolina are 81.7 and 15.0% (dry basis), respectively. As Roman-Gutierrez et al. [51] reported, the moisture sorption isotherm calculated from the isotherms on starch and gluten and their contents was almost the same as the observed moisture sorption isotherm on durum semolina.
Fig. 1-6. Sorption isotherms of water onto durum wheat flour (—○—), starch (---△---), gluten (-cdot- • -) at 30°C, and calculated value by summing the products of the fractions of constituent components and their moisture contents (···). Curves are calculated to best-fit the observed moisture contents to the GAB equation.

1.3.4. Moisture sorption onto pasta

The moisture sorption isotherm onto pasta was observed at 60°C and compared with that onto durum semolina (Fig. 1-7). Although the isotherm on pasta lay slightly over that on durum semolina, the difference was not significant except at very high water activity. Therefore, processing for pasta making had no significant effect on water sorption.
Fig. 1-7. Sorption isotherms of water onto pasta (—○—) and durum wheat flour (- - -) at 60°C. Curves are calculated to best-fit the observed moisture contents to the GAB equation.

1.4. Conclusions

The isotherms of durum semolina, starch, gluten, and pasta were well expressed by the GAB equation. Isosteric heat, $q$, for the sorption and desorption processes were larger at lower moisture contents, indicating that water molecules more strongly interact with wheat flour at the lower moisture content. Moisture contents increased in the order of gluten < durum semolina < starch.
CHAPTER 2

Dilatometric measurement of the partial molar volume of water sorbed to durum wheat flour

2.1. Introduction

Drying conditions, such as the temperature, humidity, and duration, affect the texture and appearance of the pasta. Dried pasta is consumed after rehydration. Understanding the behavior of the water during the drying and rehydration processes is necessary to efficiently manufacture dry pasta of good quality and to cook it to a good texture.

Many factors affecting the drying kinetics of pasta [13] as well as the factors affecting the rehydration kinetics of pasta [52-54] have been reported. The interaction of water molecules with the durum wheat flour plays an important role in the drying and rehydration processes. A moisture sorption isotherm, which represents the relationship between the water activity and the moisture content at a specific temperature, reflects the interaction [41-43]. The isotherm of durum wheat flour has been measured under various conditions in chapter 1 and could be expressed by the Guggenheim-Anderson-de Boer (GAB) equation [55]. The partial molar volume of water would provide useful information on the interaction, and dilatometry is a method for measuring the partial molar volume [56].

Pasta made from pre-gelatinized durum wheat flour has been prepared in order to shorten the cooking time [57]. Gelatinization made the flour more water-accessible [58], while dry-heating increased the hydrophobicity of the flour [59]. In other words, moist- or dry-heating of the flour changes its properties.

In this context, the partial molar volumes of water molecules sorbed to untreated, dry-heated, and pre-gelatinized durum wheat flour samples were measured at 25°C with various moisture contents by using dilatometry as well as the moisture sorption isotherms of the flour samples in order to better understand the interaction of water with the durum wheat flour.
2.2. Materials and Methods

2.2.1. Materials

The durum wheat flour was supplied by Nisshin Foods (Tokyo, Japan). The flour was loaded into a VL-C dessicator (As One, Osaka, Japan) connected to a GLD-051 vacuum pump (Ulvac, Kanagawa, Japan), and its moisture content was reduced to less than 0.03 kg-H₂O/kg-d.m., where d.m. indicates the dry matter, at 25°C and 510 Pa. The resulting flour was labeled untreated flour. This flour (6 g) was heated at 200°C for 8 h in a DN400 oven (Yamato Scientific Co., Tokyo, Japan) to prepare the dry-heated flour [60, 61]. The untreated flour was suspended in distilled water to produce a 30% (w/w) suspension. This suspension was poured on to a KZ-HP-1000-K hot-plate (Panasonic, Osaka, Japan), which had been heated at 160°C, and pressed with a heat block, which had also been preheated at 160°C, for 10 min with occasionally flipping [58]. The flour sheet was ground in a mortar with a muddler. The resulting flour was labeled as pre-gelatinized flour. The moisture contents of the untreated, dry-heated, and pre-gelatinized flour samples were measured with an MS-70 moisture analyzer (A & D Company, Tokyo, Japan) with a reproducibility of 0.01%.

2.2.2. Differential scanning calorimetry

A ground sample (ca. 2.0 mg), which had been precisely measured with a BM-20 electric balance (A & D Company, Tokyo, Japan), and 2.5 times its weight of water were loaded into an aluminum cell, and the cell was tightly sealed. The cell was kept at 4°C for 3 h or longer, and differential scanning calorimetric measurement was then conducted with a DSC-7020 calorimeter (Hitachi High-Tech Science Corp., Tokyo, Japan) from 5°C to 130°C at the rate of 5 °C/min. The measurement was taken twice for each sample. Alumina of the same weight as the sample was used as a reference.

2.2.3. Specific surface area and pore size distribution

The specific surface area and pore-size distribution of each ground sample were analyzed by Shimadzu Techno-Research (Kyoto, Japan) based on the adsorption of nitrogen gas to the sample by using an ASAP2010 micrometrics instrument (Shimadzu, Kyoto, Japan).
2.2.4. Moisture sorption isotherm

Each sample was dehydrated at 25°C under reduced pressure ($5.1 \times 10^2$ Pa or lower) until the moisture content became 0.03 kg-H$_2$O/kg-d.m. or lower. The moisture sorption isotherm of a sample was measured by a method similar to chapter 1. About 2 g of the sample was accurately weighed into a glass vial (15 mm I.D. $\times$ 50 mm H). The vial was placed in a PC-150K desiccator made of polypropylene (Sanplatec Corp., Osaka, Japan), the water activity being regulated to 0.11 (LiCl), 0.23 (CH$_3$COOK), 0.33 (MgCl$_2$), 0.43 (K$_2$CO$_3$), 0.53 (Mg(NO$_3$)$_2$), 0.58 (NaBr), 0.74 (NaNO$_3$), 0.75 (NaCl), or 0.84 (KCl) by using a saturated salt solution. The salts used are indicated in parentheses. The pressure in the desiccator was reduced to 2.3 kPa, and then the desiccator was placed in a DN440 oven (Yamato Scientific, Tokyo, Japan), the temperature being regulated to 25°C. The sample was weighed every a few days until its weight change became 0.05% or less. The amount of sorbed water, $M$, was calculated by Eq. (2-1):

$$M = \frac{w_e - w_d}{w_d}$$

where $w_e$ is the sample weight at equilibrium and $w_d$ is the dry weight of the sample. The moisture isotherm is expressed by the following GAB equation (Eq. (2-2)) using the Solver function of Microsoft Excel® in order to best-fit the experimental values:

$$M = \frac{abca_w}{(1 - ca_w)(1 - ca_w + bca_w)}$$

where $a_w$ is the water activity, and $a$, $b$, and $c$ are constants.

2.2.5. Partial molar volume of water

The partial molar volume of water sorbed to the sample was measured by dilatometry according to the method [56]. About 2 g of a sample, whose weight had been precisely measured, was loaded into a glass bulb (90 cm$^3$ internal volume) with a capillary, the internal diameter of which had been precisely determined to be 3.24 mm from the relationship between the amount of added water and its height, and then dodecane, which had been dried by adding molecular sieves, was added to the bulb. The sample was dispersed in the dodecane by gently stirring with a magnetic bar. The bulb was immersed in an SMT-102 water bath.
with a stirrer (As One, Osaka, Japan), a TR-2A heater (As One), and a TRL107NHF cooler (Tomas Kagaku Kiki, Tokyo, Japan). A preservative, Aqua bath (Funakoshi, Osaka, Japan), was added to the water in the bath, and the surface of the bath was covered with balls made from polypropylene in order to respectively prevent any microbial growth and evaporation. The temperature of the water in the bath was regulated at 25.0 ± 0.01°C. Water (ca. 50 mg each) was injected into the bulb up to ca. 800 mg. The molar amount of added water, Δn, was precisely evaluated by weighing before and after the injection. The height of the meniscus was read with a MON-A-300 casetometer (Nihon Koki Seisakusho, Tokyo, Japan). The partial molar volume of water, \( \bar{V} \), was calculated from the volume change, \( \Delta V \), and the \( \Delta n \) value by Eq. (2-3):

\[
\bar{V} = \frac{\Delta V}{\Delta n}
\]

2.3. Results and Discussion

2.3.1. Characteristics of the samples

Figure 2-1 shows the DSC curves for the untreated, dry-heated, and pre-gelatinized flour samples. The untreated flour exhibited an endothermic peak near 60°C which is ascribable to starch gelatinization. The pre-gelatinized flour had no peak near 60°C and it was confirmed that the flour had been gelatinized.

Table 2-1 lists the specific surface areas and mean pore sizes of the untreated, dry-heated, and pre-gelatinized flour samples. The mean pore sizes of the dry-heated and pre-gelatinized samples were slightly larger than that of the untreated sample, while there was no significant difference in the specific surface area among the flour samples.

2.3.2. Moisture sorption isotherm

Figure 2-2 presents the moisture sorption isotherms at 25°C for the untreated, dry-heated, and pre-gelatinized flour samples. Each of the observed isotherms was best-fitted to the GAB equation (Eq. (2-2)), using the Solver function of Microsoft Excel® to estimate
**Fig. 2-1.** Differential scanning colorimetric curves for the untreated (—), dry-heated (----), and pre-gelatinized (····) durum wheat flour samples.

**Fig. 2-2.** Water sorption isotherms at 25°C for the untreated (—○—), dry-heated (---□---), and pre-gelatinized (···△···) durum wheat flour samples.
Table 2-1. Specific surface areas and mean pore sizes of the untreated, dry-heated, and pre-gelatinized durum wheat flours.

<table>
<thead>
<tr>
<th>Durum wheat flour</th>
<th>Specific surface area [m²/g]</th>
<th>Mean pore size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.09</td>
<td>7.9</td>
</tr>
<tr>
<td>Dry-heated</td>
<td>0.10</td>
<td>8.4</td>
</tr>
<tr>
<td>Pre-gelatinized</td>
<td>0.10</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 2-2. Parameters of the Guggenheim-Anderson-de Boer (GAB) equation for the untreated, dry-heated, and pre-gelatinized durum wheat flours.

<table>
<thead>
<tr>
<th>Durum wheat flour</th>
<th>(a) [kg-H₂O/kg-d.m.]</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>9.19 (\times) 10⁻²</td>
<td>15.3</td>
<td>0.67</td>
</tr>
<tr>
<td>Dry-heated</td>
<td>6.89 (\times) 10⁻²</td>
<td>5.48</td>
<td>0.80</td>
</tr>
<tr>
<td>Pre-gelatinized</td>
<td>5.99 (\times) 10⁻²</td>
<td>15.1</td>
<td>0.86</td>
</tr>
</tbody>
</table>

parameters \(a\), \(b\), and \(c\). The estimated parameters are summarized in Table 2-2. The curves in the figure were calculated by using the estimated parameters. All the isotherms could be categorized as sigmoidal type II based on the classification by Brunauer et al. [42]. At low water activities, the moisture content of the untreated flour was the highest among the samples, with the pre-gelatinized and dry-heated samples following. Starch in the untreated flour sample was in the mixed state of crystalline and amorphous [57], and pre-gelatinization converted all the starch to the glass state [62]. Although dry-heating and pre-gelatinization of the flour would decrease the crystalline region and increase the amorphous one, the free volume in which the water molecules were sorbed was decreased due to structural relaxation of the glassy starch by the heat treatment [63, 64]. This would be the reason for the decrease in moisture content of the dry-heated and pre-gelatinized flour samples.

2.3.3. Partial molar volume of water

The partial molar volumes of water sorbed to the untreated, dry-heated, and pre-gelatinized flour samples are plotted versus the moisture content of the flour, or mass
ratio of water to flour, in Fig. 2-3. The $V$ value of the untreated flour sample was 9 cm$^3$/mol at a moisture content of 0.03 kg-H$_2$O/kg-d.m., and increased with increasing moisture content, reaching a constant value of 17-18 cm$^3$/mol at a moisture content of ca. 0.2 kg-H$_2$O/kg-d.m. or higher. The $V$ value was smaller at moisture contents lower than about 0.2 kg-H$_2$O/kg-d.m. It took a longer time to reach equilibrium at the lower moisture contents, e.g., 15, 7, and 2 d at respective moisture contents of 0.05, 0.15, and 0.30 kg-H$_2$O/kg-d.m. The $V$ values of the dry-heated and pre-gelatinized flour samples also exhibited similar dependence on the moisture content, indicating that dry-heating and pre-gelatinization had no significant influence on the interaction with water. These facts suggest that the water molecules more strongly interacted with the flour at the lower moisture contents. The slower drying rate at the lower moisture content [13] would have been caused by this interaction.

![Figure 2-3](image.png)

**Fig. 2-3.** Partial molar volume at 25°C of water sorbed to the untreated (○), dry-heated (□), and pre-gelatinized (△) durum wheat flour samples for various moisture contents.
The moisture sorption isotherm and the partial molar volume for the untreated flour are illustrated together in Fig. 2-4 in order to estimate the volumetric behavior of the water molecules sorbed to the flour. The water molecules would have been sorbed as a monolayer at a moisture content less than \textit{ca}. 0.1 kg-H$_2$O/kg-d.m., and such water molecules had a very low $\bar{V}$ value due to the strong interaction with or incorporation into the flour. As the water molecules became more layered, the $\bar{V}$ value became higher and reached a constant value in the multilayer region at moisture contents higher than 0.2 kg-H$_2$O/kg-d.m. The moisture content was the same as that when glass transition of the durum semolina occurred at 25°C [65]. The sorbed water molecules in the multilayer region behaved like the molecules in bulk water due to very weak interaction with the flour.
2.4. Conclusions

Moisture sorption isotherms were measured at 25°C for untreated, dry-heated, and pre-gelatinized durum wheat flour samples. The isotherms could be expressed by the Guggenheim-Anderson- de Boer equation. The amount of water sorbed to the untreated flour was highest for low water activity, with water sorbed to the pre-gelatinized and dry-heated flour samples following. The dry-heated and pre-gelatinized flour samples exhibited the same dependence of the moisture content on the partial molar volume of water at 25°C as the untreated flour. The partial molar volume of water was ca. 9 cm³/mol at a moisture content of 0.03 kg-H₂O/kg-d.m. The volume increased with increasing moisture content, and reached a constant value of ca. 17.5 cm³/mol at a moisture content of 0.2 kg-H₂O/kg-d.m. or higher.
CHAPTER 3

Prediction of pasta drying process based on a thermogravimetric analysis

3.1. Introduction

The pre-heating and constant drying-rate periods have been ignored and the decreasing drying-rate period is assumed from the beginning of drying in previous studies because the pre-heating and constant drying-rate periods are usually very short compared to the whole drying period during the production of dried pasta. Many theoretical and empirical models have been reported for describing the water transfer and its kinetics during the decreasing drying-rate period without considering the pre-heating and constant drying-rate periods. Most of them are based on Fick’s law of diffusion [66-69]. Fourteen types of empirical or semi-empirical equations are utilized to describe the drying curve [70]. These include the Newton [71], Page [72], modified Page of two types [73, 74], Henderson and Pabis [33], logarithmic [75], two term [76], two-term exponential [77], Wang and Singh [78], Thompson et al. [79], diffusion approximation [80], Verma et al. [81], modified Henderson and Pabis [82], and Midilli and Kucuk [83]. These models generally showed good agreement of the predicted results to the experimental ones in spite of the assumption of a decreasing drying-rate period from the beginning of drying. For drying Udon (Japanese noodle), it was reported that the initial drying-rate is crucial to prevent crack formation which results in a remarkable lowering of the Udon quality [84]. This fact indicates the importance of the precise prediction of the drying behavior during its early stage in which the large amount of water evaporates from the sample’s surface. However, no study has been conducted to determine the effect of the drying rate during the constant drying-rate period on the drying kinetics of pasta.

The drying rate during the constant drying-rate period and mass transfer coefficient are necessary to predict the change in the moisture content during drying. They have usually been determined by a laboratory scale experimental apparatus. Thermogravimetry is commonly
used for the analyses of thermal reaction processes including the heat decomposition gas–solid reaction, and quantitative determination of crystallization water because it allows accurately measuring a change in weight using a very small sample amount (tens of milligrams). In this context, the drying rate during the constant drying-rate period and mass transfer coefficient during drying pasta under various conditions were estimated by the thermogravimetry using a small amount of the durum semolina dough.

The objectives of this study were: (1) to estimate the drying rate during the constant drying-rate period and mass transfer coefficient during drying of pasta using thermogravimetry, and (2) to examine the applicability of the estimated parameters for predicting the drying behavior of pasta under any conditions.

3.2. Materials and Methods

3.2.1. Thermogravimetry

Durum wheat semolina supplied by Nisshin Foods, Inc., (Japan) was mixed with water to produce the moisture content of 32% (on wet basis) using an SKH-A mixer (Tiger, Japan). The hydrated semolina was packed into a single-sided open cell using a glass syringe equipped with a vacuum pump (Fig. 3-1). The sample mass was 20, 30, or 40 mg. The weight loss during drying was measured using a TGA-50 thermometer (TGA; Shimadzu, Japan) in the temperature range of 30-90°C. The relative humidity in the TGA chamber was controlled at a specific value (0-80%RH) using a saturated salt solution. Dry nitrogen gas was fed at a low flow rate into the balance in order to guard it from humid air. Each run was repeated at least twice to check the reproducibility of the drying curves. The data were analyzed using Origin 8.1J software (OriginLab, Northampton, MA, USA).

3.2.2. Pasta processing

Durum wheat semolina dough having the moisture content of 32% on a wet basis was prepared using a KitchenAid KSM150 mixer (FMI, USA). The dough was put into a pasta extruder (Magica, Bottene, Italy) equipped with a Teflon die (No. 5 or 21). During extrusion, the pressure in the extruder was maintained at about 60 kPa by evacuating the air to prevent
air bubble formation inside the pasta. The fresh pasta was hung on metallic rods and the rods were then placed on racks inside a temperature-humidity controllable chamber (SH-641, Espec, Japan). The pasta weight in the chamber was recorded every minute using an electronic balance (FX-300i, A&D, Japan) connected to a data acquisition system installed in the instrument.

3.3. Results and Discussion

3.3.1. Drying characteristics and modeling

Figure 3-2 shows an example of the drying characteristic curves obtained by thermogravimetry. The pre-heating period did not appear but the constant drying-rate period distinguished from the decreasing drying-rate one was recognized. That is, the drying rate was constant at the high moisture content, which responds to the early stage of drying, and the drying rate then decreased with the subsequent lowering of the moisture content. A similar behavior was observed under all the conditions from 30 to 90°C and from 0 to 80%RH. About 20% of the water had evaporated during the constant drying-rate period, although the period was usually very short compared to the whole drying period. The very fast drying rate is prone to forming cracks, which result in a reduced pasta quality. Inazu et al. [84] indicated from a calculation of the moisture distribution within Udon using the finite element method that the early stage of drying is a crucial step for the crack formation. Therefore, the constant drying-rate period should be taken into account to precisely predict the drying curve for
prevention of crack formation in pasta, and the drying curve was divided into two regions: one is the constant drying-rate period and another is the decreasing drying-rate one.

Figure 3-2. The drying characteristic curve obtained by thermogravimetry at 90°C and 20.6%RH.

Figure 3-3 shows the drying curves of hydrated semolina having three different thicknesses (0.7, 1.0, and 1.4 mm) at 70°C and 0%RH. The drying time axis was divided by the square of the thickness. All the plots lay on a curve during the decreasing drying-rate period. This fact indicated that the water migration in the pasta is mainly governed by water diffusion. Thus, the quotient of time by the square of the thickness, \( t/L^2 \), was replaced by time, \( t \), during the decreasing drying-rate period.

In order to simplify the model, the following assumptions were introduced: (1) the product temperature is a constant due to rapid heat transfer in the pasta; (2) the moisture diffusivity within the pasta is independent of the moisture content; (3) volumetric concentration of the pasta is also independent of the moisture content; and (4) no shrinkage occurs during drying. The drying rates during the constant and decreasing drying-rate periods are given by Eqs. (3-1) and (3-2), respectively.
Fig. 3-3. The relationship between the moisture content and the time divided by square of the thickness for the hydrated semolina having a thickness of the 0.7 mm (○), 1.0 mm (◇), or 1.4 mm (△) at 70°C in 0%RH.

\[ R_w = \frac{W}{A} \left( -\frac{dw_i}{dt} \right) \]  \hspace{1cm} (3-1)

\[ \frac{dw_i}{d(t/L^2)} = -k(w_i - w_e) \]  \hspace{1cm} (3-2)

where \( R_w \) is the drying rate, \( W \) is the dry weight of the sample, \( A \) is the drying area, \( w_i \) is the moisture content at time \( t \), \( L \) is the thickness, \( k \) is the mass transfer coefficient, and \( w_e \) is the equilibrium moisture content. Eqs. (3-3) and (3-4) are the analytical solutions for the one-dimensional rectangular and cylindrical geometries, respectively, under the assumptions that the initial moisture distribution is uniform at the moisture content \( w_0 \) and the surface are kept at the same moisture content \( w_e \) [85].

\[ \frac{w_i - w_e}{w_0 - w_e} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp \left[ -\frac{(2n-1)^2 \pi^2 D_e t}{4L^2} \right] \]  \hspace{1cm} (3-3)

\[ \frac{w_i - w_e}{w_0 - w_e} = 4 \sum_{n=1}^{\infty} \frac{1}{\delta_n^2} \exp \left( -\frac{\delta_n^2 D_e t}{\rho^2} \right) \]  \hspace{1cm} (3-4)

where \( w_0 \) is the initial moisture content, \( D_e \) is the effective diffusion coefficient of water in the
sample, $\sigma_n$ is the $n$th positive root of $J_0(\sigma_n) = 0$, $J_0(x)$ is the Bessel function of the first kind of order zero, and $r$ is the radius. Because the water diffusion controls the drying rate during the decreasing drying-rate period, the mass transfer coefficient for a slab, $k_s$, is related to that for a cylinder, $k_c$, by the following equation based on Eqs. (3-2), (3-3), and (3-4):

$$\frac{4k_s}{\pi^2} = \frac{k_c}{\delta_1} = D_e$$  \hspace{1cm} (3-5)

### 3.3.2. Dependencies of the kinetic constants on temperature and relative humidity

The drying rate during the constant drying-rate period, $R_c$, and the $k_s$ value for the decreasing drying-rate period were determined using Eqs. (3-1) and (3-2) from the drying curves obtained by thermogravimetry operated under various conditions. The estimated $R_c$ was expressed as a binominal function of the temperature, $T$, and the relative humidity, $H$, by Eq. (3-6).

$$R_c = (6.57 \times 10^{-1} + 2.69 \times 10^{-1} T - 9.48 \times 10^{-2} H - 1.10 \times 10^{-3} T^2$$

$$+ 3.26 \times 10^{-4} H^2 + 7.76 \times 10^{-4} TH) \times 10^{-5}$$  \hspace{1cm} (3-6)

The $k_s$ value, which is derived from the effective diffusion coefficient of water in the sample, $D_e$, was also expressed as a function of $T$ and $H$, because the $D_e$ depends on both the $T$ and $H$ [86, 87].

$$k_s = (-4.27 \times 10^{-1} + 6.45 \times 10^{-2} T - 1.32 \times 10^{-2} H - 2.73 \times 10^{-4} T^2$$

$$+ 4.05 \times 10^{-5} H^2 + 1.02 \times 10^{-4} TH) \times 10^{-10}$$  \hspace{1cm} (3-7)

The functions for the $R_c$ and $k_s$ are depicted in Fig. 3-4 and Fig. 3-5, respectively. The correlation coefficients, $R^2$, for the $R_c$ and $k_s$ values were 0.976 and 0.985, respectively. The $R^2$ values indicated good correlations for both the $R_c$ and $k_s$ values obtained between the observed and calculated values as shown in Fig. 3-6.
Fig. 3-4. The drying rate during the constant drying-rate period, $R_c$, as a function of the temperature and relative humidity.

Fig. 3-5. The mass transfer coefficient during the decreasing drying-rate period as a function of temperature and relative humidity.
The $R_c$ value increased with a decrease in the relative humidity at low temperatures (Fig. 3-4). This would be ascribed to the greater difference in the absolute humidity between bulk air phase and layer adjacent to sample surface at the lower humidity. On the other hand, the $R_c$ scarcely depended on the relative humidity at high temperatures. This fact suggested that the film mass transfer of water on the surface might be the rate-controlling step at high temperatures. The dependence of the $k_s$ value on the relative humidity was weak at any temperature because the diffusion of water within the sample is the rate-controlling step during the decreasing drying-rate period.

The water sorption isotherms of durum semolina and pasta over wide ranges of temperature and relative humidity were reported in chapter 1, and the isotherms of durum semolina and pasta under specific conditions overlapped expect at the relative humidity higher than 80% [55]. The Guggenheim-Anderson-de Boer equation (abbreviated GAB equation), which can describe the water sorption isotherm at a specific temperature, is expressed as a function of $H$ by Eq. (3-8). The coefficients of the GAB equation, $a$, $b$, and $c$, were expressed as a function of $T$ by Eqs. (3-9), (3-10), and (3-11) in order to estimate the equilibrium moisture content of pasta, $w_e$, at any $T$ and $H$. 

---

**Fig. 3-6.** Correlations between the observed and calculated values for $R_c$ (○) and $k_s$ (◇).
\[ w_e = \frac{abcH}{(1-cH)(1-cH+bcH)} \]  

(3-8)

\[ a = -1.08 \times 10^{-6}T^3 + 1.99 \times 10^{-3}T^2 - 1.26 \times 10^{-2}T + 3.46 \times 10^{-1} \]  

(3-9)

\[ b = 1.71 \times 10^{-4}T^3 - 2.64 \times 10^{-2}T^2 + 1.04T + 7.06 \]  

(3-10)

\[ c = 7.93 \times 10^{-8}T^3 - 1.51 \times 10^{-5}T^2 + 9.26 \times 10^{-4}T - 1.18 \times 10^{-2} \]  

(3-11)

Equations (3-8), (3-9), (3-10), and (3-11) are applicable to estimate the \( w_e \) value under any conditions in the temperature and relative humidity ranges of 30-90°C and 10-90%RH, respectively, and the \( w_e \) value is depicted as a function of \( T \) and \( H \) in Fig. 3-7.

![Fig. 3-7. The equilibrium moisture content of durum wheat semolina, \( w_e \), as a function of the temperature and relative humidity.](image)

3.3.3. Drying under programmed-drying conditions

For the practical process of manufacturing dry pasta, the temperature and humidity are step-by-step changed with time to produce a high-quality product, and such a drying process is called programmed-drying. In order to demonstrate the reliability of the above-mentioned model and the estimated parameters, the tabular and cylindrical pasta (fettuccine and spaghetti, respectively) were dried under programmed-drying conditions in the oven, and the observed
drying curves were compared to those calculated using the model and the parameters. The drying conditions are shown in Table 3-1. The fettuccine and spaghetti were dried at high- and low-temperatures, respectively. The maximum temperatures were 80 and 60°C in the former and latter cases, respectively.

Table 3-1. Conditions for drying under high-temperature (HT) and low-temperature (LT) conditions.

<table>
<thead>
<tr>
<th>Step</th>
<th>High-temperature (HT)</th>
<th>Low-temperature (LT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time [h]</td>
<td>0.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>50</td>
<td>80</td>
</tr>
<tr>
<td>Humidity [%RH]</td>
<td>60</td>
<td>75</td>
</tr>
</tbody>
</table>

Figure 3-8 and Fig. 3-9 illustrate the drying curves for the fettuccine and spaghetti, respectively. The solid curves indicate the curves calculated based on the proposed model (Eqs. (3-1) and (3-2)) using the estimated parameters, $R_c$, $k_s$, and $w_c$. The broken curves were calculated by assuming that the decreasing drying-rate period starts at the beginning of the drying process, that is, the constant drying-rate period was not considered. The insets of the figures show the drying curves during the early stage of drying. The solid curves well represented the experimental results. Especially, the drying behavior during the early stage could be well expressed by the proposed model. These facts verified the usefulness of the model and the parameters, which were estimated by thermogravimetry on a small scale, for predicting the drying curves of pasta having various geometries under any conditions.
**Fig. 3-8.** Comparison of the experimental drying curve (○) with the calculated ones with (−) and without (−−−) considering the constant drying-rate period. The pasta used was fettuccine (tabular pasta) and it was dried under the HT program conditions illustrated in Table 3-1. Inset: The extended figure for the early stage of drying.

**Fig. 3-9.** Comparison of the experimental drying curve (○) with the calculated ones with (−) and without (−−−) considering the constant drying-rate period. Spaghetti (cylindrical pasta) was dried under the LT program condition illustrated in Table 3-1. Inset: The extended figure for the early stage of drying.
3.4. Conclusions

The drying processes of pasta were measured by thermogravimetry in the temperature and relative humidity range of 30-90°C and 0-80%RH, respectively. The constant drying-rate period was recognized before the constant drying-rate period under all conditions. About 20% of the water evaporated during the constant drying-rate period, although no thought was given for calculating the drying curve. The drying rate during the constant drying-rate period and the mass transfer coefficient during the decreasing drying-rate period were evaluated under the stated conditions, and were formulated as binominal functions of the temperature and relative humidity. The appropriateness of the parameters were demonstrated by comparing the drying curves of the tubular and cylindrical pasta dried in an oven under programmed-drying conditions with the curves calculated using the estimated parameters taking into consideration the constant drying-rate period. A good agreement of the experimental and calculated curves demonstrated the validity of the proposed model and the estimated parameters.
CHAPTER 4

Thermal analysis of drying process of durum wheat dough under the programmed temperature-rising conditions

4.1. Introduction

A typical drying curve for pasta, which reflects the transient change in moisture content, is concave, i.e., the moisture content rapidly decreases during the early stages of drying, and gradually decelerates to become very low at later stages [13]. As a result, a large part of the entire drying period is occupied by drying the low-moisture regime, suggesting that any increase in drying rate in this region will reduce drying time.

During drying, pasta transforms from a rubbery state to a glassy state with a concomitant decrease in moisture content [88]. A similar transition has been reported for drying of strawberries [89], tomatoes [90], apricots [91], wheat [65], and starch [92, 93]. The drying process can usually be described by Fick's law of diffusion [66, 67, 94-97]. Unfortunately, near the glass transition point of durum wheat flour, the law cannot exactly predict drying behavior of pasta because of the occurrence of non-Fickian phenomena [88, 98]. As a consequence, it is difficult to precisely predict the drying behavior in the low moisture-content region where this glass transition occurs. For rational design of the pasta drying process, knowledge of how the drying rate varies over a wide range of temperatures and moisture contents is required.

To evaluate constant drying rates and mass-transfer coefficients in the regime where rates decrease, the drying processes based on a decrease in weight of the dough were analyzed in chapter 3, as measured using a thermogravimeter at constant temperatures and humidities [13]. The change in moisture content of pasta that was dried in a laboratory-scale oven under programmed conditions, i.e., simulating the changes in temperature and humidity in the industrial production of pasta, could be successfully predicted using the constant-drying rates and mass-transfer coefficients obtained. This observation indicated thermogravimetric analysis of dough to be effective for studying the physical phenomena underlying drying of
The objective of this study is to examine the effects of temperature and moisture content on the drying behavior of pasta. The drying rate of durum wheat dough was measured using a thermogravimeter at various temperature-rising rates to estimate the dependence of the activation energy on moisture content. Differential scanning calorimetric measurements (DSC) were also performed under the same conditions as the thermogravimetric ones. Based on these measurements, the effects of the temperature and the moisture content on the drying rate of pasta were discussed.

4.2. Materials and Methods

4.2.1. Sample preparation

Durum wheat semolina with moisture content of 0.163 kg-H2O/kg-d.m. was supplied by Nisshin Foods, Inc. (Tokyo, Japan). The durum wheat semolina (100 g-w.m.) was mixed with water (30 g) using an SKH-A100 mixer (Tiger Corporation, Osaka, Japan) for 5 min, after which the mixture stood at room temperature for at least 3 h to produce the dough.

4.2.2. Thermogravimetry

The hydrated semolina dough (20 mg) was pressed into a single-sided open platinum cell. The weight loss during drying was measured using a TGA-50 thermogravimeter (Shimadzu, Kyoto, Japan) under a flow of dry nitrogen at 20 mL/min. Before drying, dry nitrogen gas was fed for 30 min. Because the dry nitrogen was flowing, the relative humidity of the dough surface was assumed to be 0%. The weight loss of the sample was measured from room temperature to 100°C under linearly rising-temperature conditions of 0.2-1.0 °C/min, and the sample was dried at 135°C for 5 h to estimate its bone-dry weight. The drying rate was evaluated by differentiating the weight loss with time at various moisture contents using Origin 8.1J (OriginLab, Northampton, MA, USA). Measurements were performed at least twice to confirm reproducibility.
4.2.3. Activation energy

Because the change in sample weight was measured under a flow of dry nitrogen, the equilibrium amount of water sorbed onto the flour should be zero. Therefore, the fraction of water remaining on the flour, $Y$, was calculated by the following equation:

$$Y = \frac{w}{w_0}$$  \hspace{1cm} (4-1)

where $w_0$ and $w$ are the initial moisture content and the moisture content at time $t$, respectively.

The activation energy, $E$, at a specific $Y$ value was estimated by an isoconversion method using the drying data obtained at various temperature-rising rates. Among the various methods available [99], the method of the differential type proposed by Friedman was adopted [100]. The change in the $Y$ value with time, $dY/dt$, corresponding to the drying rate, can then be expressed by Eq. (4-2):

$$\frac{dY}{dt} = k f(Y)$$  \hspace{1cm} (4-2)

where $f(Y)$ is a kinetic function concerning the driving force for drying, and $k$ is the mass transfer coefficient. The temperature dependence of this coefficient, $k$, can be expressed by the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E}{RT}\right)$$  \hspace{1cm} (4-3)

where $k_0$ is the frequency factor, $E$ is the activation energy, $R$ is the gas constant, and $T$ is the absolute temperature. Substituting Eq. (4-3) into Eq. (4-2) gives the following equation:

$$\ln\left(\frac{dY}{dt}\right) = -\frac{E}{RT} + \ln[k_0 f(Y)]$$  \hspace{1cm} (4-4)

To estimate the activation energy, the $dY/dt$ values at a specific value of $Y$ were evaluated by numerical differentiation of the drying curve obtained at different temperature-rising rates, and plotted versus $1/T$ on a semi-logarithmic scale.
4.2.4. Differential scanning calorimetry

DSC analysis was performed under the same conditions as those of the thermogravimetric (TG) analysis, using a DSC-50 (Shamadzu, Kyoto, Japan). Measurements were performed at least twice to confirm reproducibility.

4.3. Results and Discussion

4.3.1. Thermogravimetric analysis of the drying process

Figure 4-1 shows the change in the fraction of water remaining on the flour, i.e., $Y$, and the temperature during drying at the different temperature-rising rates, as measured by TG analysis.

**Fig. 4-1.** Drying curves under programmed temperature-rising conditions of 0.2 (— -), 0.4 (—), 0.6 (—), 0.8 ( - - -), and 1.0 (– –) °C/min. The parameter $Y$ (ordinate axis) indicates the fraction of water remaining on the flour.
All drying curves under the temperature-rising conditions were concave and similar to those under isothermal drying conditions in chapter 3. The drying rate was higher at increased temperature-rising rates, and became increasingly low at low moisture contents.

The applicability of Eq. (4-4) was examined by plotting the value of $dY/dt$ versus $1/T$ on a semi-logarithmic scale, as shown in Fig. 4-2 for number of $Y$ values. For each $Y$ value, the points were fitted to a straight line to obtain $E$ and $k_0f(Y)$.

![Fig. 4-2](image1)

**Fig. 4-2.** Temperature dependences of the drying rate at the fractions of water remaining on the flour, $Y$, of 0.8 (○), 0.7 (△), 0.6 (□), 0.5 (◇), 0.4 (◇), 0.3 (◇), and 0.2 (◇).

Figure 4-3 shows the estimated $E$ values, plotted against $Y$ values ranging from 0.2 to 0.8. The $E$ values at $Y$ values above 0.35, corresponding to a moisture content of 0.14 kg-H₂O/kg-d.m., were fairly constant at 32 kJ/mol, while they were larger at $Y$ values below 0.35. For the fraction of water remaining on the flour of $Y$ = 0.2, the activation energy was $E = 53.0$ kJ/mol. These facts indicate the drying rates to markedly decrease in the later stages of drying.
4.3.2. Differential scanning calorimetric measurement

Figure 4-4 shows the DSC curves at various temperature-rising rates. All curves exhibited endothermic peaks. Because such peaks were observed at low moisture contents, it was reasoned that they resulted from the enthalpy recovery of amorphous starch rather than from gelatinization. This assumption appeared to be supported by the fact that the endothermic peak was broader at lower temperature-rising rate and that the structure of amorphous starch was more relaxed because of the longer aging time at lower rate. Typically, using a hermetic cell, the glass transition can be observed at temperatures above the endothermic peak during the early stage of enthalpy relaxation in DSC [101]. In this study, the glass transition could not clearly be observed because measurements were carried out using an open cell and the moisture content gradually decreased. However, a slightly endothermic shoulder after the endothermic peak seemed to suggest the occurrence of a glass transition.

The DSC curves re-drawn as a function of the moisture content, based on the TG and DSC measurements results, are shown in Fig. 4-5. Endothermic peaks were observed between moisture contents of 0.10-0.20 kg-H₂O/kg-d.m., with the peak shifting to lower moisture contents for the drying process at higher temperature-rising rates.
Fig. 4-4. DSC curves at 0.2 (a), 0.4 (b), 0.6 (c), 0.8 (d), and 1.0 (e) °C/min during drying. The upward- and downward-facing arrows show the peak and conclusion of the endotherms, respectively.

Fig. 4-5. Relationship between moisture content and endotherm during drying, as determined by DSC and TG at 0.2 (a), 0.4 (b), 0.6 (c), 0.8 (d), and 1.0 (e) °C/min. The arrows indicate the location of the endothermic peaks.
4.3.3. Effect of moisture content on the drying rate

The drying rate is plotted against moisture content in Fig. 4-6 for all temperature-rising rates, where it was observed that the constant drying rate was higher at higher temperature-rising rates. This result is ascribed to the fact that the temperature at a given moisture content is higher at higher temperature-rising rates. The drying rate markedly decreased at moisture contents of 0.15-0.20 kg-H₂O/kg-d.m. or lower, where roughly corresponded to that moisture content where activation energy started to increase (Fig. 4-3).

![Drying characteristics curves under programmed rising temperature conditions](image)

**Fig. 4-6.** Drying characteristics curves under programmed rising temperature conditions at 0.2 (a), 0.4 (b), 0.6 (c), 0.8 (d), and 1.0 (e) °C/min. The arrow indicates the inflection point of the decreasing drying rate of 1.0 °C/min.

Figure 4-7 shows the relationship between the conclusion temperature of the endothermic peak in the DSC measurements and moisture content, as well as those between the temperature where the drying rate started to decrease rapidly or the glass transition temperature of durum semolina flour with moisture content [65]. The plot for the conclusion temperatures of the endothermic peaks coincides with the glass transition curve, which strongly suggests the glass transition to occur after the endothermic peak. The plots for the
temperature of the inflection points of the drying characteristics curves (Fig. 4-6) were located near the glass transition curve as well. Therefore, the glass transition of dough from the rubbery to the glassy state produced a rapid increase in activation energy and a rapid decrease in drying rate.

![Graph showing moisture content vs. temperature](image)

**Fig. 4-7.** Relationship between the moisture content and the temperature of the inflection points of the drying characteristic curves (○), as well as those between the conclusion of the endothermic peaks in DSC (△) or the glass transition temperature (■). The glass transition temperature was adopted from literature [65].

### 4.4. Conclusions

The activation energy of the mass transfer coefficient for the drying of durum semolina dough was determined to be ca. 32 kJ/mol at a moisture content of 0.14 kg-H₂O/kg-d.m. or higher, yet markedly increased as the moisture content dropped below 0.14 kg-H₂O/kg-d.m. TG and DSC measurements indicated an endothermic peak resulting from enthalpy recovery of amorphous starch at moisture contents of 0.10-0.20 kg-H₂O/kg-d.m. A large decrease in drying rate was, furthermore, observed at moisture contents of 0.15-0.20 kg-H₂O/kg-d.m. or below. Both the conclusion temperature of the endothermic peak in the DSC measurements and the temperature of the inflection points of the drying characteristics curves were located
near the glass transition curve of durum semolina flour. In summary, these observations indicated the glass transition to play an important role in the drying rate.
CHAPTER 5

Shrinkage and tensile stress of sheet-like and cylindrical pastas with various moisture contents

5.1. Introduction

A drying curve of pasta, which is the relationship between the drying time and the moisture content, is usually concave, and the drying rate is fast during the early stage but gradually decelerates with time [13]. The reasonable design of the drying process requires an adequate model for describing the water migration within a material to be dehydrated during the processing. Some mathematical models have been proposed for the drying of pasta [87, 102-105]. The applicability of Fick's second law of diffusion for the prediction of the moisture change during drying has been demonstrated for cylindrical and sheet-like pastas by Migliori et al. [104] and Temmerman et al. [105, 106], respectively. The apparent moisture diffusivity estimated by the law was reported to be lowered at a higher relative humidity of drying air even at the same temperature [107]. The difference in the moisture content between the center and the surface of pasta sample also became smaller at the higher humidity [108]. These facts indicate that the drying conditions largely affect the moisture distribution within pasta. Moreover, the decrease in the moisture content during the drying results in the glass transition of pasta [88], and the region in a glass state is extended from the surface to center of pasta sample with the progress in drying.

The mechanical properties of a food material, such as a stress-strain curve [109] and critical stress [5-7], also provide useful information for optimization of the drying process because they depend on product's moisture content. The apparent strength, apparent stress-relaxation coefficient, Young's modulus, strain, and yield stress of pasta have been measured by many researchers [108, 110-112]. Pasta shrinks in association with evaporation of water. The locally heterogeneous properties in stress and shrinkage within pasta occurred during drying would result in the generation of cracks, which largely degrade the pasta quality [108, 113]. In order to find the conditions in which no crack occurs during drying, it is
important to precisely predict the moisture distribution within the pasta that causes shrinkage and stress formation. In this study, the shrinkage and tensile stress of cylindrical and sheet-like pastas having various moisture contents with different distributions was examined.

5.2. Materials and Methods

5.2.1. Materials

Durum wheat semolina was supplied by Nisshin Foods, Inc., Tokyo, Japan. Sodium bromide and potassium chloride were purchased from Nacalai Tesque, Inc., Kyoto, Japan.

5.2.2. Sample preparation

Durum semolina of 700 g was mixed with water to produce the moisture content of 32% (on wet basis) using a kitchen-aid blender (KSM150, FMI, USA) for 10 min. The mixture was then put into a pasta-making machine (Magica, Bottene, Italy) which was refurbished and connected to a diaphragm pump (DTC-2, Technosigma, Matsudo, Japan) to reduce the pressure inside the machine. The two types of model pastas, the cylindrical or sheet-like pastas, were pushed out by single-screw extruder at a speed of $3.7 \pm 0.1$ cm/s under reduced pressure of 30 kPa abs through a die. The length and inner diameter of the teflon die used to produce a cylindrical pasta were 5 mm and 3.6 mm, respectively. The direction of extrusion of the pasta was the same with that in length of the cylindrical pasta and width of sheet-like pasta, respectively. The sizes of the cylindrical pasta and sheet-like pastas were $3.67 \pm 0.10$ mm in diameter and 39.8-51.9 mm in length, and 42.2-50.8 mm in width, 22.2-27.2 mm in height, and $1.18 \pm 0.02$ mm in depth, respectively. The distance between the two points marked at a 27-mm interval on cylindrical pasta was measured exactly before and after drying to estimate the shrinkage in the length direction. Similarly, shrinkages in width and height directions were evaluated from the distances of two points, which were separated about 43 mm and 20 mm, respectively, before and after drying for sheet-like pasta. Shrinkages in diameter direction of cylindrical pasta and in depth direction of a sheet-like pasta were directly evaluated from the changes in the diameter and depth before and after drying. Each measurement was at least repeated 30 times.
In order to examine the effect of the moisture distribution in the pasta on the shrinkage, the fresh pasta was dried under three different conditions. In the first case, the pasta was dried at 50°C and 40% relative humidity at every 5-10 min for 8 h in a temperature-humidity controllable chamber (SH-641, Espec, Japan). In the second case, the temperature was the same as in the first case, but the relative humidity was controlled at 80% at every 5-10 min for 6 h in order to dry the pasta more slowly than in the first case. Because a sample was placed on a plain weave stainless steel mesh (wire diameter of 0.4 mm, sieve mesh size of 2.1 mm) in the chamber in these cases, water in the sample was evaporated from all the surfaces of the sample. The shrinkage and average moisture content of the pastas were measured immediately after their preparation. In the third case, the pasta prepared under the conditions of the second case were put into a plastic bag and stored at 50°C for two days to make the moisture distribution homogeneous after the bag was tightly sealed. The pasta samples dried in the first, second, and third cases were designated as 40%, 80%, and equilibrated samples, respectively.

The average moisture content of the pasta, \( x \), was estimated by weighing the pasta, which was not pulverized, before and after drying it at 135°C for 5 h:
\[
  x = \frac{w_1 - w_2}{w_2}
\]

where \( w_1 \) and \( w_2 \) are the sample weights before and after drying, respectively.

5.2.3. Shrinkage strain

The width, height, and depth of the sheet-like pasta were measured before and after drying using a vernier caliper, the precision of which was 0.01 mm (CD-S15C, Mitsutoyo, Kawasaki, Japan), and the shrinkage strain, \( \varepsilon \), for each direction was calculated by Eq. (5-2).
\[
  \varepsilon = \frac{L_1 - L_2}{L_1}
\]

where \( L_1 \) and \( L_2 \) are the sample lengths before and after drying, respectively. The shrinkage coefficient was estimated from the slope of a line obtained by plotting the \( \varepsilon \) values versus the average moisture contents of the pastas, and the shrinkage ratio of the height direction to width one was also estimated from the line obtained by plotting the \( \varepsilon \) values for the height versus those for the width.
For the cylindrical pasta, the shrinkage strains for the length and diameter were also measured by a method similar to that for the sheet-like pasta. The shrinkage ratio of the length direction to diameter one was also estimated from the line obtained by plotting the shrinkage strains for the length versus those for the diameter.

5.2.4. **Tensile stress**

A dumbbell specimen was prepared by cutting the sheet-like pasta using a die blade. The specimen was dried under the same conditions as the sheet-like and cylindrical pastas. The specimen was stretched at a tension rate of 0.5 mm/s using an RE2-33005S rheometer (Yamaden, Tokyo) to record the strain and tensile stress. The tensile stress was calculated from the tensile force divided by the initial cross-sectional area of the dumbbell specimen, which was accurately determined using the vernier caliper. At the beginning of the stretching, elastic deformation, where the tensile stress linearly increases with the strain, occurred. The Young’s modulus was estimated from the slope of the line. The air, the humidity of which was regulated at 51%RH or 81%RH by passing through saturated sodium bromide or potassium chloride at 50°C, was pumped over the measurement site of the rheometer. The tensile strain, \( \gamma \), was calculated by Eq. (5-3).

\[
\gamma = \frac{\Delta l}{l_1}
\]

where \( l_1 \) is the sample length and \( \Delta l \) is the tensile distance.

5.3. **Results and Discussion**

5.3.1. **Shrinkage of sheet-like pasta**

Figure 5-1(a)-(c) shows the dependencies of the shrinkage strains for the width, height, and depth, respectively, on the average moisture content of sheet-like pasta having different moisture distributions. The slope of the plots for each sample gives the shrinkage coefficient. The coefficients for the width, height, and depth of the 40% and 80% samples were 0.13, 0.12, and 1.03 and 0.20, 0.21, and 1.14, respectively. For the equilibrated sample, the coefficient for the width and height were 0.29 and 0.26, but the coefficient for the depth could not be
accurately evaluated due to adhesion of the samples to the plastic bag. The coefficient for the 40% samples was the lowest in all the directions, and those for the 80% and equilibrated samples followed. The moisture distribution of the 40% sample was more uneven than that of the 80% sample, while the equilibrated sample had even distribution. These facts suggested that the moisture distribution within the pasta affected its shrinkage. During the early stage of drying, the moisture content of the sample surface more rapidly decreased to form a rigid layer near the surface in the air having the lower humidity. This layer would prevent the shrinkage and produce the lowest shrinkage coefficient for the 40% sample. On the other hand, the equilibrated sample would gradually and evenly shrink with a decrease in the moisture and result in the highest shrinkage coefficient.

Fig. 5-1. Shrinkage strain in the width (a), height (b), and depth (c) directions of the sheet-like pasta having different moisture contents. The pasta was dried at 50°C and 40% relative humidity (---○---) and at 50°C and 80% relative humidity (- -△- -). The symbol (– –□– –) indicates the pasta prepared at 50°C and 80% relative humidity and stored at 50°C for two days to make the moisture distribution homogeneous.

The shrinkage strain in the depth direction was negative and the pasta expanded during the early stage of drying (Fig. 5-1(c)). The pressure on the pasta during extrusion was the highest in the depth direction. Therefore, shrinkage occurred in the width and height directions from the beginning of drying, but the compression relaxation was predominant over shrinkage in the depth direction resulting in expansion during the early stage of drying.

The relationship in the shrinkage strain between the height and width directions was linear (Fig. 5-2). The shrinkage ratios, which are the slopes of the lines, were 0.93, 0.96, and 0.94 for the 40%, 80%, and equilibrated samples, respectively. The ratios less than unity
indicated that the pasta shrinkage was anisotropic and that the pasta shrank more in the width direction than in the height direction. The shrinkage anisotropy might be ascribed to the network of polymer constituents such as gluten and starch. The polymer constituents were stretched in the width direction during extrusion, and their creep recovery rapidly occurred during drying. This recovery would result in the shrinkage ratio being less than unity.

![Graph showing relationships between shrinkage strain in the height and width directions](image)

**Fig. 5-2.** Relationships between the shrinkage strain in the height direction to that in the width one for the sheet-like pasta. The pasta was dried at 50°C and 40% relative humidity (---○---) and at 50°C and 80% relative humidity (- -△- -). The symbol (---□---) indicates the pasta prepared at 50°C and 80% relative humidity and stored at 50°C for two days to make the moisture distribution homogeneous.

### 5.3.2. Shrinkage of cylindrical pasta

Figure 5-3 shows the shrinkage strain of the cylindrical pasta prepared at 50°C and 80% relative humidity. The shrinkage coefficient in the longitudinal direction was 0.23. The shrinkage strain in the diametric direction linearly increased with the decrease in the moisture content, but the strain mostly increased at the moisture contents less than 0.17. As shown in Fig. 5-4, the shrinkage ratio was 0.73 at the high moisture contents (less than 0.10 in the shrinkage strain in the diametric direction) at which the shrinkage strain linearly increased.
Fig. 5-3. Shrinkage strain in the longitudinal (—○—) and diametric (- -△- -) directions of the cylindrical pasta prepared at 50°C and 80% relative humidity and having various moisture contents.

Fig. 5-4. Relationships between the shrinkage strain in the longitudinal direction to that in the diametric one for the cylindrical pasta.
with the decrease in the moisture content, indicating the anisotropy that the longitudinal shrinkage was predominant over the diametric one. For the moisture contents less than 0.17, the shrinkage ratio significantly increased corresponding to the increase in the shrinkage strain in the diametric direction.

The previous report indicated that the glass transition temperature of the durum semolina decreased as its moisture content increased because water acts as a plasticizer [65]. The glass transition of the durum semolina at 50°C was reported to occur at the moisture content of 0.17. The glass transition of the durum semolina affected the mechanical properties, such as the strength, stress relaxation, and tensile stress strain [110, 111]. Therefore, the major changes in the shrinkage strain and the shrinkage ratio at the moisture contents less than 0.17 would be ascribed to the glass transition.

The creep relaxation of the polymeric constituents occurred during the early stage of drying, resulting in the high shrinkage in the longitudinal direction. On the other hand, during the late stage of drying, the longitudinal shrinkage scarcely progressed, but the diametric shrinkage occurred. Therefore, it is postulated that the shrinkage ratio became high at the lower moisture contents.

### 5.3.3. Tensile strain

The dumbbell specimen of the durum semolina dough equilibrated at a specific moisture was stretched at 0.5 mm/s and the tensile stress was measured as a function of the strain as shown in the inset of Fig. 5-5. The tensile stress was proportional to the strain during the early stage of stretching, and the slope of the straight line determined the Young's modulus. The modulus of the pasta was measured for the samples having various moisture contents (Fig. 5-5). The plots for all the 40%, 80%, and equilibrated samples lay on a single curve. The modulus became high as the moisture content decreased. The modulus then became almost constant at the moisture contents less than 0.17 where the pasta was transformed from the rubber state to a glass one [65].

Young's modulus did not depend on the drying conditions, indicating that the modulus was not affected by the moisture distribution within the pasta. This fact suggested that the hard surface of the pasta scarcely contributed to its strength against the tensile strain.
Fig. 5-5. Young's modulus of dumbbell specimens of durum semolina dough having different moisture contents. The specimens were dried at 50°C and 40% relative humidity (○) and at 50°C and 80% relative humidity (△). The symbol (□) indicates the pasta prepared at 50°C and 80% relative humidity and stored at 50°C for two days to make the moisture distribution homogeneous. Inset: Tensile stress-strain curve for the dumbbell specimens dried at 50°C and 40% relative humidity, and having the moisture content of 0.51.

5.4. Conclusions

Sheet-like and cylindrical pastas were dried under different conditions to prepare samples having different moisture distributions. A slight anisotropy was observed during shrinkage of the pasta with both shapes. The Young's modulus of the dumbbell specimen of the durum semolina dough was almost constant at the moisture contents when the pasta was transformed from the rubber state to a glass one. Pasta having a more heterogeneous moisture distribution exhibited a low shrinkage coefficient, but the heterogeneity in the moisture distribution scarcely affected Young's modulus of the pasta.
PART 2

Rehydration kinetics of pasta
CHAPTER 6

Estimation of the gelatinization temperature of noodles from rehydration curves under temperature-programmed heating conditions

6.1. Introduction

Temperature greatly affects the drying of wet food material and the rehydration of dried food. The rehydration capacity of starchy food is greater at temperatures higher than the gelatinization temperature [52]. Hence, it is important to determine the gelatinization temperature of a starchy food for reasonable design of its manufacturing and cooking processes. There are methods of estimating gelatinization temperature, including amylography, polarization microscopy, and differential scanning calorimetry (DSC) [114]. Among these, DSC is most often used. Most of these methods require pulverization of a sample and require expensive instruments.

Based on a report that the driving force necessary for rehydration of dried starchy food was large and that the rehydration rate increased at temperatures higher than that of gelatinization [115], a novel method of estimating the gelatinization temperature of starch-containing foods, without pulverization of a sample from a rehydration curve under temperature-programmed heating conditions, was developed. Udon and kishimen are noodles made of wheat flour, and they are different in width and flatness. Juwari-soba is a noodle made of buckwheat flour alone, and hachiwari-soba is made from a mixture of buckwheat and plain wheat flours at a weight ratio of 8:2. Common soba is made of a mixture of buckwheat and plain wheat flours, and its content of plain wheat flour is more than that of hachiwari-soba. The major constituent of Malony®, winter cuisine in a pot, is potato starch. Kuzukiri was originally made of ground arrowroot, but most commercially available today is made of potato starch. Pasta is made of durum wheat semolina. The gelatinization temperatures estimated by the proposed method were compared with those estimated by DSC.
6.2. Materials and Methods

6.2.1. Materials

The two kinds of pasta were supplied by Nissin Foods (Tokyo), and they were prepared at different maximum temperatures during the drying process. Pasta dried at high- and at low-temperature were designated HT- and LT-pasta, respectively. All the other dried noodles were purchased from a supermarket in Kyoto, Japan. All the noodles were cut into 5-cm-long samples.

6.2.2. Rehydration

A noodle, the initial weight of which was measured, was fixed to a hook bar and immersed in a 1-L glass beaker with distilled water. The initial temperature of the water was adjusted to 30.0 ± 0.1°C, and the temperature was raised to 100°C at a specific rate using an immersion heater dipped into the beaker. The rate of temperature rise was controlled using a programmable temperature-controller (TXN-700, As One, Osaka, Japan). The water in the beaker was stirred gently, and the temperature was measured regularly using a thermometer. After a specific duration, the noodle was removed from the beaker, immediately blotted to remove any superficial water, and weighed. The noodle was dried at 135°C for 5 h in a DN400 convection drying oven (Yamato, Tokyo, Japan). The amount of water rehydrated, $X$, was estimated by the following equation:

$$X = \frac{W_2 - W_1}{W_0}$$

(6-1)

where $W_0$ is the initial absolute dry weight of the noodle, and $W_1$ and $W_2$ are the weights of the noodle before and after rehydration.

The rehydration curve for HT-pasta was obtained at average temperature-increase rates of 0.50, 0.77, 1.00, and 1.38 °C/min in order to examine the effect of the temperature-raising rate on the estimated gelatinization temperature. The curves for the other noodles were measured at a temperature-raising rate of 1.38 °C/min.
6.2.3. Differential scanning calorimetry

Each noodle was ground in a mortar with a muddler. The ground noodle (1.5 mg) and distilled water (15 mg) were placed in a 201-53090 aluminum cell (Shimadzu, Kyoto, Japan), and the cell was tightly sealed. The cell was kept in a refrigerator for 5 h or longer, and differential scanning calorimetric measurement was carried out using with a DSC-50 calorimeter (Shimadzu) from 30°C to 120°C at a rate of 5 °C/min.

6.3. Results and Discussion

6.3.1. Rehydration curves

Figure 6-1 shows the rehydration curves for HT-pasta obtained at various temperature-raising rates. Each curve has a point at which the rehydration rate increased markedly, and the temperature at that point was about 52°C. In order to facilitate evaluation of the temperature at the inflection point, the amount of water rehydrated was plotted against the temperature for the data near that point (Fig. 6-1, inset). The inflection-point temperatures for the curves at temperature-raising rates of 0.50, 0.77, 1.00, and 1.38 °C/min were 51.9, 52.7, 52.4, and 52.3°C respectively. The mean value and standard deviation of the temperatures were 52.3 ± 0.3°C. Because the temperature-raising rate scarcely affected the inflection-point temperature, the rehydration curves for the other noodles were observed at a temperature-raising rate of 1.38 °C/min.

6.3.2. Relationships of gelatinization temperatures and inflection-point temperature

The amounts of water rehydrated are plotted against temperature for all the noodles tested (Fig. 6-2). In order to distinguish the curves, they were adequately displaced in a longitudinal direction. For all the noodles, distinct inflection points were recognized. The inflection-point temperature of LT-pasta was 53.1°C, almost the same as that of HT-pasta (52.3°C). The temperatures were close to the gelatinization temperature of durum wheat semolina [14]. The temperatures of udon and kishimen, both made of plain wheat flour, were 57.0 and 57.8°C, respectively, close to the previously reported value [116]. The temperature
of kuzukiri (potato starch) was 49.1°C. Malony is also rich in potato starch, and its temperature was 48.4°C. These inflection-point temperatures were similar due to the similarity of the major constituents. The temperatures of juwari-soba, hachiwari-soba, and common soba were 61.1, 59.6, and 57.4°C, respectively. The inflection-point temperature was higher for soba, with a higher content of buckwheat flour.

![Rehydration curves for HT-pasta at various temperature-increase rates.](image)

**Fig. 6-1.** Rehydration curves for HT-pasta at various temperature-increase rates. The temperature-raising rates were 0.50 (\(\nabla\)), 0.77 (\(\square\)), 1.00 (\(\triangle\)), and 1.38 (\(\bigcirc\)) °C/min. Inset: amount of water rehydrated at temperatures near the inflection point.

The DSC curves for the noodles except for Malony were determined. Endothermic peaks were observed for all the noodles in a temperature range of 45 to 80°C, and the onset, peak, and conclusion temperatures of each type of noodle were estimated. The temperatures were plotted against the inflection-point temperatures observed by the proposed method (Fig. 6-3). As the figure shows, the inflection-point temperatures were between the onset and peak temperatures. It is known that the gelatinization temperature of starchy food depends somewhat on the measurement technique [114]. Hence, the inflection-point temperature should reflect the gelatinization temperature of each type of noodle.
Fig. 6-2. Rehydration curves for LT-pasta (▼), udon (◇), kishimen (□), juwari-soba (■), hachiwari-soba (●), common soba (▲), Malony (○), and kuzukiri (△) at a temperature-raising rate of 1.38 °C/min.
6.4. Conclusions

The proposed method is a simple method of estimating the gelatinization temperature of dried foods without pulverization, and does not require specialized expensive equipment.
CHAPTER 7

Rehydration kinetics of pasta at different temperatures

7.1. Introduction

A quantitative understanding of the change in the moisture content of pasta at any temperature of the rehydrated water is necessary to know the mechanical properties and the optimal rehydration time of pasta [111, 117, 118]. The moisture content of the pasta at any rehydration time can be well predicted using Peleg's model and the Weibull distribution function [28]. However, the temperature dependence of rehydration kinetics does not seem to be properly characterized. In particular, the effect of the starch gelatinization on the characteristics of rehydration kinetics has not been revealed. In addition, the reported equations cannot apply to pasta of a different diameter, even if the material is identical to each other.

In this study, the effects of the temperature of the rehydration water on the characteristics of rehydration kinetics, such as the equilibrium moisture content and the initial rate of rehydration, were investigated in detail. The temperature of the rehydrated water was varied from 20 to 90°C for an extended time period (4 h) to systematically observe the phenomena during rehydration. On the basis of the observations, an equation, which is a function of the initial diameter of the pasta, rehydration time, and temperature of the rehydrated water, was proposed to describe the moisture content under any conditions.

7.2. Materials and Methods

7.2.1. Materials

Ma·Ma (Nisshin Foods, Inc., Tokyo, Japan), purchased from a local supermarket, was used in all the experiments. The carbohydrate content of the pasta was 72 wt%. The initial diameters of the pasta were 1.4 mm (lot No. T0913 L), 1.6 mm (lot No. T1332 N), and 1.8 mm (lot No. 10.11.26 DS).
7.2.2. Rehydration

Initial moisture contents of pasta based on dry solid, $X_0$, were determined by drying about 0.2 g of sample, the weight of which had been accurately measured, in a convection drying oven (DO-300FA, As One, Japan) at 105°C for 4 days. The measurement was repeated three times. Culture tubes containing about 50 cm$^3$ of distilled water were equilibrated at 20, 40, 50, 55, 60, 70, 80, or 90°C in an SD thermominder and Personal-11 water bath (Taitec, Saitama, Japan). A sample cut into 9-cm long, the weight of which was about 0.20 g, 0.26 g, and 0.33 g for the 1.4-mm, 1.6-mm, and 1.8-mm pasta, respectively, was rehydrated into a tube (about 15 tubes were prepared under a specific condition). At a given time, the sample was removed from the tube, immediately blotted to remove any superficial water, and weighed, $W_0$. The samples were dried in the convection drying oven at 105°C for 4 days, and weighed, $W_1$.

7.2.3. Volume measurement

After the rehydration for a given period, the sample was immersed in a burette containing hexane (25°C), and the sample volume was measured from the increase in the volume in the burette, assuming that a penetration of hexane into the pasta can be ignored. The samples were then dried in the convection drying oven at 105°C for 4 days, and weighed.

7.2.4. Thermal analysis

The gelatinization of spaghetti samples was measured by differential scanning calorimetry (DSC-50, Shimadzu, Kyoto, Japan). The sample was ground into a fine powder by using a pestle and mortar. The ground sample was accurately weighed (1.5 mg) using a thermogravimetric analyzer (TGA-50, Shimadzu) and moistened with distilled water at a weight ratio of dry sample to water of around 1:6.5. The sample was sealed into an aluminum cell (seal cell 201-53090, Shimadzu) using a SSC-30 sealer crimper (Shimadzu). The cell was placed in a DSC pan with another cell in which the same amount of distilled water was sealed as a reference. The samples were heated in the DSC at 5 °C/min from 20 to 120°C. The start ($T_s$), peak ($T_p$), and conclusion ($T_c$) temperatures for an endothermic peak were computed.
using analysis software supplied with the instrument. Each experiment was carried out in
duplicate.

7.2.5. Pore analysis

7.2.5.1. Pore-size distribution

The pore-size distribution of pasta was analyzed by mercury intrusion porosimetry
(Autopore 9520, Shimadzu) applying a pressure of up to 414 MPa. The pore diameter was
calculated according to the Washburn equation [119]:

\[ P_m = -\frac{4\gamma \cos \theta}{d_c} \]  (7-1)

where \( P_m \) is the pressure, \( \gamma \) is the surface tension of the mercury, \( \theta \) is the contact angle
between mercury and the sample, and \( d_c \) is the diameter of the capillary. The surface tension
of the mercury of \( 4.85 \times 10^{-1} \) N/m and the contact angle of 130° were used to calculate the
pore size from the pressure measurement. The volume of mercury intruded at the maximum
pressure was considered to be the total porosity. A sample of approximately 3 g was kept
under vacuum at room temperature for 15 h for intrusion. An initial pressure was 7 kPa. The
measurement was carried out in duplicate.

7.2.5.2. Atomic force microscopy

The surface of pasta was observed by a SPM-9500 atomic force microscope (AFM)
(Shimadzu) with a silicon nitride triangular cantilever with a sharpened pyramidal tip
(OMCL-TR800PSA-1, Olympus, Tokyo, Japan) having a nominal spring constant of
0.15 N/m. The imaging was performed in the constant contact force mode with a nominal
imaging force of 16 nN. The scan area was 25 μm² with a scan frequency at 1.0 Hz. The
image was modified using the analysis software installed in the instrument.

7.2.6. Statistical analysis

The coefficients of the nonlinear regression between the observed and calculated values
were determined using Solver in Microsoft Office Excel® 2007. An accidental error of the
The coefficient was evaluated with a confidence level of 95% \((P < 0.05)\) by linearization [120]. The good fit of the model was evaluated on the basis of the coefficient of the determination \((R^2)\) and the root-mean-square deviation (RMSD). The RMSD is defined as [121]:

\[
\text{RMSD} = \frac{1}{n} \sqrt{\frac{1}{n} \sum_{i=1}^{n} (X_i - X_{pi})^2}
\]

(7-2)

where \(n\) is the number of experimental points, \(X_i\) is the experimental moisture content, and \(X_{pi}\) is the predicted moisture content.

### 7.3. Results and Discussion

#### 7.3.1. Loss of pasta mass

The pasta components leak into the rehydrated water during rehydration, resulting in the loss of its mass. The amount of the loss of pasta mass is generally significant, although a small amount of loss is preferred for a high quality of cooked pasta [122]. However, no correction was made for the loss in previous studies focused on the modeling of the moisture content. Figure 7-1 shows the relationship between the amount of the loss of pasta mass (initial matter (i.m.) basis), \(M_t\), and the quotient of time by square of the diameter, \(t/d^2\), where \(d\) is the initial diameter of the pasta at 20, 50, and 90°C. The \(M_t\) value was greater at the longer rehydration time and at the higher temperature of the rehydrated water. The \(M_t\) value reached approximately 0.2 kg/kg-i.m., which corresponded to approximately 20% of the pasta mass.

The optimal “boiled condition” for dried pasta, called *al dente*, is cooked so as to be firm but not hard. The \(M_t\) value at *al dente*, which was attained around 7 min for 1.6 mm diameter pasta in Fig. 7-1, was about 0.032 kg/kg-i.m. The moisture content at the early stage of rehydration, such as the condition of *al dente*, was only slightly affected by the loss. On the other hand, the effect of the loss on the moisture content at the latter stage became significant. Therefore, the loss should be considered to characterize the rehydration process.
Fig. 7-1. Amount of loss of the pasta mass during rehydration at 90°C for the pastas with initial diameters of 1.6 mm (○), at 50°C for the pastas with initial diameters of 1.4 mm (△), 1.6 mm (□), 1.8 mm (◇), and at 20°C for the pastas with initial diameters of 1.6 mm (<). The amount of loss was expressed as kg/kg-initial matter (i.m.).

Fig. 7-2. Temperature dependencies of the equilibrium amount of loss \( M_e \) (○) and the rate constant \( k \) (△).
The plots of $M_t$ versus $t/d^2$ for the pastas of 3 different diameters (1.4, 1.6, and 1.8 mm) at 50°C lay on a curve (Fig. 7-1). This fact indicated that the amount of loss of the pasta mass depends on the surface area of the pasta because the square of the diameter is proportional to the surface area. Equation (7-3) could express the observed amount of loss during rehydration as a function of time:

$$M_t = M_e \left[1 - \exp\left(-\frac{kt}{d^2}\right)\right]$$

where $M_e$ is the equilibrium amount of the loss of pasta mass and $k$ is the rate constant. The maximum value of RMSD for the observed and calculated $M_t$ values was 0.450, which demonstrates the suitability of Eq. (7-3) for describing the experimental loss of the pasta mass. Figure 7-2 shows the temperature dependencies of the $M_e$ and $k$ values. The $k$ value was not affected by temperature, but the $M_e$ value became large in reverse proportion to the absolute temperature. This result suggested that the leaking of pasta components into the rehydrated water during rehydration is a mechanical change such as exfoliation, not the chemical or physical changes such as the hydrogen bond breaking, diffusion, or absorption.

**Fig. 7-3.** Changes in the moisture content at 50°C (closed symbols) and 80°C (open symbols) for the pastas with initial diameters of 1.4 mm ($\triangle$, •), 1.6 mm (□, ■), and 1.8 mm (◇, ◆).
7.3.2. Rehydration at various temperatures

Figure 7-3 shows the relationship between the moisture content, $X_t$, and the quotient of time by square of the diameter, $t/d^2$, for the 1.4, 1.6, and 1.8 mm diameter pastas at 50 and 80°C. The moisture content based on the net mass of pasta, $X_t$, was calculated by Eq. (7-4):

$$X_t = \frac{W_0 - W_1}{W_1} \quad (7-4)$$

The $X_t$ values were larger at a higher temperature. The plots of $X_t$ versus $t/d^2$ for the pastas of 3 different diameters lay on a curve at any temperature. This fact indicated that the rehydration of pasta is governed mainly by the water diffusion.

The hyperbolic equation has been applied to describe the moisture content of pasta as a function of time $t$ [22, 24, 28]. In this study, the equation of hyperbolic type (Eq. (7-5)) to describe the $X_t$ value using the $t/d^2$ as an independent variable instead of time $t$ was applied:

$$X_t = \frac{a \times (t/d^2)}{b + (t/d^2)} + X_0 \quad (7-5)$$

where $a$ and $b$ are constants. Figure 7-4 illustrates the rehydration process at 20-90°C. The solid curves were calculated using the estimated $a$ and $b$ values. The maximum value of RMSD for the observed and calculated $X_t$ values was 0.030, which demonstrates the appropriateness of Eq. (7-5) for describing the experimental rehydration characteristics of pasta.

The constants, $a$ and $b$, were estimated to best-fit the calculated $X_t$ values to the experimental ones using the Solver in Microsoft Excel®. The solid curves in Fig. 7-3 and Fig. 7-4 were drawn using the estimated $a$ and $b$ values.
7.3.3. Equilibrium moisture content

The equilibrium moisture content at \( t = \infty \), \( X_e \), is given by Eq. (7-6):

\[
X_e = \lim_{t \to \infty} X_t = a + X_0
\]

(7-6)

The equilibrium moisture content, \( X_e \), can be approximated by \( a \) because the \( X_0 \) value is much less than the \( a \) value. The temperature dependence of the \( a \) value was analyzed using Eq. (7-7) based on van’t Hoff’s equation:

\[
\frac{\text{d} \ln a}{\text{d}(1/T)} = -\frac{\Delta H}{R}
\]

(7-7)

where \( \Delta H \) is a change in the enthalpy of the rehydration and \( R \) is the gas constant (8.314 J/(mol \cdot K)). The \( a \) values were plotted versus the reciprocal of the absolute temperature (Fig. 7-5). The plots would be separated in 3 regions: high temperature, transition, and low temperature regions. The gelatinization temperatures, \( T_s \) (45.3°C), \( T_p \) (60.5°C), and \( T_c \) (69.8°C), were obtained from the analysis of the DSC curve. The start and end temperatures of the transition region were 45 and 60°C, respectively. These results indicated that starch in
pasta was not gelatinized in the low temperature region but completely gelatinized in the high temperature region. In the low temperature region, the $\Delta H$ value was 1.44 kJ/mol (the value of $a$ at $T = \infty$ was 2.06 kg-H$_2$O/kg-d.m.) and the $a$ value was small. On the other hand, in the high temperature region, the $\Delta H$ value was 25.1 kJ/mol ($R^2 > 0.992$) (the value of $a$ at $T = \infty$ was $3.16 \times 10^4$ kg-H$_2$O/kg-d.m.) and the $a$ value was large.

![Figure 7-5](image)

**Fig. 7-5.** Temperature dependencies of the equilibrium moisture content $a$ (○) and the initial rate of rehydration $a/b$ (△). The $a$ and $a/b$ values were determined at the confidence level of 95%.

The moisture content significantly increases with the starch gelatinization due to the high carbohydrate content of the pasta (72%) [123]. Starch sorbs water reversibly, and the water is mainly held in an amorphous region of the starch at temperatures lower than the gelatinization temperature (i.e., in the low temperature region in Fig. 7-5) [123]. That is, the water would interact with the pasta components by a weak force such as van der Waals' force. The reversible interaction with the weak attractive force resulted in a small $\Delta H$ value and water retention in the pores resulted in a small $a$ value in the low temperature region. On the other hand, the heating of the starch with water at temperatures higher than the gelatinization temperature (i.e., in the high temperature region in Fig. 7-5) causes an irreversible change in
both the amorphous and crystalline regions [57, 123] to break intra- and/or intermolecular hydrogen bonds of amylopectin and amylose, which both maintain the structure of starch. The rehydrated water would form a hydrogen bond with the hydroxyl group of the exposed sugar residues. The force of the hydrogen bond is much stronger than van der Waals’. The irreversible reaction with a strong adhesive force resulted in an extremely large $\Delta H$ value and the swelling by starch gelatinization resulted in a large $a$ value in the high temperature region.

7.3.4. Specific volume of water

Figure 7-6 shows the relationship between the increase in the volume of the pasta and the weight of the rehydrated water. The slope of the line gives the apparent specific volume of water in the pasta. The volumes were $1.02 \pm 1.5 \times 10^{-1}$ and $0.99 \pm 2.2 \times 10^{-2}$ mL/g ($P < 0.05$) at 40°C ($< T_s$) and 80°C ($> T_p$), respectively. Although the difference in the specific volume was not significant, the specific volume at 40°C was larger than that at 80°C. Rehydrated water would fill the pores of the pasta at temperatures lower than the gelatinization temperature, but the water would also penetrate into the gelatinized region of the pasta at higher temperatures. Water which penetrated into the region seemed to result in a smaller volume. However, further studies are required to elucidate the reason for the difference in the specific volume of water in pasta.
7.3.5. Initial rate of rehydration

The initial rate of rehydration, \( v_0 \), which is a derivative of \( X_t \) at \( t = 0 \), is given by the \( a/b \) value (Eq. (7-8)):

\[
v_0 = \left. \frac{dX_t}{dt} \right|_{t=0} = \frac{a}{b}
\]

(7-8)

The temperature dependence of the initial rate of rehydration is reported to be expressed by the Arrhenius equation Eq. (7-9) [27]:

\[
v_0 = \frac{a}{b} = A_0 \exp \left( -\frac{E_a}{RT} \right)
\]

(7-9)

where \( A_0 \) is the frequency factor and \( E_a \) is the activation energy. Figure 7-5 shows the relationship between the initial rate of rehydration and the reciprocal of the absolute temperature. The plots lie on a line \( (R^2 = 0.969) \) in the entire temperature range. The \( E_a \) and \( A_0 \) values were estimated to be 30.5 kJ/mol and \( 1.36 \times 10^{-4} \) m\(^2\) · kg-H\(_2\)O/(s · kg-d.m.), respectively.
The temperature dependence of the $a$ value in the high temperature region was different from that in the low temperature region, being significantly affected by the starch gelatinization. On the other hand, the temperature dependence of $a/b$ could be expressed by Eq. (7-9) in the entire temperature range. This result indicated that the initial rate of rehydration was not affected by the starch gelatinization.

Figure 7-7 shows the pore-size distribution of pasta by mercury intrusion porosimetry, and Fig. 7-8 shows the AFM image of the pasta surface. These results showed that pasta was a porous material and the pores of around 0.7 μm were distributed on the surface. The water diffused from the surface to the center of the pasta through the pores would form the hydrogen bond with a hydroxyl group at temperatures higher than the gelatinization temperature. The hydration rate is, however, assumed to be much faster than the diffusion rate of water. Thus, the rate of rehydration was governed by the diffusion rate of water, although the equilibrium moisture content was limited by the state of the starch gelatinization. Therefore, the initial rate of rehydration was not slightly affected by the starch gelatinization.

![Image of pore-size distribution](image.png)

**Fig. 7-7.** The pore-size distribution of pasta by the mercury intrusion porosimetry, where $V$ is the cumulative intrusion of mercury. The median and mode radii were 0.66 and 0.75 μm, respectively.
The initial rate of rehydration has a close relationship to the optimal rehydration time because *al dente* is the state at the early stage of the rehydration. The initial rate of rehydration was significantly affected by the diffusion rate of water through the pores. Therefore, in order to shorten the rehydration time, it would be necessary to enlarge the pores of pasta.

![AFM image of the pasta surface](image)

*Fig. 7-8.* AFM image of the pasta surface. The *x* and *y* scan sizes were both 5 μm. The *z* max was 308.90 nm.

### 7.4. Conclusions

The loss of pasta mass should be considered to predict the moisture content of the pasta with a high accuracy. The equation to predict the amount of loss of pasta mass during rehydration which was proportional to the surface area of pasta was proposed. The leakage of pasta components into rehydrated water during rehydration was thought to be the mechanical change such as exfoliation. The equilibrium moisture content showed the temperature dependence of van’t Hoff type separately at the temperatures higher than *T*<sub>p</sub> and lower than *T*<sub>s</sub>. The initial rate of rehydration showed a temperature dependence of the Arrhenius type in the temperature range of 20-90°C. The rate of rehydration was governed by the water diffusion through the pores of the pasta, because the hydration rate seemed to be much faster than the diffusion rate of water. On the other hand, the equilibrium moisture content was limited by
the state of starch gelatinization at any temperature. The empirical equation, the parameters of which were the diameter of pasta, rehydration time, and temperature of the rehydrated water, was proposed to predict the moisture content, taking into consideration the effect of starch gelatinization.
CHAPTER 8

Effect of salts on rehydration kinetics of pasta

8.1. Introduction

The rehydration process of pasta at various temperatures has been measured and a hyperbolic equation in terms of the rehydration time for empirically describing the change in the moisture content with time has been proposed in chapter 7. This equation contained two parameters to reflect the equilibrium moisture content and the initial rehydration rate. Evaluating these parameters at various temperatures indicated the equilibrium moisture content of pasta to be controlled by water diffusion at low temperatures, but by gelatinization of the starch at high temperatures. The evaluation also indicated the initial rehydration rate to be governed only by the diffusion of water into the pasta.

Although previous studies [28, 29, 52, 124] have been performed by using demineralized water, dried pasta is usually cooked in water containing 0.1-1% (w/v) NaCl. The aim of this present study was therefore to reveal the effect of salts on the rehydration kinetics of dried pasta. The rehydration process was measured in a 1.83 mol/L NaCl solution, equivalent to 10% (w/v), at 20-90°C. The process was also measured in water containing LiCl, KCl, NaBr, or NaI at 1.83 mol/L. Although salts other than NaCl were unrealistic for cooking and their concentrations were extremely high, the conditions were adopted in order to understand the role of NaCl and the other salts in the rehydration process of pasta.

8.2. Materials and Methods

8.2.1. Materials

Commercially available pasta (Ma·Ma spaghetti, Nisshin Foods, Tokyo, Japan), whose carbohydrate content was 72% (w/w), was used in all the experiments. The initial diameter of the cylindrical pasta was approximately 1.6 mm (lot no. T1332N). The chosen salts were of analytical grade (Wako Pure Chemical Industries, Osaka, Japan) and each was dissolved in
8.2.2. Rehydration of salt solution

Culture tubes containing about 50 mL of each salt solution were equilibrated in a temperature range of 20-90°C in an SD ther mominder and Personal-11 water bath (Taitec, Saitama, Japan). A 9-cm-long sample, weighing approximately 0.26 g, was immersed in each tube (15 tubes were prepared under each specific condition). The sample was removed from the salt solution at specified times, immediately blotted to remove any superficial salt solution, and weighed. Each sample was dried in a DO-300FA convection drying oven (As One, Japan) at 105°C for 4 d, and then weighed. The initial water content of the pasta based on a dry solid, $w_0$, was determined by drying approximately 0.2 g of the sample at 105°C for 4 d. The initial water content was measured in triplicate.

8.2.3. Amount of rehydrated solution

Some of the pasta components leaked into the solution during rehydration, resulting in a loss of mass. The amount of loss in the pasta mass is generally significant, although a small amount of loss is preferred for high-quality cooked pasta [122]. This loss of pasta mass became more significant during the latter stage of rehydration [52]. The amount of the rehydrated solution, $w_t$, at any time $t$ was estimated by taking into consideration this loss under the assumptions that the concentration of the salt solution was the same as that in the bulk solution, and that only water was evaporated and salt remained in the sample when the sample was dried. The $w_t$ term, therefore, has units of kg-solution/kg-d.m.

8.2.4. Differential scanning calorimetry

The gelatinization of pasta, which had been ground into a fine powder with a pestle and mortar, was measured by differential scanning calorimetry (DSC-50, Shimadzu, Kyoto, Japan). A 1.5-mg ground sample was accurately weighed with a TGA-50 thermogravimetric analyzer (Shimadzu) and moistened with a salt solution at a weight ratio of the dry sample to salt solution of around 1:6.5. The sample was sealed in a 201-53090 aluminum cell
(Shimadzu) which was sealed with an SSC-30 sealer crimper (Shimadzu). The cell was placed in a DSC pan with a reference cell which contained the same amount of distilled water as the sample. The samples were heated in the DSC at 5 °C/min from 20°C to 120°C. The starting and peak temperatures for the endothermic peak, $T_s$ and $T_p$, respectively, were computed by using the analysis software supplied with the instrument. Each experiment was carried out in duplicate.

8.2.5. **Statistical analysis**

The parameters for a non-linear equation were estimated to best-fit the calculated curve to the experimental points by using Solver of Microsoft Office Excel® 2007, and the flat-surface regression between the observed and calculated values was obtained by using Origin 8.1 (OriginLab, Northampton, MA, USA). The accidental error of the coefficient was evaluated with a confidence level of 95% ($p < 0.05$) by linearization [120]. The fit of the curve to the experimental points was evaluated on the basis of the coefficient of determination ($R^2$) and the root-mean-square deviation (RMSD) which is defined as [121]:

$$\text{RMSD} = \frac{1}{n} \sqrt{\sum_{i=1}^{n} (w_i - w_{pi})^2}$$ (8-1)

where $n$ is the number of experimental points, $w_i$ is the experimental $w_i$ value, and $w_{pi}$ is the predicted value.

8.3. **Results and Discussion**

8.3.1. **Rehydration kinetics of pasta**

Figure 8-1 shows the changes in the amount of the solution rehydrated by pasta immersed in the 1.83 mol/L NaCl solution at various temperatures. Since the initial diameter of the pasta was slightly different from sample to sample, $w_i$ was plotted versus the rehydration time divided by the square of the initial diameter according to chapter 7. The $w_i$ values gradually increased with increasing temperature from 20°C to 60°C, and markedly increased at temperatures above 60°C. The $w_i$ values for the pasta immersed in NaCl solutions of various concentrations were also measured at 80°C (Fig. 8-2). The $w_i$ values increased with
Fig. 8-1. Amount of the rehydrated solution of dried pasta at 90°C (○), 80°C (△), 70°C (□), 60°C (▷), 55°C (◇), 50°C (▽), 40°C (◆), and 20°C (◁) in a 1.83 mol/L NaCl solution.

Fig. 8-2. Amount of the rehydrated solution of dried pasta at 80°C in 0 (●), 0.09 (○), 0.88 (◇), 1.83 (△), and 3.92 (□) mol/L NaCl solutions.
decreasing NaCl concentration.

According to the results of chapter 7, the rehydration processes shown in Figs. 8-1 and 8-2 can be expressed by Eq. (8-2).

\[ w_t = \frac{a(t/d^2)}{b + (t/d^2)} + w_0 \]  

(8-2)

where \( t \) is the time, \( d \) is the initial diameter of the dried pasta, and \( a \) and \( b \) are constants. The \( a \) and \( b \) values for each rehydration process were estimated to best-fit the calculated \( w_t \) values to the experimental ones. The curves in the figures have been drawn by using the estimated \( a \) and \( b \) values. Minimum correlation coefficient \( R^2 \) and maximum RMSD for the observed and calculated values in Figs. 8-1 and 8-2 were 0.993 and 0.029, respectively. These values indicate the accuracy of Eq. (8-2) for describing the experimental rehydration kinetics under any condition. The equilibrium amount of the rehydrated solution at \( t = \infty \), \( w_e \), and the initial rehydration rate, which is a derivative of \( w_t \) at \( t = 0 \), \( v_0 \), are respectively given by Eqs. (8-3) and (8-4) [52].

\[ w_e = \lim_{t \to \infty} w_t = a + w_0 \approx a \]  

(8-3)

\[ v_0 = \frac{dw_t}{d(t/d^2)} \bigg|_{t=0} = \frac{a}{b} \]  

(8-4)

8.3.2. Temperature dependence of the equilibrium amount of rehydrated solution

The temperature-dependence characteristics of the equilibrium amount of the rehydrated solution, \( a \), in water and in the 1.83 mol/L NaCl solution are shown in Fig. 8-3. The \( a \) values in water are cited from the results of chapter 7. The temperature dependence of the \( a \) value can be divided into three regions: low- and high-temperature regions and their transition region. The boundary temperatures of the transition region for rehydration in water, 45.3°C and 60.5°C, are the same as the starting and peak temperatures for gelatinization, \( T_s \) and \( T_p \), observed by DSC for the mixture of water and ground pasta [52]. The transition could therefore be ascribed to the gelatinization of starch. The boundary temperatures for rehydration in the 1.83 mol/L NaCl solution were approximately 62°C and 70°C which are also the same as the respective \( T_s \) (62.2°C) and \( T_p \) (70.8°C) values obtained by DSC.
Fig. 8-3. Temperature dependence of the $a$ ($\circ$, ⭕) and $a/b$ ($\triangle$, ▲) values. The unfilled and filled symbols represent rehydration in the 1.83 mol/L NaCl solution and in water, respectively. The data in water were taken from Fig. 7-5.

At temperatures higher than the boundary value, gelatinization of the starch played an important role in the rehydration kinetics of pasta because of its high carbohydrate content. The plots of the logarithmic $a$ values versus the reciprocal of the absolute temperature, $T$, in the low- and high-temperature regions lay on separate lines. The slope of each line corresponds to the change in the enthalpy of rehydration, $\Delta H$, based on the following equation:

\[
\frac{\text{d} \ln a}{\text{d}(1/T)} = -\frac{\Delta H}{R}
\]

where $T$ is the absolute temperature, $\Delta H$ is the change in enthalpy, and $R$ (8.314 J/mol·K) is the gas constant. The $\Delta H$ values in the low- and high-temperature regions for rehydration in the 1.83 mol/L NaCl solution were respectively evaluated to be 1.08 and 33.1 kJ/mol. The $\Delta H$ value in the NaCl solution was nearly equal to that in water (1.44 kJ/mol [52]) in the low-temperature region, while the $\Delta H$ value in the NaCl solution was higher than that in water (25.1 kJ/mol [52]) in the high-temperature region. The $\Delta H$ value in the
high-temperature region, being much greater than that in the low-temperature region, reflects the gelatinization enthalpy of starch, because hydrogen bonds among the hydroxyl groups of the starch are reconstructed by gelatinization at temperatures higher than $T_s$ [52]. It has been reported that the gelatinization enthalpy obtained in a ca. 2.0 mol/L NaCl solution was 0.94 J/g greater than that obtained in water [125]. The results in that report are basically consistent with these observations in this study. The difference between the $\Delta H$ value in the high-temperature region in the NaCl solution and that in water is assumed to reflect the difference in the gelatinization enthalpy.

Table 8-1 lists the equilibrium amounts of the rehydrated solution, $a$, for rehydration at 55°C and 60°C in the various salt solutions. The $a$ value for rehydration in salt solutions of the alkaline metal ions with chloride is in the order of LiCl < NaCl < KCl. The halogen ion of the sodium salt also affected the $a$ value in the order of NaCl < NaBr < NaI. These orders are in reverse to the Hofmeister (lyotropic) series [126-129], where Li$^+$ > Na$^+$ > K$^+$ for alkaline metal ions with the same anion counterpart and Cl$^-$ > Br$^-$ > I$^-$ for halogen ions coupled with a constant cation.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Salt</th>
<th>Equilibrium amount of rehydrated solution $a$ [kg-solution/kg-d.m.]</th>
<th>Initial rehydration rate $a/b$ [m$^2$·kg-solution/(kg-d.m.·s)]</th>
<th>RMSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>60°C</td>
<td>LiCl</td>
<td>1.16 ± 0.06</td>
<td>(1.24 ± 0.22) × 10$^9$</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>1.22 ± 0.06</td>
<td>(1.43 ± 0.37) × 10$^9$</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>KCl</td>
<td>1.43 ± 0.04</td>
<td>(1.86 ± 0.19) × 10$^9$</td>
<td>0.006</td>
</tr>
<tr>
<td>55°C</td>
<td>NaCl</td>
<td>1.01 ± 0.05</td>
<td>(1.57 ± 0.26) × 10$^9$</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>NaBr</td>
<td>4.63 ± 1.35</td>
<td>(1.33 ± 0.31) × 10$^9$</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>NaI</td>
<td>9.43 ± 1.68</td>
<td>(3.68 ± 0.74) × 10$^9$</td>
<td>0.033</td>
</tr>
</tbody>
</table>
8.3.3. Initial rehydration rate

Figure 8-3 also shows the temperature dependence of the initial rehydration rates in water and in the 1.83 mol/L NaCl solution. The plots of the \( a/b \) values, which correspond to the initial rehydration rates, lie on a line in the tested temperature range for each case. This fact would indicate that the rate of starch gelatinization in the high-temperature region was much faster than that of water diffusion and that the initial rehydration rate was governed by this diffusion. The activation energy values for the diffusion were evaluated from the slope of the lines to be 30.5 [52] and 25.6 kJ/mol for the respective rehydration in water and in the 1.83 mol/L NaCl solution.

Based on Fick’s second law of diffusion, apparent diffusion coefficient \( D_a \) can be estimated for cylindrical pasta according to the following equation [85]:

\[
\frac{w_t - w_e}{w_0 - w_e} = 4 \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp \left( -\frac{\beta_n^2 D_a t}{(d/2)^2} \right)
\]

where \( \beta_n \) is the Bessel function roots (\( \beta_1 = 2.4048 \)). Equation (8-6) can be approximated by only the first term in the series for long times or small diameters. The \( D_a \) value was thus estimated by plotting \( (w_t - w_e)/(w_0 - w_e) \) versus time \( t \) for rehydration [28].

Figure 8-4 shows that the plot for a specific NaCl concentration gave a straight line with an \( R^2 \) value > 0.977 to estimate the \( D_a \) value. The \( D_a \) value at 80°C was lower with higher NaCl concentrations. Both the sodium and chloride ions are larger in volume than water. Since the sodium ion positively hydrates, it would migrate in the solution accompanied by several water molecules. The sodium ion also migrates together with the chloride ion due to electro-neutrality. The presence of more NaCl would thus restrict water diffusion, resulting in the lower \( D_a \) value.

The \( D_a \) values at 60°C were obtained in 1.83 mol/L LiCl, NaCl, and KCl solutions (Fig. 8-5). The \( D_a \) value was higher for the salt of an alkaline metal ion with chloride having a larger crystal radius. This trend would not be reasonably acceptable. As already mentioned, the alkaline metal ions migrated in water in the hydrated state. Therefore, the \( D_a \) values are plotted versus the Stokes radii of the hydrated ions [130] in Fig. 8-5. The \( D_a \) value in the salt solution with the larger hydrate radius was lower, indicating that hydration of the ions played an important role in the rehydration of pasta.
Fig. 8-4. Estimation of the apparent diffusion coefficients for rehydration at 80°C in 0 (●), 0.09 (○), 0.88 (◇), 1.83 (△), and 3.92 (□) mol/L NaCl solutions.

Fig. 8-5. Relationships between the apparent diffusion coefficient at 60°C, the crystalline radius (filled symbols) and the stokes radius (unfilled symbols) for 1.83 mol/L LiCl (○), NaCl (□), and KCl (△) solutions.
8.3.4. Estimation of the amount of rehydrated solution under any condition

Coefficients $a$ and $b$ for the high-, transition-, and low-temperature regions were formulated as functions of temperature $T$ and NaCl concentration $C$ by the following equations:

$$\ln a = p_1 - p_2T - p_3C \quad (8-7a)$$

$$\ln b = q_1 - q_2T - q_3C \quad (8-7b)$$

The values for $p_1$ to $p_3$ and $q_1$ to $q_3$ are listed in Table 8-2. Minimum $R^2$ or maximum RMSD for the $a$ and $b$ values were 0.995 or 0.012 and 0.869 or 0.024, respectively, and good correlation for both $a$ and $b$ were obtained between the observed and calculated values as shown in Fig. 8-6. Equations (8-7a) and (8-7b) enable us to predict the rehydration processes for pasta under any conditions of temperature and NaCl concentration.

![Graph](image-url)

**Fig. 8-6.** Correlation between the observed and calculated values for $a$ (unfilled symbols) and $b$ (filled symbols) in the high-temperature ($\bigodot$, $\bullet$), transition-temperature ($\triangle$, $\blacktriangle$), and low-temperature ($\lozenge$, $\blacklozenge$) regions.
Table 8-2. Coefficients $p_1$ to $p_3$ and $q_1$ to $q_3$ for correlating parameters $a$ and $b$ with temperature $T$ and NaCl concentration $C$.

<table>
<thead>
<tr>
<th>Region</th>
<th>$p_1$</th>
<th>$p_2$</th>
<th>$p_3$</th>
<th>$q_1$</th>
<th>$q_2$</th>
<th>$q_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>High temp.</td>
<td>$1.04 \times 10^1$</td>
<td>3.03</td>
<td>$4.25 \times 10^{-2}$</td>
<td>$1.72 \times 10^1$</td>
<td>1.33</td>
<td>$2.02 \times 10^{-1}$</td>
</tr>
<tr>
<td>Transition</td>
<td>$2.81 \times 10^1$</td>
<td>9.19</td>
<td>$5.56 \times 10^{-1}$</td>
<td>$3.60 \times 10^1$</td>
<td>4.90</td>
<td>$3.45 \times 10^{-1}$</td>
</tr>
<tr>
<td>Low temp.</td>
<td>1.14</td>
<td>$2.87 \times 10^{-1}$</td>
<td>$7.37 \times 10^{-2}$</td>
<td>$1.29 \times 10^1$</td>
<td>2.49</td>
<td>$2.47 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

8.4. Conclusions

The equilibrium amount of the rehydrated solution showed separate temperature dependence of the van’t Hoff type at temperatures higher than $T_p$ and lower than $T_s$. At temperatures higher than $T_p$, the change in enthalpy of the rehydration, $DH$, in the 1.83 mol/L NaCl solution was 33.1 kJ/mol, this being greater than the $DH$ value in water. The initial rehydration rate showed temperature dependence of the Arrhenius type in the temperature range of 20-90°C. The activation energy for rehydration, $E$, in the salt solution was 25.6 kJ/mol, which is slightly lower than the $E$ value in water. The Hofmeister series of ions provides an index for their effect on the equilibrium amount of rehydrated solution of pasta. The apparent diffusion coefficient of water into pasta was not correlated with the crystal radii of the salts, but with the Stokes radii of the hydrated ions. Equations were also formulated to predict the rehydration kinetics under any conditions of temperature and NaCl concentration.
CHAPTER 9

Rehydration kinetics of pasta prepared under different drying conditions

9.1. Introduction

Pasta is also dried under various conditions, where both temperature and humidity are changed with time. Dried pasta is eaten after cooking or rehydration. Drying conditions affect the properties of cooked pasta. The properties of cooked pasta or the differences in the properties of pasta were compared before and after cooking [14, 15, 38-40]. However, quantitative studies on the rehydration of pasta prepared under various drying conditions are insufficient.

Peleg’s [9-12] and Weibull’s [9-8] models were used to express the rehydration processes of some dried foods [32, 131-134]. However, the temperature dependence of the rehydration behavior, particularly the effects of starch gelatinization on this behavior, has not fully been assessed. The expression of a hyperbolic type, in which the rehydration time was divided by the square of the initial diameter of pasta, was reported in chapter 7 and 8 to be useful for describing the rehydration processes of pasta having different initial diameters and estimating the equilibrium moisture content and the initial rate of rehydration [52].

In this study, the rehydration processes of pasta dried under different conditions were measured and analyzed based on the kinetic expression of hyperbolic type in order to elucidate the effects of the drying conditions on the rehydration of pasta.

9.2. Materials and Methods

9.2.1. Materials

Three types of pasta processed under different programmed drying conditions were supplied by Nisshin Foods Co., Ltd. (Tokyo, Japan). The maximum temperature and duration were 50°C and 20 h, 70°C and 11 h, and 85°C and 6 h for the pasta prepared under low-,
high-, and very-high-temperature conditions, respectively. The pasta is designated as LT-, HT-, and VHT-pasta, respectively. The initial diameters of the pasta were about 1.6 mm, which was exactly measured for each sample.

9.2.2. Differential scanning calorimetry

The gelatinization of pasta samples was measured using a DSC-50 different scanning calorimeter (Shimadzu, Kyoto, Japan). The sample was ground into a fine powder using a pestle and mortar. The ground sample was accurately weighed (1.5 mg) using a TGA-50 thermogravimetric analyzer (Shimadzu) and moistened with distilled water at a weight ratio of dry sample to water of around 1:6. The sample was sealed into an aluminum cell (sealed cell 201-53090; Shimadzu) using a SSC-30 sealer crimper (Shimadzu). The cell was placed on a DSC pan with another cell in which the same amount of distilled water was sealed as a reference. The samples were heated in the DSC at 5 °C/min from 31.5 to 120°C. The onset, peak, and conclusion temperatures for an endothermic peak were computed using analysis software supplied with the instrument. Each experiment was repeated at least twice.

9.2.3. Rehydration

The initial moisture contents of pasta based on the dry solid, \( X_0 \), were determined by drying 0.3 g of sample, the weight of which had been accurately measured, in a convection drying oven (DO-300FA; As One, Osaka, Japan) at 105°C for 3 days. The measurement was repeated five times. Culture tubes containing 50 cm\(^3\) of distilled water were equilibrated at a temperature from 20°C to 90°C at 10°C-intervals in an SD thermominder and Personal-11 water bath (Taitec, Saitama, Japan), and at 97°C in a stainless-steel tray placed on a digital hot plate (DP-1S; As One). A sample cut into an 8-cm sections was weighed \( W_1 \) and immersed into a tube (about 15 tubes were prepared under a specific condition). At a given time, the sample was removed from the tube, immediately blotted to remove any superficial water, and weighed, \( W_2 \). Samples were dried in a convection drying oven at 105°C for 3 days and weighed, \( W_3 \).

The moisture content of pasta, \( X_t \), was calculated by Eq. (9-1).
Weight loss occurred during rehydration due to leakage of constituents from the pasta, and the amount of loss of pasta mass at any time, $M_t$, was calculated by the following equation:

$$M_t = \frac{W_1 - W_2(1 + X_0)}{W_1}$$

(9-2)

9.3. Results and Discussion

9.3.1. Differential scanning calorimetric measurement

Figure 9-1 shows DSC thermograms of ground LT-, HT-, and VHT-pasta. The onset, peak, and conclusion temperatures were 51.1, 59.8, and 67.0°C for LT-pasta, 51.7, 59.5, and 68.5°C for HT-pasta, and 52.1, 60.3, and 70.0°C for VHT-pasta, respectively. The gelatinization temperatures tended to be higher for pasta prepared at higher temperatures, as shown by broken lines, and a similar trend was reported by Petitot et al. [37] and Guler et al. [14]. This suggests that the structure of starch is more rigid in pasta dried at higher temperatures.

9.3.2. Rehydration at various temperatures

Figure 9-2 shows the loss of pasta mass during rehydration at 80°C for the LT-, HT-, and VHT-pasta. Loss of pasta mass was measured for all the pasta samples at the temperatures at which the rehydration was measured. The amount of loss for any pasta could be empirically expressed as a function of rehydration time, $t$, and the initial diameter of the pasta, $d$, by Eq. (9-3) [52].

$$M_t = M_e \left[ 1 - \exp \left( -\frac{kt}{d^2} \right) \right]$$

(9-3)

where $M_e$ is the equilibrium loss of pasta mass, and $k$ is the rate constant. The parameters, $k$ and $M_e$, were evaluated to best-fit the calculated $M_t$ values to the experimental ones using the Solver in Microsoft Excel®, and the values at 80°C are listed in Table 9-1. The equilibrium loss of pasta mass was smaller for the pasta dried at higher temperature as Guler et al. [14]
Fig. 9-1. DSC thermograms of pasta dried under low- (a), high- (b), and very-high-temperature (c) conditions.

Fig. 9-2. Loss of pasta mass during rehydration at 80°C for pasta dried under low- (△), high- (□), and very-high-temperature (◇) conditions.
Fig. 9-3. Rehydration processes of pasta dried under low- (a), high- (b), and very-high-temperature (c) conditions at 20°C (▲), 30°C (▼), 40°C (○), 50°C (□), 60°C (△), 70°C (◇), 80°C (◇), 90°C (◇), and 97°C (◇).
had reported. The structure formed by protein in pasta would affect the loss of its mass during cooking [135], and drying at higher temperature more significantly denatured protein [38, 136]. Therefore, it is thought that the firmer network of gluten formed during drying at higher temperature resulted in a lower loss of pasta mass. Although the rate constant, $k$, tended to be larger for the pasta dried at higher temperature, the difference in $k$ value was not significant.

Figure 9-3 shows the rehydration processes of the LT-, HT-, and VHT-pasta at various temperatures. As defined by Eq. (9-1), the moisture content, $X_t$, was expressed as the amount of water rehydrated per unit weight of dry material, taking the loss of pasta mass into consideration. The initial diameter of pasta, which was slightly different sample by sample, affects the rehydration kinetics. Therefore, the $X_t$ values were plotted against rehydration time divided by the square of the initial diameter according to chapter 7. For all pasta samples, rehydration progressed more quickly at higher cooking temperatures. At a specific temperature, the pasta dried at lower temperature was more likely to rehydrate water. The rehydration processes were input into the following hyperbolic-type equation [52]:

$$X_t = \frac{a \times (t/d^2)}{b + (t/d^2)} + X_0$$  \hspace{1cm} (9-4)

where $a$ and $b$ are constants. The constants were estimated to best-fit the calculated $X_t$ values to the experimental values using the Solver in Microsoft Excel®. Solid curves in Fig. 9-3 were drawn using the estimated $a$ and $b$, and the coefficient of determination, $R^2$, was larger than 0.97 for any rehydration process.

**9.3.3. Temperature dependencies of equilibrium moisture content and initial rate of rehydration**

As shown in Fig. 9-3, Eq. (9-4) was adequate for empirically characterizing the rehydration process of any pasta at various cooking temperatures, and the $a$ and $b$ values for any data set shown in Fig. 9-3 were evaluated. The equilibrium moisture content, $X_e$, is defined as the moisture content at $t = \infty$ and is given by $a + X_0$. In any case, the $X_e$ value was assumed to be equal to the $a$ value because the $X_0$ value was much less than the $a$ value. The $a$ values were plotted against the reciprocal of the cooking absolute temperature, $T$, (Fig. 9-4). For any pasta, the plots were separated into low temperature, transition, and high temperature
Fig. 9-4. Temperature dependence of equilibrium moisture content for pasta dried under various conditions. Symbols are the same as in Fig. 9-2.

Table 9-1. Equilibrium loss of pasta mass, $M_e$, and rate constant $k$ for the loss of pasta mass at 80°C, and the change in enthalpy for equilibrium moisture content, $\Delta H$, and activation energy, $E$, and the frequency factor, $A_0$, for initial rehydration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Loss of pasta mass</th>
<th>$\Delta H$ [kJ/mol]</th>
<th>$E$ [kJ/mol]</th>
<th>$A_0$ $[m^2 \cdot kg-H_2O/(s \cdot kg-d.m.)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_e$ [kg/kg-i.m.]</td>
<td>$K \times 10^{-10}$ [m$^2$/s]</td>
<td>Low temperature region</td>
<td>High temperature region</td>
</tr>
<tr>
<td>LT-pasta</td>
<td>0.164</td>
<td>8.58 ± 4.70</td>
<td>4.12</td>
<td>20.5</td>
</tr>
<tr>
<td>HT-pasta</td>
<td>0.145</td>
<td>9.16 ± 3.55</td>
<td>1.66</td>
<td>20.9</td>
</tr>
<tr>
<td>VHT-pasta</td>
<td>0.116</td>
<td>10.8 ± 4.04</td>
<td>3.09</td>
<td>27.1</td>
</tr>
</tbody>
</table>

regions [52]. The temperature of the transition regions ranged from 40°C to 60°C, which corresponded to the gelatinization temperatures observed by differential scanning calorimetry. Therefore, the temperature dependence of the equilibrium moisture content was analyzed separately in the low and high temperature regions according to the van’t Hoff equation.
\[
\frac{d \ln X_e}{d(1/T)} \approx \frac{d \ln a}{d(1/T)} = -\frac{\Delta H}{R}
\]

where \(\Delta H\) is the change in enthalpy of rehydration and \(R\) is the gas constant. The \(\Delta H\) values in the low and high temperature regions were evaluated from the slopes of the lines in Fig. 9-4 for the LT-, HT-, and VHT-pasta (Table 9-1). The \(\Delta H\) value of the VHT-pasta was large when compared with those of the LT- and HT-pasta.

The \(\Delta H\) values in the high temperature regions were much larger than those in the low temperature region. Because of the high carbohydrate content of pasta, starch gelatinization plays an important role in rehydration. In the low temperature region, water molecules would reversibly interact with carbohydrates via a weak force such as van der Waals’ force, and the weak interaction resulted in a small \(\Delta H\) value. On the other hand, the hydrogen bonds of water molecules with carboxyl groups of starch are easily formed in the high temperature region higher than the gelatinization temperature, and a large \(\Delta H\) value would be ascribed to the strong adhesive force. The \(\Delta H\) value for gelatinization was larger for the pasta dried at higher temperature [14, 37]. Although the \(\Delta H\) value for gelatinization has a different meaning from the \(\Delta H\) value for rehydration, the drying temperature also seems to affect the \(\Delta H\) value for rehydration.

The initial rate of rehydration, \(v_0\), is given by differentiating Eq. (9-4) at \(t = 0\) to be \(a/b\). Figure 9-5 shows the relationships between the \(v_0\) values and the reciprocal of the cooking absolute temperature. For each pasta, the plots lay on a straight line, indicating that the temperature dependence of the \(v_0\) value could be expressed by the Arrhenius equation.

\[
v_0 = \left. \frac{dX_e}{d(t/d^2)} \right|_{t=0} = \frac{a}{b} = A_0 \exp \left( -\frac{E}{RT} \right)
\]

where \(E\) is the activation energy and \(A_0\) is the frequency factor. The \(E\) and \(A_0\) values for the LT-, HT-, and VHT-pasta are listed in Table 9-1. Because pasta has pores and the diffusion of water in the pores is the rate-limiting step in the early stages of rehydration [137], the activation energy for the initial rehydration would reflect the water diffusion in the pores. However, there were no significant differences in \(E\) value among the LT-, HT-, and VHT-pasta. Therefore, the maximum temperature during drying would scarcely affect the initial water intake of pasta.
9.4. Conclusions

The loss of pasta mass during rehydration was lower for the pasta dried at higher temperature. Rehydration temperature markedly affected the change in enthalpy of rehydration, $\Delta H$, for the pasta dried at any temperature, and the $\Delta H$ values were estimated in the regions lower and higher than the gelatinization temperature. The $\Delta H$ value in the high temperature region was affected by the drying temperature, and the $\Delta H$ value was large for the pasta dried under the very-high-temperature conditions. The initial rate of rehydration, which was governed by water diffusion into pasta pores, scarcely depended on the maximum temperature of drying.
CHAPTER 10

Properties and rehydration characteristics of pasta prepared using various dies

10.1. Introduction

Pastas prepared using the dies made of Teflon and bronze have smooth and rough surfaces, respectively. It has been reported that pasta prepared using the bronze die has higher porosity, lower density, lower rupture strength, and larger effective diffusion coefficient of water during drying than that prepared using the Teflon die [6, 7]. These facts suggest that the die material affects inner structure of pasta as well as the surface structure. Dry pasta is consumed after rehydration. However, effects of die material, which is used for extruding the durum semolina dough, on the rehydration behaviors of dry pasta have not sufficiently been examined.

The objective of this study is to examine the effects of the die material on the properties of fresh pasta and the rehydration behaviors of the dried ones. Aluminum, polypropylene, and polycarbonate dies were used as well as Teflon and bronze dies, which have been usually used, for prepare the pastas having different properties.

10.2. Materials and Methods

10.2.1. Materials

Durum wheat semolina was supplied by Nisshin Foods, Inc., Tokyo, Japan. Sodium chloride was purchased from Nacalai Tesque, Inc., Kyoto, Japan.

10.2.2. Preparation of pasta

Durum wheat semolina (700 g) and water (224 g) were mixed using a kitchen-aid blender (KSM150, FMI, Tokyo, Japan) for 20 min. The mixture was then put into a pasta-making machine (Magica, Bottene, Italy) equipped with a die made of Teflon,
polypropylene, polycarbonate, aluminum, or bronze and extruded under reduced pressure (60 kPa) through the die to prepare the fresh pasta. The orifice diameter and length of each die were 1.8 and 5 mm, respectively. The fresh pasta was dried in a temperature-humidity controllable chamber (SH-641, Espec, Osaka, Japan) to produce the dried product having the moisture content of $0.120 \pm 0.004$ kg-H$_2$O/kg-d.m. under the conditions that the temperature and humidity were increased from 50 to 85°C and 40% to 75%, respectively, during the first 50 min, were kept at 85°C and 75% for 250 min, decreased to 60°C and 65%, and kept at the levels for 10 min.

10.2.3. Observation of surface morphology

The surface of the pasta was observed at 200- or 1000-fold magnification and recorded using a VHX-1000 digital microscope (Keyence Corp., Osaka, Japan). The pasta was also cut and the bright-field image of the cross-section was observed at 100-fold magnification using an SUR-KE optical microscope (Nikon, Tokyo).

10.2.4. Extrusion velocity

Pasta extruded from the pasta-making machine was cut every 5 s, and the length of the pasta stick was measured with a ruler to calculate the extrusion velocity. The measurement was repeated 11 times for each sample.

10.2.5. Apparent bulk density

The apparent bulk density of the pasta was measured by a powder-substitution method using cross-linked polymethylmethacrylate particles having a mean diameter of 50 μm and a 5-mL graduated cylinder. The density of the particles was 0.769 g/mL. Pasta of about 3.5 g, which was precisely weighed, was put into the cylinder and the void space was tightly filled with particles (about 1 g) under vibration. The bulk density was evaluated from the sample weight and the sample volume calculated from the weight of the particles. The measurement was repeated 5 times for each sample.
10.2.6. Rupture strength

The breaking load and strain of the pasta prepared using Teflon, polycarbonate, and bronze dies were measured using a rheometer (RE2-33005S Rheoner II, Yamaden, Tokyo) fitted with a No. 49 plunger and a 20-N load cell at the moving velocity of 0.5 mm/s. The measurement was repeated 12 times for each sample.

10.2.7. Gelatinization temperature

The pasta was ground in a mortar using a pestle. The ground pasta of about 1.5 mg, which had been precisely measured, and distilled water of tenfold weight (ca. 15 mg) were placed in an aluminum cell (201-53090, Shimadzu, Kyoto), and then the cell was tightly sealed using a clamper (SSC-30, Shimadzu). The cell was kept at 4°C for 5 h or longer. A differential scanning calorimetric measurement was carried out using a DSC-50 calorimeter (Shimadzu). Distilled water of the same weight as that in the sample was used as a reference. The temperature was changed from 30 to 120°C at the rate of 5 ºC/min. The measurement was repeated 5 times for each sample.

10.2.8. Rehydration curve

The initial moisture content of pasta, $X_0$, was measured as follows: pasta of about 5 g, which was weighed ($W_1$) to an accuracy of 1 mg, was dried at 105°C for 4 d in a DN400 convection drying oven, and the bone-dry weight of the pasta ($W_0$) was measured. The $X_0$ was estimated by the following equation:

$$X_0 = \frac{W_1 - W_0}{W_0}$$

(10-1)

Culture tubes containing about 50 cm$^3$ of 0.5% (w/v) sodium chloride were put in a stainless steel container filled with boiling water, which was heated using a DP-1S hot-stirrer (As One, Osaka). The temperature of the sodium chloride solution was regulated at 99.7 ± 0.3°C, which was measured using a CT-1200D digital temperature indicator (Custom, Tokyo). The pasta was cut into 8-cm-long sticks. The initial diameter and length of the pasta were measured in several places of a stick using a CD-S15C vernier caliper (Mitsutoyo, Kanagawa,
Japan) for 50 samples. The surface area of the stick, \( S \), was calculated from the mean diameter and length without respect to surface asperity assuming a columnar shape. The weight of each stick, \( W_1 \), was measured. The stick was placed into the culture tube. At a given time, the sample was removed from the tube, immediately blotted to remove any superficial water and weighed, \( W_2 \). The samples were dried in the oven at 105°C for 4 d, and then weighed, \( W_3 \). The amount of water rehydrated at any time, \( t \), was defined in 2 ways. One was the moisture content based on the bone-dry weight of the sample, \( X_t \), and the other was the amount of water rehydrated per unit surface area (\( S \)), \( x_t \). They were calculated by Eqs. (10-2) and (10-3), respectively.

\[
X_t = \frac{W_2 - W_3}{W_3} \tag{10-2}
\]

\[
x_t = \frac{W_3 - W_1}{S} \tag{10-3}
\]

The plots of the moisture content based on the bone-dry weight of the sample, \( X_t \), of the rehydration time, \( t \), divided by the square of the initial diameter, \( d^2 \), could be expressed by Eq. (10-4) of the hyperbolic type [52]. The constants, \( a \) and \( b \), were determined to best-fit the calculated curve to the experimental points using Solver of Microsoft Excel®.

\[
X_t = \frac{a \times (t / d^2)}{b + (t / d^2)} + X_0 \tag{10-4}
\]

The optimal condition for cooked dried pasta is called al dente, and the moisture content of the al dente pasta was defined to be 1.70 kg-H₂O/kg-d.m. in this study. The rehydration time for each pasta to reach the condition of al dente was estimated by interpolating the discrete experimental points.

These measurements were repeated at least 3 times for each item.

10.2.9. Statistical analysis

The data were statistically evaluated by ANOVA. The least significant difference test was applied to compare the mean values.
10.3. Results and Discussion

10.3.1. Microscopic images

Figures 10-1(A) and 10-1(B) illustrate the surface images of the dried pasta prepared using the Teflon, polypropylene, polycarbonate, aluminum, and bronze dies at 200- and 100-fold magnifications, respectively. The observation at the 200-fold magnification revealed that the surfaces of the pasta prepared using the Teflon, polypropylene, and polycarbonate dies were smooth, while those of the pasta prepared using the aluminum and bronze dies were rough. The surface of the pasta prepared using the Teflon die looked smooth even based on observations at 1000-fold magnification. The digital microscopic observations indicated that the pasta prepared using the Teflon die had the smoothest surface, while those prepared using the polypropylene, polycarbonate, aluminum, and bronze dies followed in this order. The difference in the surface roughness among the pasta would be ascribed to the surface profile and the sliding frictional coefficient of the dies. Optical microscopic observations of the segments of the pasta cross-sections also indicated that the surfaces of the pasta prepared using the aluminum and bronze dies were bumpy (Fig. 10-2). On the other hand, optical microscopic observations at 100-fold magnification could not show a difference in the inner structure.

10.3.2. Properties of dried and rehydrated pasta

Table 10-1 lists the properties of pasta prepared using the different dies. The extrusion velocity was the highest for the pasta prepared using the Teflon die, the surface of which was the smoothest, while the velocities for the pasta prepared using the polypropylene, polycarbonate, aluminum, and bronze dies followed in this order, which was the same as that for the surface smoothness observed by the digital microscope.

The bulk densities of the pasta prepared using the Teflon, polypropylene, polycarbonate, aluminum, and bronze dies were increased in this order, and the density was correlated to the extrusion velocity at $R^2 = 0.91$. The difference in the density among the pasta prepared using the Teflon die, those prepared using the polypropylene or polycarbonate one, and those prepared using the aluminum or bronze one was significant ($P < 0.05$). It was also reported
Fig. 10-1. Surface images at 200- (A) and 1000-fold (B) magnifications of pasta prepared using the dies made of Teflon (a), polypropylene (b), polycarbonate (c), aluminum (d), and bronze (e). The images were observed using a digital microscope.

Based on mercury porosimetric measurements that inner structure of pasta prepared using a Teflon die was dense with a lower porosity than that prepared using the bronze die [6]. There was a tendency that the pasta having the higher density was stronger based on the fracture
assessment. These facts suggested that the pasta, which passed faster through a die, had the denser structure and the higher mechanical strength.

The onset, peak, and conclusion temperatures during gelatinization, $T_o$, $T_p$, and $T_c$, of the pasta did not depend on the die material. The temperatures decreased when the starch was damaged [138, 139]. The pasta underwent pressure when passing through a die and the pressure depended on the die material. No difference in the gelatinization temperatures among the pastas indicated that the pressure was too low to damage the starch of the durum wheat.

Fig. 10-2. Optical microscopic images at 100-fold magnification of the cross-section segments of pasta prepared using the dies made of Teflon (a), polypropylene (b), polycarbonate (c), aluminum (d), and bronze (e).

10.3.3. Rehydration kinetics

The moisture content based on the bone-dry weight of the sample, $X_t$, is plotted compared with the rehydration time, $t$, divided by the square of the initial diameter, $d^2$, for all the tested pastas in Fig. 10-3.
Fig. 10-3. Rehydration of pasta prepared using the dies made of Teflon (□), polypropylene (△), polycarbonate (○), aluminum (▽), and bronze (◇).

Fig. 10-4. Rehydration during the early stage of cooking for the pasta prepared using various dies. The symbols are the same as in Fig. 10-3.
Table 10-1. Properties and rehydration kinetics of pasta prepared using different dies (average ± SD).

<table>
<thead>
<tr>
<th>Die material</th>
<th>Teflon</th>
<th>Polypoplyren</th>
<th>Polycarbonate</th>
<th>Aluminum</th>
<th>Bronze</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial diameter [mm]</td>
<td>1.77 ± 0.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.74 ± 0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.78 ± 0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.80 ± 0.06&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.75 ± 0.06&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Extrusion velocity [cm/s]</td>
<td>3.7 ± 0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.0 ± 0.1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.6 ± 0.0&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.5 ± 0.1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.5 ± 0.1&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Apparent bulk density [g/cm³]</td>
<td>1.36 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.35 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.35 ± 0.01&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.32 ± 0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.31 ± 0.02&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Breaking load [N]</td>
<td>5.6 ± 0.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>—</td>
<td>5.6 ± 0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>—</td>
<td>4.1 ± 0.5&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Breaking strain [%]</td>
<td>39.9 ± 3.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>—</td>
<td>37.8 ± 4.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>—</td>
<td>40.7 ± 2.8&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gelatinization Onset</td>
<td>50.1 ± 1.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50.2 ± 0.9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50.4 ± 0.9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>49.8 ± 1.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50.2 ± 1.4&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gelatinization Peak</td>
<td>58.1 ± 0.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>57.9 ± 0.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>58.0 ± 0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>58.1 ± 0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>58.0 ± 0.8&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Gelatinization Conclusion</td>
<td>67.9 ± 1.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>69.2 ± 1.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>69.2 ± 0.9&lt;sup&gt;a&lt;/sup&gt;</td>
<td>68.1 ± 0.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>68.4 ± 1.7&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Momentarily-rehydrated amount of water ×10² [kg-rehydrated water/m²]</td>
<td>3.2 ± 0.2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.4 ± 0.4&lt;sup&gt;ab&lt;/sup&gt;</td>
<td>3.9 ± 0.2&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5.6 ± 0.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6.2 ± 0.4&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Equilibrium amount of water rehydrated [kg-H₂O/kg-d.m.]</td>
<td>9.0 ± 0.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.4 ± 0.3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.3 ± 0.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9.0 ± 0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.7 ± 0.5&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a, b, c, and d</sup> Averages with different letters indicate significant differences (p < 0.05) between the samples.

The \(a/b\) and \(a + X_0\) values in Eq. (10-4) correspond to the initial rehydration velocity and the equilibrium amount of water rehydrated, respectively. Because the early stage of rehydration could not be well expressed by Eq. (10-4) as mentioned above, only the \(a + X_0\) value was estimated using Eq. (10-4). The initial diameter would affect the rehydration velocity. Therefore, the rehydration during the early stage within 60 s was characterized based on the \(x_t\) value, which represents the amount of water rehydrated per unit surface area. The plots of the \(x_t\) value compared with the rehydration time \(t\) were expressed by a quadratic equation, and \(x_0\), which responded to the momentarily-rehydrated amount of water when the sample was immersed in the boiling water, was estimated by extrapolating the equation to \(t = 0\) (Fig. 10-4).

The \(x_0\) and \(a + X_0\) values for all the tested pastas are summarized in Table 10-1. The \(x_0\) was higher in the order of the pasta prepared using the bronze, aluminum, polycarbonate, polypropylene, and Teflon dies. The order was the same as that for the surface roughness. The
difference in the $x_0$ value between the pasta prepared using the Teflon die, polypropylene, or polycarbonate one, and aluminum or bronze one was significant ($p < 0.05$). Based on the estimation of the surface area of the sample, it was assumed that the sample was a satiny column-shaped stick. However, the surface of practical pasta was irregular and the surface area was higher for the rougher pasta. The pasta having rougher surface would more rapidly rehydrate water. This would be the reason for the high $x_0$ values of the pasta prepared using the bronze and aluminum dies.

There was no significant difference in the $a + X_0$ value among the tested pasta. The gelatinization of starch in pasta enhanced the rehydration [140]. However, the gelatinization temperature was not affected by the die material. This fact would be the reason for no difference in the $a + X_0$ values.

The time to reach the state of *al dente*, when the moisture content was 1.70 kg-H$_2$O/kg-d.m., was estimated using Eq. (10-4) and the best-fitted $a$ and $b$ values for each pasta. The times for the pasta prepared using the Teflon, polypropylene, polycarbonate, aluminum, and bronze dies were 11.3, 11.2, 11.3, 10.0, and 10.3 min, respectively. There was about a 1-min difference between the pasta having a smooth surface and those having rough ones. Pasta having a rougher surface can be cooked in a shorter time.

### 10.4. Conclusions

The die material affected the extrusion velocity of the durum wheat dough, the surface roughness, bulk density, and rapture strength of the dried pasta, while it did not affect the gelatinization temperature. The equilibrium amount of water rehydrated in boiling 0.5% (w/v) sodium chloride was almost the same for all the pastas prepared using the dies made from the various materials. However, the momentarily-rehydrated amount of water, which was estimated by extrapolating the experimental points within 60 s, depended on the die material.
CHAPTER 11

Measurement of moisture profiles in pasta during rehydration based on image processing

11.1. Introduction

Many papers have focused on the rehydration of dried food, such as apple [141], orange [142], date palm fruit [143], shiitake mushrooms [144], candied mango [145], mango [146], carrot [147, 148], and water chestnut [149]. The rehydration process is typically analyzed based on Fick's second law of diffusion. The process of air drying Morchella esculenta mushrooms [22], broccoli stem [26], and chickpeas [150] was investigated and could be well expressed by the law at different temperatures. Moreover, the rehydration process of fresh penne pasta at 20-80°C was reported to be characterized by two effective diffusion coefficients using the law [28]. However, a recent study showed that the actual process of moisture migration is not diffusion-controlled, proposing instead several other mechanisms, such as water imbibition, capillarity, and flow in porous media [21, 151]. Although many models have been proposed to describe water migration in dried food during rehydration, the key mechanism controlling migration remains unclear.

The average moisture content of an entire sample is usually measured in order to validate a proposed model, although the moisture profile is numerically solved [105]. One reason for taking such a measurement is the absence of an adequate method to obtain a precise moisture profile of the sample and to verify the numerical results. The absence of an adequate method makes it difficult to discern or interpret the mechanism controlling water migration during rehydration. Rehydration curves, which express changes in the average moisture content over time and are obtained by numerically solving the various models based on Fick's second law of diffusion, are of the hyperbolic type and satisfactorily fit the experimental data [22, 26, 28, 29, 150]. However, such results are insufficient to judge the appropriateness of the models, and the actual measurement of a precise moisture profile is unavailable for verification.
Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) are powerful techniques to measure the moisture profile of foods. The moisture profiles of rice grains during cooking [152], noodles during drying or rehydration [124, 153-155], and cheese during brining [156] were measured using these techniques. Although these techniques can provide information regarding moisture profiles, the accuracy of the measurement is insufficient to verify the numerically calculated profile due to the following four limitations: The minimum moisture content measurable by the techniques is high. For example, a moisture content less than 0.67 kg-H₂O/kg-d.m. cannot be measured for pasta due to fast water proton relaxation [155], although the pasta is rehydrated from a moisture content of approximately 0.11 kg-H₂O/kg-dm. Another limitation is low spatial resolution. During MRI measurement, the moisture content is evaluated every 65 μm at best [152]. That is, only about 12 points of data can be obtained for pasta having a radius of 0.8 mm. Additionally, the measurement is time consuming. The MRI technique takes a few minutes to obtain a moisture profile of a sample; however, the moisture profile of a sample, such as pasta, changes within a few minutes. Finally, the cost of equipment, such as NMR and MRI, is high. Therefore, the development of a method without these limitations would aid in elucidating the mechanism controlling water migration in dried foods.

Dried pasta is yellowish or yellowish brown and becomes lighter as the moisture content increases. The color change of pasta during rehydration was focused in developing a new method, using a digital camera, to precisely measure the moisture content (0.1 kg-H₂O/kg-d.m. or higher) of pasta. Notably, the sample must be cut in order to measure the cross-sectional moisture profile. A digital camera can acquire the color distribution of a sample, and currently available cameras have high pixels, which provides high-resolution images. The moisture profile measured by this method would enable us to elucidate the phenomena in the rehydration process. Moreover, development of this method is the first step in understanding the mechanism controlling water migration during food rehydration.

11.2. Materials and Methods

11.2.1. Materials

Two kinds of dried pasta were used. One was cylindrical pasta (spaghettini) supplied by
Nisshin Foods, Inc. (Tokyo, Japan) and another was slab pasta (lasagna; De Cecco, Fara San Martino, Italy) purchased from a local supermarket.

The spaghettini was made from durum semolina. The sample was prepared under the following conditions: the drying temperature was increased from 50 to 85°C during the first 60 min, maintained at 85°C for 300 min, and decreased to 30°C during the last 30 min. After the drying process, the cylindrical sample had an initial diameter of 1.60 mm and an initial moisture content of 0.11 kg-H₂O/kg-d.m. The carbohydrate, protein, and fat contents were 72, 13, and 2% (w/w), respectively.

The lasagna was also made from durum semolina. The sample had an initial thickness of 1.04 mm and an initial moisture content of 0.10 kg-H₂O/kg-d.m.

11.2.2. Rehydration

Culture tubes containing approximately 50 mL of distilled water were equilibrated at 100°C in a DP-1S hot-stirrer (As one, Osaka, Japan). The spaghettini and lasagna were cut into 9-cm lengths, of approximately 0.27 g, and 6.5-cm lengths × 2-cm depths, of approximately 1.90 g, respectively, and rehydrated by immersion in the culture tube. The sample was removed from the tube at the specified time, as shown later, and immediately carefully blotted with Kimtowels and Kimwipes (Nippon Paper Crecia, Tokyo, Japan) to remove excess water. One sample was used for each rehydration time.

11.2.3. Apparent density

After rehydration, the sample was wrapped in polyethylene sealing film to prevent moisture loss and then placed in the temperature-controlled oven at 70°C for 3 days in order to equalize the moisture distribution in the sample. Next, sample volume, \( V \), was measured by a displacement technique using a pycnometer (25 mL; Sogorikagaku Glass Works, Kyoto, Japan) containing dodecane (density = 749 kg/m³), with the assumption that dodecane penetration into the sample can be ignored. The apparent density of the rehydrated pasta, \( \rho \), was calculated using Eq. (11-1).

\[
\rho = \frac{w_0}{V}
\]  

(11-1)
where \( w_0 \) is the sample weight after 3 days at 70°C, measured by an AUW320 electronic balance (Shimadzu, Kyoto, Japan) prior to volume measurement. Each experiment was performed in duplicate.

11.2.4. Proposed method

As mentioned above, the method proposed in this study is based on the increase in sample color brightness with increasing moisture content. To obtain the moisture profile, a cross-sectional image of the sample is taken. The method consists of the five following steps:

The first step is the preparation of two sets of rehydrated pasta samples: one is used to measure the moisture profile and the other is used for making a calibration curve. The samples used for measuring the moisture profile and for making a calibration curve were rehydrated for 1, 10.2, 14.7, and 20 min and for 1, 3, 6, 9, 12, 15, 21, 25, and 30 min, respectively, under the same conditions. Then, only the samples for making a calibration curve were wrapped in polyethylene sealing film to prevent moisture loss and placed in a temperature-controlled oven at 70°C for 3 days to equalize the moisture distribution in the samples. Both sets of samples were subjected to steps 2 and 3.

![Equipment used in the proposed method.](image)

**Fig. 11-1.** Equipment used in the proposed method.

In step 2, cross-sectional images were taken using a digital camera (Fig. 11-1). The rehydrated sample was cut crosswise using a sharp stainless steel blade and covered with a light shield, the diameter or the thickness of which was the same as that of the sample. Both the light shield and the inner surface of an illumination box had an emissivity of 0.94. The
cross section of the laterally shielded sample was illuminated by two cold light illuminators (PICL-NSX; NPI, Tokyo, Japan) from both sides of the sample and photographed using a high-resolution digital camera (EOS-40D; Canon, Tokyo, Japan) with a 65-mm lens (MP-E 65 mm; Canon) in JPEG format. One image was taken for each sample. The image had $3,888 \times 2,592$ pixels, indicating that the spatial resolution of the proposed method was about 1.6 $\mu$m/pixel, which was about 40 times higher in the spatial resolution than those of MRI methods [152, 153, 155]. Then, the area without the cross section of sample in the image was manually eliminated using Photoshop CS4 extended (Adobe Systems Inc., San Jose, CA, USA).

The third step involved digital image processing using two software packages: Mathematica 7 (Wolfram Research, Champaign, IL, USA) and Origin 8.1J (OriginLab, Northampton, MA, USA). The original 24-bit RGB color image, obtained in step 2, was pixelated into red, green, and blue images. Although the red, green, and blue images had the same quality and could be equally used in principle, the blue image was used in this paper as an example. The image was converted into an 8-bit gray-scale format using the Origin 8.1J. In order to visually clarify the gray level of the image, the original gray-level $G_0$ of each pixel was converted to the level $G_\gamma$ through a gamma correction [157] using Eq. (11-2), and $G_\gamma$ was further converted to the level $G_c$ through a contrast correction [157] using Eq. (11-3).

$$G_\gamma = 255 \left( \frac{G_0}{255} \right)^{0.5}$$  \hspace{1cm} (11-2)

$$G_c = 2 \times G_\gamma - \frac{255}{2}$$  \hspace{1cm} (11-3)

In step 4, the calibration curve was prepared, which correlates the corrected gray level $G_c$ with the moisture content $X$, determined by drying each sample at 135°C for 5 h in a convection drying oven (DO-300FA; As One, Osaka, Japan) immediately after the image acquisition in step 2. Moisture content was determined using the following equation:

$$X = \frac{w_0 - w_1}{w_1}$$  \hspace{1cm} (11-4)

where $w_0$ and $w_1$ are the sample weights before and after drying, respectively.

In the final step, the corrected gray level $G_c$ of each pixel in the sample image was
converted to the moisture content using the calibration curve, in order to obtain the moisture profile of the rehydrated pasta.

The measurements were conducted in at least duplicate for every sample rehydrated for different times. The reliability of the moisture profiles was examined as shown in the following section. The accuracy of the calibration curves was expressed by standard deviation for each point.

### 11.2.5. Verification of accuracy

The root mean square error (RMSE) (Eq. (11-5)) was used to evaluate the accuracy of the proposed method.

\[
RMSE = \sqrt{\frac{\sum (\bar{X}_{\text{cal}} - \bar{X}_{\text{obs}})^2}{N}}
\]  

(11-5)

where \( \bar{X}_{\text{cal}} \) and \( \bar{X}_{\text{obs}} \) are the average moisture content of a sample calculated by Eq. (11-6) from the moisture profile and the experimentally observed one (Eq. (11-4)), respectively, and \( N \) is the number of experimental values.

\[
\bar{X}_{\text{cal}} = \int_{V} \frac{\rho(X) \cdot X}{X + 1} dV / \int_{V} \frac{\rho(X)}{X + 1} dV
\]  

(11-6)

where \( \rho(X) \) is the apparent density at the moisture content \( X \). The dependence of \( X \) on \( \rho(X) \) is empirically represented by Eq. (11-7).

\[
\rho(X) = A + B \exp(CX)
\]  

(11-7)

where \( A, B, \) and \( C \) are constants.

### 11.3. Results and Discussion

#### 11.3.1. Gray level profile

Figure 11-2 shows images of the cross sections of spaghettini and lasagna rehydrated for 10.2 and 14.7 min, respectively, at which points the pastas were optimally cooked to the state termed *al dente*. Images (a) and (b) in Fig. 11-2 are the original and processed ones, respectively. The color of the circumferential (A) and rectangular (B) regions in which the water penetrated was brightened and whitened in images (a) and (b) in Fig. 11-2, respectively.
Fig. 11-2. Cross-sectional images of the spaghettini rehydrated for 10.2 min (A) and the lasagna rehydrated for 14.7 min (B). Original image (a) and digitally processed image (b). *Broken lines* show the segments of moisture profiles as an example.

Fig. 11-3. Gray-level profile of the cross-sectional image of spaghettini rehydrated for 10.2 min. Inset: The extended profile.

A gray-level profiles in the radial direction (A-b) and the thickness one (B-b) of the cross-sectional images of Fig. 11-2 were converted to the moisture profiles using the calibration curves (see below) and are represented by the thin line in Fig. 11-3 (shown only for spaghettini). The inset in Fig. 11-3 is the extended profile in the x-axis range of 0.325 to 0.365. Although the thin line appears to have a jagged pattern, there are obviously convex or concave patterns, as shown by the circles in the extended profile. Each circle corresponds to a pixel. Therefore, the jagged thin line was not ascribed to measurement noise, but to the high spatial resolution of the proposed method.

Starch gelatinization does not occur uniformly [123]. Large starch granules usually
gelatinize faster, and gelatinization begins in an amorphous region of the starch granule. The pitch of the convex or concave pattern was about 20 μm, which was in the same order as the 2- to 40-μm size of a starch granule [123]. Therefore, the jagged patterns expressed by the thin line in Fig. 11-3 can be ascribed to the nonuniformity of the starch gelatinization. The spatial resolution of 1.6 μm in the proposed method allows for the estimation of nonhomogeneous rehydration behavior in pasta.

11.3.2. Calibration curve

The insets in Fig. 11-4 show cross-sectional images of the spaghettini with different, but homogeneous moisture contents. As the moisture content increased, the color of the image changed from black to white. The calibration curve, which correlates the gray level $G_c$ ($0 \leq G_c \leq 255$) to the moisture content $X$, is shown in Fig. 11-4 and can be expressed by the quadratic function Eq. (11-8).

$$X = aG_c^2 + bG_c + c$$  \hspace{1cm} (11-8)

where $a$, $b$, and $c$ are constants. The $G_c$ values were obtained by averaging the gray levels of all pixels in the cross-sectional image. The gray levels of 0 and 255 represent black and white, respectively. The constants $a$, $b$, and $c$ were determined to best-fit the observed moisture contents to the calculated ones using the Solver of Microsoft Office Excel® 2010 and were $4.54 \times 10^{-5}$, $4.03 \times 10^{-3}$, and $-3.06 \times 10^{-1}$ for spaghettini, respectively, and $4.24 \times 10^{-5}$, $2.69 \times 10^{-3}$, and $-6.17 \times 10^{-2}$ for lasagna, respectively. The correlation coefficient ($R^2$) was 0.978 at minimum, indicating the accuracy of Eq. (11-8) and the validity of the proposed method.

Moisture contents lower than 0.67 kg-H$_2$O/kg-d.m. cannot be measured by the currently used MRI method due to fast water proton relaxation [155]. The calibration curve showed a clear one-to-one relationship in the moisture content range of 0.10 to 2.85 kg-H$_2$O/kg-d.m. Therefore, the proposed method can satisfactorily obtain moisture profiles for samples with low moisture content.
Fig. 11-4. Relationships between the moisture content and gray level in spaghettini (—○—) and lasagna (- - ● - -) with homogeneous moisture distribution. Bars indicate standard deviation. The pictures in the figure are the digitally processed cross-sectional images obtained from spaghettini with homogeneous moisture contents of 1.12 ± 0.02 and 2.89 ± 0.12 kg-H₂O/kg-d.m., indicated by arrows.

11.3.3. Moisture profile

The thick line in Fig. 11-3 shows the gray-level profile, which was obtained by dividing the image into ten segments shown by broken lines in Fig. 11-2 A-b, B-b and by averaging the gray levels at the same distance from the center of the segments. The profile expressed by the thin line indicates, in detail, the rehydration behavior. On the other hand, the thick line shows the averaged moisture profile in the sample. Figure 11-5A, B shows the averaged moisture profiles of spaghettini rehydrated for 0, 1, 10.2, and 20 min and lasagna rehydrated for 0, 1, 14.7, and 20 min, respectively. The profile at 0 min represents the dried pasta. The moisture profile in the *al dente* pasta, which was rehydrated for 10.2 and 14.7 min for spaghettini and lasagna, respectively, was measured by the proposed method for the first time, as this method was able to measure a lower moisture content than the currently used method.
The spaghettini and lasagna have different characteristics, such as compositions, shape, drying condition, microstructure, initial moisture content, and degree of gelatinization. However, the moisture profiles during their rehydration were similar in shape. This fact indicates that the phenomena controlling water migration during rehydration are the same even if some characteristics of pasta are different.

During the first 1 min, swelling occurred in an approx. 0.2-mm region near the surface, and the moisture content remained at the same level as that of the dried pasta in the inner region. The profiles at 0 and 1 min indicated that water quickly penetrated only near the
surface. Based on SEM measurements, many small holes and cracks were reported on the surface of the pasta [158, 159]. Water entered the pasta through these small surface holes and cracks. The fact that the region near the surface had a flat moisture profile, and that there was no gradient in the profile, suggested that water imbibition during the early stage was not attributable to water diffusion, but water filling of the holes and cracks.

The extent of gelatinization was assessed by observing the birefringence in the starch/water system during heat treatment, revealing that gelatinization was complete within 1 min [115]. This indicated that starch gelatinization is a fast process. However, the moisture content on the surface gradually increased with time (Fig. 11-5). The previous result (chapter 7) showed that the average moisture content of pasta increased up to about 9 kg-H₂O/kg-dm. This indicated that the gelatinization of starch granules in the sample, even with 20-min rehydration, did not reach equilibrium, and that swelling of the granules was restricted. In previous studies, while dried pasta showed a homogeneous internal structure, such that the starch granules were deeply embedded in a protein matrix, the structure below the surface appeared to be a honeycomb-like structure after a 4-min rehydration [158, 159]. The protein matrix, which had shrunk during drying, appeared to relax in structure during rehydration, and the starch granules gradually swelled due to gelatinization. Therefore, the structural relaxation process of the protein matrix appears to play an important role in alterations in the moisture content of samples during rehydration.

The moisture profiles observed for the samples rehydrated for 10.2 or 14.7 and 20 min showed two features. One was the flat moisture profile near the surface, and the other was the parabolic distribution of the moisture content in the inner region. The latter feature suggested that the water migration in the region was diffusion controlled, while the former feature suggested that the diffusion of water was not the rate-limiting step for rehydration near the surface. As mentioned above, the moisture content near the surface of the sample rehydrated for 20 min was much lower than the equilibrium content, and the starch granules in the sample had the potential to absorb more water. Therefore, most of the water supplied from the bulk phase would be rehydrated by the starch granules that increased the moisture content near the surface. In the inner region, diffusion of water occurred according to the gradient in the moisture content, and the profile gradually shifted to the higher level. However, the
consumption of water by starch granule rehydration near the surface restricted the penetration of water into the inner region. The rehydration near the surface expanded the region with the flat moisture profile, as can be seen from the profiles at 10.2 or 14.7 and 20 min.

### 11.3.4. Accuracy of measurement

The constants $A$, $B$, and $C$ in Eq. (11-7) were 1.12, 0.415, and $-0.785$ for the spaghettini, respectively, and 1.08, 0.500, and $-1.455$ for the lasagna, respectively. The correlation coefficient ($R^2$) was 0.985 at minimum, indicating the accuracy of Eq. (11-7) as shown in Fig. 11-6. The $\bar{X}_{\text{cal}}$ and $\bar{X}_{\text{obs}}$ values for the spaghettini rehydrated for 0, 1, 10.2, and 20 min and for the lasagna rehydrated for 0, 1, 14.7, and 20 min are plotted in Fig. 11-7. The RMSE was 0.149 and 0.175 for spaghettini and lasagna, respectively, indicating the high accuracy of the proposed method for moisture content determinations in pasta.

![Fig. 11-6. Dependence of apparent density on average moisture content in spaghettini (---○---) and lasagna (---●---). Bars indicate standard deviation.](image-url)
Fig. 11-7. Correlation between the experimentally observed average moisture content, $\bar{X}_{\text{obs}}$, and the moisture content calculated from the moisture profile, $\bar{X}_{\text{cal}}$, in spaghettini rehydrated for 0 min ($\triangle$), 1 min ($\bigcirc$), 10.2 min ($\vartriangle$), and 20 min ($\square$) and lasagna rehydrated for 0 min ($\blacktriangle$), 1 min ($\bullet$), 14.7 min ($\blacktriangledown$), and 20 min ($\blacksquare$). Bars indicating the standard deviation are behind the symbols.

11.4. Conclusions

When pasta is rehydrated, its color brightness is altered. Based on this fact, a method was developed to measure the moisture profile in pasta using a digital camera and an image processing technique. The method allowed for the precise quantification of a moisture content of 0.1 kg-H$_2$O/kg-d.m., with a spatial resolution of 1.6 μm. The high-resolution profile revealed that starch granules were non-uniformly gelatinized during rehydration. The average moisture content, calculated from the moisture profile, was well correlated with that experimentally observed. The good correlation demonstrated the accuracy of the proposed method. The changes in the profile over time suggested that small holes and cracks near the pasta surface were quickly filled with water, and that the region near the surface gradually expanded due to structural relaxation of the protein matrix. It was also suggested that water migration occurred via diffusion in the inner region, and that gelatinization of the starch granules restricted the water diffusion. Moreover, it was shown that the phenomena
controlling water migration during rehydration are common for spaghettini and lasagna, which are different in some characteristics.
CHAPTER 12

Effects of relaxation of gluten network on rehydration kinetics of pasta

12.1. Introduction

The transient change in the average moisture content of dried pasta and other dried foods during rehydration is exponential [28]. Therefore, the diffusion equation based on Fick’s law can be applied to describe the rehydration processes.

Using the method developed in chapter 11, the moisture distribution within pasta during rehydration at 100°C revealed that the moisture content on the surface of pasta gradually increased instead of quickly reaching equilibrium [161]. In addition, the region with constant moisture content was determined to be near the surface, and the moisture distribution near the center of pasta was hyperbolic [161]. Thus, the overall moisture distribution resembled the reversed shape of a billycock and could not be reasonably explained by the diffusion model based on Fick’s law.

The non-Fickian diffusion of a low-molecular-weight molecule into a matrix of high-molecular-weight molecules is attributed to the slow reconfiguration of high-molecular-weight molecule segments after accepting the penetrant [162]. This phenomenon has been observed in many high-molecular-weight polymer-penetrant systems [163]. Moreover, the diffusion coefficient of water directly measured using a pulsed-field-gradient NMR method was larger than the value indirectly estimated from the diffusion model [164, 165]. Therefore, the key factor controlling water migration within pasta may not only be the diffusion of low-molecular-weight molecules (water) but also the relaxation of high-molecular-weight molecules (components of wheat flour). Previous studies on the rehydration of dried food have extensively focused on water diffusion, but few have investigated the relaxation of high-molecular-weight molecules.

In this study, we examined the rehydration kinetics of pasta having an infinitely small diameter in boiling water, where the effects of water diffusion on rehydration are negligible in
In order to examine the relaxation of high-molecular-weight molecules. High-molecular-weight molecules have not been reported to govern water migration within pasta during rehydration. Pasta mainly consists of starch and gluten. Starch granules are deeply embedded in the honeycomb structural-network of gluten in pasta. The rate of starch gelatinization, which is completed within a minute [115], is much faster than that of water diffusion [52, 160]. In this context, gluten was assumed to be the high-molecular-weight molecule that governed rehydration rates. The aim of this study was to investigate the effects of the relaxation of the gluten network on the rehydration kinetics of pasta in boiling water. Free from the effects of water diffusion, the moisture content was estimated by extrapolating the average moisture content of durum pasta of various diameters to 0 mm.

12.2. Materials and Methods

12.2.1. Pasta preparation

Cylindrical durum pasta with the initial diameters of 1.30 mm, 1.35 mm, 1.63 mm, and 1.71 mm were supplied by Nisshin Foods, Inc. (Tokyo, Japan). The carbohydrate, protein, and fat contents were 72%, 13%, and 2% (w/w), respectively. Gluten pasta made of gluten isolated from durum wheat flour (Nisshin Foods, Inc.) was prepared [57]. Durum wheat flour (500 g) was mixed with water (350 g) for 20 min to produce dough using a KitchenAid KSM150 mixer (FMI, USA). The dough was kept at 25°C for 1 h and subsequently washed in water at 20°C until the water became clear. The gluten isolated from the durum wheat flour was freeze-dried by FDU-1200 (Tokyo Rika-ikkai, Tokyo, Japan) to lower its moisture content to 0.13 kg-H2O/kg-d.m. Water was then added to the freeze-dried gluten to moisten 32% of gluten on a wet basis using an SKH-A mixer (Tiger, Osaka, Japan). The moistened gluten was placed in an electric rolling noodle-machine (STMJ-180, Sanshodou-jitsugyou, Tokyo, Japan) and cut into pieces 80 mm in length, 3 mm in width, and 4 mm in depth to produce fresh gluten pasta. The fresh gluten pasta was placed on metallic meshes, which were then placed on racks in a temperature-humidity controllable chamber (SH-641, Espec, Japan) to prepare dried gluten pasta.

After drying at the maximum temperature of 90°C for 6 h, the average moisture contents of durum pasta and gluten pasta were 0.12 kg-H2O/kg-d.m. and 0.10 kg-H2O/kg-d.m.,
respectively. The average moisture content of each type of pasta was determined based on the sample weights before \(W_t\) and after \(W_0\) drying at 135°C for 5 h:

\[X_t = \frac{W_t - W_0}{W_0}\] (12-1)

**12.2.2. Rehydration**

Culture tubes containing approximately 50 mL of distilled water were placed in a stainless steel container filled with boiling water, which was heated using a DP-1S hot-stirrer (As one, Osaka, Japan). Approximately 80-mm-long pasta was immersed in culture tubes for a specific time. Then, samples were removed from the tube and immediately blotted carefully with Kimtowels and Kimwipes (Nippon Paper Crecia, Tokyo, Japan) to remove excess water. Rehydration experiments were repeated in triplicate under each condition.

**12.2.3. Statistical analysis**

The fitness of the calculated values to experimental values was evaluated using the coefficient of the determination \((R^2)\) and the root mean square deviation (RMSD) as follows (Eq. (12-2)):

\[\text{RMSD} = \frac{1}{n} \sqrt{\sum (X_{\text{cal}} - X_{\text{obs}})^2}\] (12-2)

where \(X_{\text{cal}}\) and \(X_{\text{obs}}\) are the calculated and the experimental average moisture contents, respectively, and \(n\) represents the number of experimental data points.

**12.3. Results and Discussion**

**12.3.1. Estimation of the moisture content in infinitely thin pasta**

Figure 12-1 shows the transient changes in the average moisture content of durum pasta of various initial diameters. The moisture content of all durum pasta rapidly increased in the early stages of rehydration and gradually increased toward equilibrium in the later half. Durum pasta rehydrated faster because of its shorter diameter. To estimate the moisture content of infinitely thin durum pasta (Fig. 12-2), which is designated as 0-mm pasta, the average moisture content at a specific time was plotted against pasta diameters and
Fig. 12-1. The rehydration process of durum pasta with the initial diameters of 1.30 mm (○), 1.35 mm (△), 1.63 mm (◇), and 1.71 mm (□). Bars indicate the standard deviations.

Fig. 12-2. Estimation of the moisture content of infinitely thin durum pasta by extrapolation at the rehydration times of 5 min (―), 20 min (· · ·), 40 min (―), and 80 min (· · ·). The symbols are the same as those in Fig. 12-1. Bars indicate the standard deviation and most of them are behind the symbols.
extrapolated to 0 mm with a straight line. The minimum correlation coefficient, $R^2$, of the extrapolation line was 0.94, indicating that a linear approximation was appropriate for estimating the moisture content of 0-mm durum pasta from the $y$-intercept of the line. Thus, the transient changes in the moisture content of 0-mm durum pasta can be obtained by plotting the moisture content against the rehydration time.

12.3.2. Rehydration at the surface of pasta in boiling water

Figure 12-3 shows the changes in the normalized moisture contents for 0-mm durum pasta and at the surface of pasta, which was obtained from the moisture distribution in chapter 11 [161]. The normalized moisture content at the surface was lower than that of 0-mm durum pasta, which could be attributed to the removal of excess water on the surface before moisture-distribution measurements. The moisture distribution also underestimated the moisture content at the surface of pasta in boiling water. However, the transient changes in the normalized moisture content of 0-mm durum pasta and the moisture content at the pasta surface estimated from the moisture distribution were both exponential. Therefore, we concluded that the rehydration behavior of 0-mm durum pasta, which was estimated by extrapolating the average moisture contents to 0 mm, adequately reflected the behavior at the pasta surface.

The diffusion equations (differential equations) used to describe the rehydration kinetics of pasta require boundary conditions to be solved. Most studies assume a constant surface moisture content or mass transfer through fluid film near the surface, which is proportional to the difference in the moisture content between the surface and bulk phase. However, the present study showed that these boundary conditions were inadequate for simulating the pasta rehydration process because the moisture content at the pasta surface estimated at 0-mm for durum pasta gradually increased over time.

The moisture content of 0-mm durum pasta gradually increased and did not reach equilibrium even after 1 h of rehydration (Fig. 12-3). The rehydration process for 0-mm durum pasta was very slow, although a sufficient amount of water was supplied from the surroundings without the diffusion limitation of water, and the starch gelatinized within a few minutes [115]. These observations suggest that slow phenomena control rehydration kinetics at the surface of pasta.
12.3.3. Effects of the gluten network on rehydration at the pasta surface

Figure 12-3 also shows the rehydration kinetics of gluten pasta. The transient changes in the moisture contents of gluten pasta and 0-mm durum pasta were exponential. The rehydration process could be modeled by the following equation [166], which is used to describe the gradual increase in the surface concentration of organic low-molecular-weight molecules for polymer films [162]:

$$\frac{X_t - X_0}{X_e - X_0} = 1 - \exp(-kt)$$  \hspace{1cm} (12-3)

where $X_t$ is the moisture content at time $t$, $X_0$ is the initial moisture content, $X_e$ is the equilibrium moisture content, and $k$ is the rate constant. The parameters $k$ and $X_e$ were determined to best fit the calculated curve based on experimental data points using Solver of Microsoft Excel® 2010. The $X_e$ and $k$ values for 0-mm durum pasta were estimated to be 11.35 kg-H2O/kg-d.m. and $7.53 \times 10^{-4}$ 1/s, respectively. With regards to gluten pasta, its $X_e$
and $k$ values were estimated to be 1.21 kg-H$_2$O/kg-d.m. and $7.42 \times 10^{-4}$ 1/s, respectively. The maximum RMSD values for 0-mm durum pasta and gluten pasta were 0.030 and 0.025, respectively, demonstrating that Eq. (12-3) could be used to describe the rehydration processes of both 0-mm durum pasta and gluten pasta. In Figure 12-3, the calculated curves for 0-mm durum pasta and gluten pasta are shown in solid and broken curves, respectively. The $X_e$ value of 0-mm durum pasta was much larger than that of gluten pasta because unlike gluten pasta, durum pasta contains starch. On the other hand, the $k$ value of 0-mm durum pasta was very close to that of gluten pasta, indicating that the rehydration rates were the same for 0-mm durum pasta and gluten pasta even though the rehydration capacity of 0-mm durum pasta differed from that of gluten pasta.

Dried pasta has a compact amorphous structure. The starch granules are deeply embedded in the honeycomb structural-network of gluten in pasta, although starch granules are unrecognizable in dried pasta. Light microscopy and SEM images showed that the compact structure of pasta changed to a filamentous network in the direction of its surface to center during rehydration and the network gradually loosened during rehydration [159, 167]. The similar $k$ values for 0-mm durum pasta and gluten pasta indicate that rehydration kinetics at the pasta surface is governed by the gluten network. Although the starch granules swell via gelatinization immediately after water intake from their surrounding because of the very high gelatinization rate of starch, the gluten network prevents the swelling of starch granules. Then, amyllose begins to leak from the swollen starch granules at a certain degree of gelatinization. Therefore, the structure of pasta changes the filamentous gluten network during rehydration. The gradual increase in the moisture content may be due to the prevention of the swelling of starch granules, even though the rehydration capacity of the pasta at equilibrium was approximately 9 kg-H$_2$O/kg-d.m. [52, 160]. Rehydration at the pasta surface may proceed along with the relaxation of the gluten network because of the rehydration of gluten and the swelling force of gelatinizing starch granules.

The relaxation of the gluten network could be an important mechanism in the rehydration of pasta. The previous result in chapter 11 showed that starch gelatinization played an important role, especially near the pasta surface where sufficient water is supplied. Furthermore, water diffusion could not be ignored because the diffusion coefficient of water
by pulsed-field-gradient NMR method was only one order of magnitude larger than that estimated from the diffusion model [28, 164, 165]. Therefore, the relaxation of the gluten network, water diffusion and starch gelatinization occur simultaneously during the rehydration of pasta. These simultaneously occurring phenomena would result in the unique non-Fickian moisture distribution obtained in chapter 11.

12.4. Conclusions

The rehydration process of infinitely thin pasta was determined by extrapolating the average moisture content of pasta with various diameters to 0 mm. The process reflected well the change in the moisture content at the surface of pasta. The rehydration curve of 0-mm durum pasta suggested that the gradual increase in the moisture content should be considered as a boundary condition when numerically solving the differential equation modelling pasta rehydration kinetics. The moisture content for 0-mm durum pasta did not reach equilibrium even after 1 h of rehydration. The rate constants calculated for 0-mm durum pasta and gluten pasta using the Long and Richman equation were the almost same, indicating that the rehydration kinetic at the pasta surface is governed by the gluten network. Although starch gelatinization is a fast process and starch granules begin to swell immediately after water penetration, the gluten network prevents starch from swelling. Thus, rehydration at the pasta surface proceeds with the relaxation of the gluten network.
CONCLUDING REMARKS

PART 1

CHAPTER 1

The moisture sorption isotherms of durum semolina were observed in the temperature range of 30 to 80°C for both the sorption and desorption processes. The isotherms of its constituent starch and gluten were observed at 30°C and that of pasta was observed at 60°C. All the isotherms were well expressed by the Guggenheim-Anderson-de Boer equation. The isotherm for the desorption process lay over that for the sorption one at any temperature, and a slight hysteresis was recognized. Isosteric heats, $q$, for sorption and desorption processes were estimated according to the Clausius-Clapeyron equation as a function of the moisture content of durum semolina. The $q$ values were larger at lower moisture contents, indicating that water molecules more strongly interact with the wheat flour at lower moisture contents. The $q$ values for the desorption process were greater than those for sorption. The isotherms of starch lay over those of gluten at any water activity, and those of pasta were located between those of starch and gluten.

CHAPTER 2

Moisture sorption isotherms were measured at 25°C for untreated, dry-heated and pre-gelatinized durum wheat flour samples. The isotherms could be expressed by the Guggenheim-Anderson-de Boer equation. The amount of water sorbed to the untreated flour was highest for low water activity, with water sorbed to the pre-gelatinized and dry-heated flour samples following. The dry-heated and pre-gelatinized flour samples exhibited the same dependence of the moisture content on the partial molar volume of water at 25°C as the untreated flour. The partial molar volume of water was ca. 9 cm$^3$/mol at a moisture content of 0.03 kg-H$_2$O/kg-d.m. The volume increased with increasing moisture content, and reached a constant value of ca. 17.5 cm$^3$/mol at a moisture content of 0.2 kg-H$_2$O/kg-d.m. or higher.
CHAPTER 3

The drying process of durum wheat semolina dough was measured by thermogravimetry in the temperature and relative humidity ranges of 30 to 90°C and 0 to 80%, respectively, in order to predict the drying process of pasta under any drying conditions. About 20% of the water was evaporated during the constant drying-rate period which has been ignored in previous studies. It is demonstrated that the constant drying-rate period should be taken into account in order to predict the drying curve with a high accuracy. The drying rate during the constant drying-rate period and the mass transfer coefficient estimated by the thermogravimetric analysis were expressed as functions of the temperature and relative humidity, and they were useful for predicting the drying processes of pasta under any drying conditions including the programmed ones.

CHAPTER 4

The effects of temperature and moisture content on the drying rate of durum wheat pasta were examined using thermogravimetry and differential scanning calorimetry (DSC) at temperature-rising rates of 0.2 to 1.0 °C/min. The activation energy for the mass transfer coefficient of drying was estimated to be ca. 32 kJ/mol at moisture contents of 0.14 kg-H2O/kg-d.m. or higher, but increased rapidly as the moisture content dropped below this level. The conclusion temperature of the endothermic peak in the DSC and the temperature of the inflection point of the drying characteristics curve were located near the glass transition curve of the durum semolina flour.

CHAPTER 5

The shrinkage of sheet-like and cylindrical pastas of different moisture contents and distributions was measured. A slight anisotropy in shrinkage was observed for both the pastas. The shrinkage ratio of the height to the width directions for the sheet-like pasta slightly depended on the drying conditions and was 0.93 to 0.96. The shrinkage coefficient in the longitudinal direction scarcely depended on the moisture content and was 0.23 for the cylindrical pasta. Although the shrinkage coefficient in the diametric direction for both the
pastas was 0.21 at moisture contents higher than 0.17, the coefficient increased for the moisture contents lower than 0.17. The Young’s modulus of the dumbbell specimen of pasta did not depend on the drying conditions. However, it decreased with a decrease in the moisture content and became almost constant at the moisture contents lower than 0.17. These facts suggested that glass transition significantly affected mechanical properties of pasta.

PART 2

CHAPTER 6

A novel method in which the rehydration curve is observed under linearly temperature-raising conditions was proposed to estimate the gelatinization temperature of starch-containing foods; it was applied in an estimation of the gelatinization temperatures of dried noodles. The gelatinization temperatures of two kinds of pasta, dried at high and low temperature, were 52.3 and 53.1°C, and those of udon, kishimen, juwari-soba, hachiwari-soba, so-called common soba, Malony®, and kuzukiri were 57.0, 57.8, 61.1, 59.6, 57.4, 48.4, and 49.1°C. The gelatinization temperatures estimated by the method were between the onset and peak temperatures obtained by differential scanning calorimetric measurement.

CHAPTER 7

The rehydration kinetics of pasta was measured in the temperature range of 20-90°C to investigate the temperature dependencies of an equilibrium moisture content and an initial rate of rehydration. The dependencies indicated the mechanism of rehydration: the equilibrium moisture content is limited by the state of starch gelatinization and the initial rate of rehydration is governed by the water diffusion through the pores of the pasta regardless of the starch gelatinization. The empirical equations were proposed to predict the amount of loss of the pasta mass during rehydration which results in the quality loss of cooked pasta and the moisture content which affects the mechanical properties and an optimal rehydration time. The equation of the moisture content, taking the effect of starch gelatinization into consideration, has the initial diameter of pasta, rehydration time, and temperature of rehydrated water as parameters to predict under any conditions.
CHAPTER 8

The rehydration kinetics of dried pasta were measured in the 20-90°C range in 1.83 mol/L of NaCl and at 80°C in 1.83 mol/L of LiCl, KCl, NaBr, and NaI solutions in order to elucidate the role of salt in the kinetics. At the temperatures higher than 70.8°C, the change in the enthalpy of rehydration, DH, in the 1.83 mol/L NaCl solution was 33.1 kJ/mol, which was greater than the DH value in water, and the activation energy for the rehydration, \( E \), in the salt solution was 25.6 kJ/mol, which was slightly lower than the \( E \) value in water. The Hofmeister series of ions was an index for their effect on the equilibrium amount of the rehydrated solution of pasta. The apparent diffusion coefficient of water into pasta was not correlated with the crystal radius of the salts, but was with the Stokes radius of the hydrated ions. Equations were formulated to predict the amount of rehydrated solution under any condition of temperature and NaCl concentration.

CHAPTER 9

The drying conditions of pasta affect its properties, such as appearance, hardness, and rehydration. The dried pasta is eaten after cooking. In this context, the rehydration kinetics of pasta dried under different conditions was measured at various rehydration temperatures. The pasta was characterized by the maximum temperature during the drying: 50°C, 70°C, and 85°C. The rehydration processes of the pasta at any rehydration temperature could be expressed by an empirical kinetic equation of the hyperbolic type, and the equilibrium moisture content and the initial rate of rehydration were estimated, taking the loss of pasta mass during rehydration into consideration. The loss of pasta mass was lower for pasta dried at higher temperature. Maximum temperature affected the change in the enthalpy of rehydration in the temperature region to a greater degree than the gelatinization temperature of starch in the pasta, while it had no effect on the activation energy for the initial rate of rehydration.

CHAPTER 10

Pasta was prepared using dies made of different materials. The surface was observed
using digital and optical microscopes, and was rougher for the pastas prepared using the Teflon, polypropylene, polycarbonate, aluminum, and bronze dies in this order. The extrusion velocity when passing through the die was faster, the bulk density was higher, and the rupture strength was greater for the pasta having the smoother surface. The die material did not affect the gelatinization temperature. The rehydration curves in boiling water containing 0.5% (w/v) sodium chloride were also observed. The curves were expressed by an equation of the hyperbolic type except for the early stage of rehydration in order to estimate the equilibrium amount of water rehydrated based on the bone-dry sample. The momentarily-rehydrated amount of water, which is a hypothetical quantity to characterize the initial water intake, was estimated by fitting the experimental points within 60 s. The amount was higher for the pasta having the rougher surface.

**CHAPTER 11**

A method using an image processing technique was developed to measure the moisture profile in pasta during its rehydration process. The method is based on the increase in sample color brightness with increasing moisture content. Compared to currently used methods, this method has the advantage that moisture contents around 0.1 kg-H₂O/kg-d.m. can be easily measured at a spatial resolution of 1.6 µm. The moisture profiles obtained by this method suggested that penetration of water into small holes and cracks on the pasta surface, water diffusion in the pasta, and structural relaxation of the protein matrix play important roles in the rehydration mechanism. It was also suggested that starch granule gelatinization prevented water migration into the interior portion of the pasta.

**CHAPTER 12**

The aim of this study was to investigate the effects of the relaxation of the gluten network on pasta rehydration kinetics. The moisture content of pasta, under conditions where the effects of the diffusion of water on the moisture content were negligible, was estimated by extrapolating the average moisture content of pasta of various diameters to 0 mm. The moisture content of imaginary, infinitely thin pasta (0-mm durum pasta) did not reach equilibrium even after 1 h of rehydration. The rehydration of pasta made of only gluten
(gluten pasta) was also measured. The rate constants estimated by the Long and Richman equation for 0-mm durum pasta and gluten pasta were $7.53 \times 10^{-4}$ and $7.42 \times 10^{-4}$ 1/s, respectively, indicating that the rehydration kinetics of 0-mm durum pasta were similar to those of gluten pasta. These results suggest that the swelling of starch by fast gelatinization was restricted by the honeycomb structural network of gluten and the relaxation of the gluten network controlled pasta rehydration kinetics.
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