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◇◇◇ Original Paper ◇◇◇

Water Holding Capacity Profile that Governs Water Migration in Starchy Food During Boiling

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A starchy food that is initially a single-phase body turns into a multiphase body during boiling because of starch gelatinization. Fick's law is applicable only to a homogeneous system and is not applicable to such a multiphase system. Relative Water Content (RWC) model has been proposed as an alternative model that is able to describe water migration in multiphase food systems. In the RWC model, water migration is driven by the gradient of water content divided by the water holding capacity (WHC), m/m*. In this study a WHC profile (WHC plotted against water content with which starchy food is heat-treated) was assumed based on information concerning starch gelatinization. Using this WHC profile, the correlation between WHC profile and transient water content profile in a wheat flour dough slab during boiling was examined. A modified WHC profile was found to be applicable for describing certain characteristic features of the transient water content profile in a slab of wheat flour dough during boiling.

Key words: relative water content model, water holding capacity, water migration, multiphase food, starchy food

1. Introduction

Water content distribution in a food body plays an important role in food qualities such as texture and shelf life. For this reason, water migration has been among the topics of interest for research in the academic field as well as in the food industry [1–4]. Water migration in food has been explained using models based on Fick's diffusion law, while the gravimetric method has been used in measuring water content inside a food body [5–7]. Unfortunately, however, the gravimetric method is not suitable for identifying water content distribution in a starchy food body that is small in size, such as a rice grain or a noodle strand. Consequently, the change in water content profile in this kind of food could not be verified by experiment.

With the availability of MRI (magnetic resonance imaging) for observation of changes in water content profile in food bodies, the irregular changes in water content profiles were sometimes reported in starchy foods that were soaked at a temperature higher than the gelatinization temperature (boiling) [8,9]. It was found that some of the changes could not be explained using Fick's Law of diffusion [10–12]. We recognized that this irregular behavior was caused by the fact that some kinds of food, such as starchy foods, change from single–phase to multiphase during boiling [13, 14]. This is because water holding capacity of a food body changes as starch gelatinization proceeds during boiling; namely, the distribution of water holding capacity becomes uneven throughout the body [15]. Since Fick's diffusion law is applicable only to homogeneous systems, it cannot be applied to such a multiphase system.

The Relative Water Content (RWC) model was proposed as an alternative model that is able to describe water migration in a multiphase food system [13, 14]. In the RWC model (Eq.1), water migration is driven by the gradient of water content divided by the water holding capacity (WHC), m/m*, whereas it is driven by the gradient of water content, m, in Fick's law. WHC is defined as the maximum water content that a food body can absorb at equilibrium.

$$j = -\rho_{\text{solid}} D m^* \frac{\partial}{\partial x}\left(\frac{m}{m^*}\right) \qquad (1)$$

In order to make the diffusion model available, we need

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information on WHC as a function of position and time in the food body. WHC of starchy food is known to change when it is heat-treated. For example, when it is immersed in water at room temperature, a rice grain (ungelatinized) absorbs water only up to 0.43 kg-water/kg-solid [16]. On the other hand, a grain of "instant rice" (pregelatinized and dried), absorbs several times more water [17]. The equilibrium water content values are WHC values. This suggests that WHC of the starchy food depends on the extent of starch gelatinization.

A starchy food, either ungelatinized or partly gelatinized, may have an even WHC profile in its body and keep the even WHC profile during immersion, if WHC does not change during immersion by keeping the water temperature low enough to prevent further starch gelatinization. In this case, the transient water content profiles in the food body may be described by Fick's diffusion equation. However, what about the case when the water temperature is high such as the case of boiling? The change of WHC should take place during immersion.

Although it is an important factor for predicting water migration in starchy food during boiling, how does WHC change during boiling is left unknown. In this study, a slab of wheat flour dough was selected as a model food. A profile of WHC against water content at heat-treatment was assumed based on the information concerning starch gelatinization. Then transient water content profile in the flour dough slab during boiling was calculated by RWC model using this WHC profile. The calculated water content profile was compared with that of measured profile reported elsewhere by Fukuoka *et al.* [11]. The effect of the shape of WHC profile on the transient water content profile was examined and the WHC profile was shaped up so that the calculated water content profile was able to mimic the measured water content profile.

2. Methods

2.1 Modeling

We set the problem to be solved as follows: Suppose a slab (3.8 mm thickness) of wheat flour dough is boiled in hot water (100℃); simulate the change of water content profile in the slab during boiling. The size and the initial water content of the dough slab is the same as those used by Fukuoka *et al.* [11]. The simulated water content profile will be compared with the measured profile reported by Fukuoka *et al.*

Since water diffusion process is several tens of times slower than the heat transfer process, the water content profile inside the slab may be taken to be governed by the water diffusion process at constant temperature (100℃). When the diffusion flux equation (Eq. (1)) is combined with the equation of continuity, we have a diffusion equation:

$$\frac{\partial m}{\partial t}(\rho_{\text{solid}} m) = \frac{\partial}{\partial x}\left\{\rho_{\text{solid}} D m^* \frac{\partial}{\partial x}\left(\frac{m}{m^*}\right)\right\} \qquad (2)$$

In a system where expansion or shrinkage is negligibly small, we have a simple form of diffusion equation:

$$\frac{\partial m}{\partial t} = \frac{\partial}{\partial x}\left(D m^* \frac{\partial}{\partial x}\left(\frac{m}{m^*}\right)\right) \qquad (3)$$

To solve Eq. (3), we need information on water diffusivity (D), WHC, initial water content, and surface boundary condition. Although water diffusivity in the wheat flour/water system at 100℃ is reported to range from the order of 10^{-10} to 10^{-9} m^2/s [18], a constant diffusivity value (5×10^{-10} m^2/s) was used in this paper, so that the effect of WHC on water content profile simulation was highlighted. The initial water content is set to 0.72 (kg-water/kg-solid), which is the initial water content of the dough used in the experiment of Fukuoka *et al.* [11].

The water content at the surface is very hard to be assumed because it becomes extraordinarily high due to destruction of the food structure when the boiling period is prolonged. Consequently, in this paper, the measured water content values (using MRI method) at the position about 0.1 mm under the slab surface was used as the boundary condition in the calculation. When the MRI data of the dough slab during boiling reported by Fukuoka *et al.* [11] was analyzed, the water content at about 0.1 mm under the surface was found to rise linearly as the time increased as follows:

$$m = 0.000555\, t + 0.7333 \qquad m \le 1.7 \qquad (4)$$

This equation was included in the boundary condition in this study.

2.2 WHC profile

As explained in the previous section, WHC of starchy food depends on the extent of starch gelatinization. When starch granules/water system was observed by differential scanning calorimetry (DSC) [19] and by NMR [20], starch granules were gelatinized rapidly to reach specified extent of gelatinization within 1 or 2 min. This upper limit in the extent of gelatinization is termed as the terminal extent of gelatinization (TEG) that depends on temperature and water content. TEG in wheat starch/water system was measured by DSC in the temperature range from 60℃ to 100℃. The result of the experiment was examined to give the empirical equation [21] as:

$$\mathrm{TEG}=\frac{3.15m/(1+m)-0.946}{1+\exp[-0.1792(\theta-69.1)]}\quad (0.54<m<1.5) \quad (5)$$

where m and θ are, respectively, water content [kg-water/kg-solid] and temperature [℃] with which heat-treatment is conducted.

In Fig. 1, TEG calculated by Eq.(5) is plotted against water content for selected temperature. This figure indicates that the extent of starch gelatinization reached by boiling (85–100℃) is governed by the water content with which the heat-treatment is conducted. Wheat starch with water less than 0.4 kg-water/kg-solid can not be gelatinized and that with water more than 1.7 kg-water/kg-solid may be fully gelatinized. Suppose that WHC is deeply influenced by TEG, WHC may also be governed by the water content with which heat-treatment is conducted. Consequently, the problem is to find an appropriate form of WHC profile (85–100℃) as a function of water content.

The minimum WHC value in the WHC profile should be that of ungelatinized wheat flour dough. For the minimum, we selected 0.95 kg-water/kg-solid, which is the value measured by soaking the dough in pure water at room temperature [22].

The maximum WHC value in the WHC profile is selected as 1.7 kg-water/kg-solid, which is the measured water content value in the dough slab during boiling [11]. Water content at a position slightly under the surface of the dough slab reached 1.7 kg-water/kg-solid after 30 min boiling, while the water content value leveled off at this value through the dough slab after 120 min boiling (Fig. 4). For this reason, this value is taken as the maximum WHC value of this dough.

WHC value should increase from the minimum value (0.95 kg-water/kg-solid) to the maximum value (1.7 kg-water/kg-solid), in the range of water content from $m=0.4$ kg-water/kg-solid to $m=1.7$ kg-water/ kg-solid. Three schematics of WHC profiles connecting point M ($m=0.4$, WHC=0.95) and point N ($m=1.7$, WHC=1.7) were examined (Fig. 2). One is line A connecting M and N with a straight line. Another is line B connecting M and N with a convex line bended at a point ($m=1.25$, WHC=1.6). The other is line C connecting M and N with a concave line bended at a point ($m=1.25$, WHC=1.3). Using each of these three lines as the WHC profile, transient water content profile in the model food (slab of wheat flour dough during boiling) was calculated.

3. Results and discussion

The change of water content profile that is calculated by solving Eq. (3) using line A (Fig. 2) as the WHC profile, is shown in Fig. 3a. The shape of the water content profile is apparently similar to that of water content profiles calculated by Fickian diffusion equation. However, when WHC profile with a bending point is used, an obvious bending point emerges in each of water content profile at the water content which coincides with the bending water content in the WHC profile (1.25 kg-water/kg-solid). In addition, it is found that convex (or concave) shape of WHC profile at the bending point is reflected on the convex (or concave) shape in water content profile, respectively (Figs. 3b and 3c).

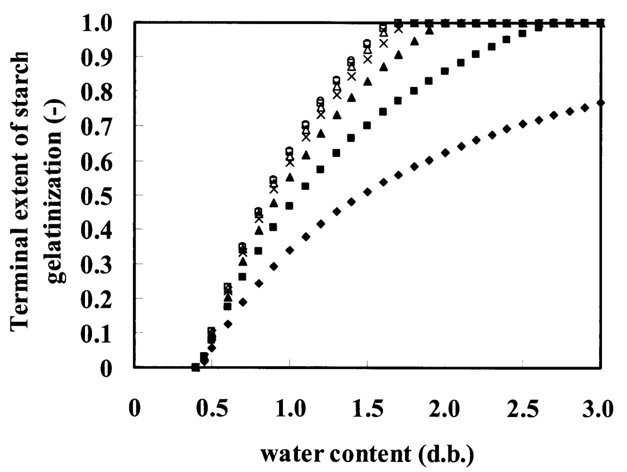

Fig. 1 Terminal extent of starch gelatinization values plotted against water content (calculated from the published data of Fukuoka *et al.* [11]). ◆70℃, ■75℃, ▲80℃, ×85℃, △90℃, □95℃, ○100℃. d.b. means dry basis (kg-water/kg-solid).

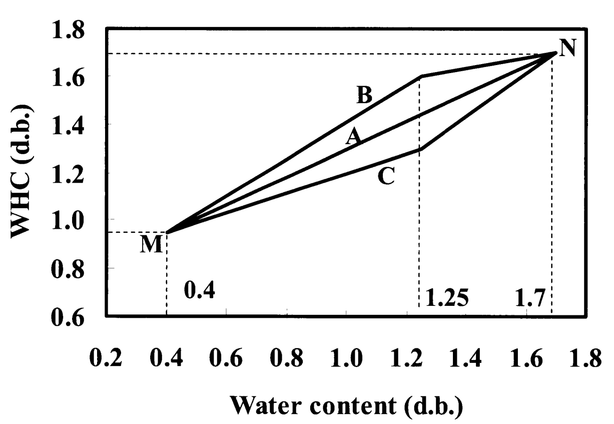

Fig. 2 WHC profile used for the calculation of transient water content profile in a slab of wheat flour dough during boiling. A: Linearly varying WHC profile, B: WHC profile with a breaking point at $m=1.25$ (d.b.), WHC=1.6, C: WHC profile with a breaking point at $m=1.25$ (d.b.), WHC=1.3. d.b. means dry basis (kg-water/kg-solid).

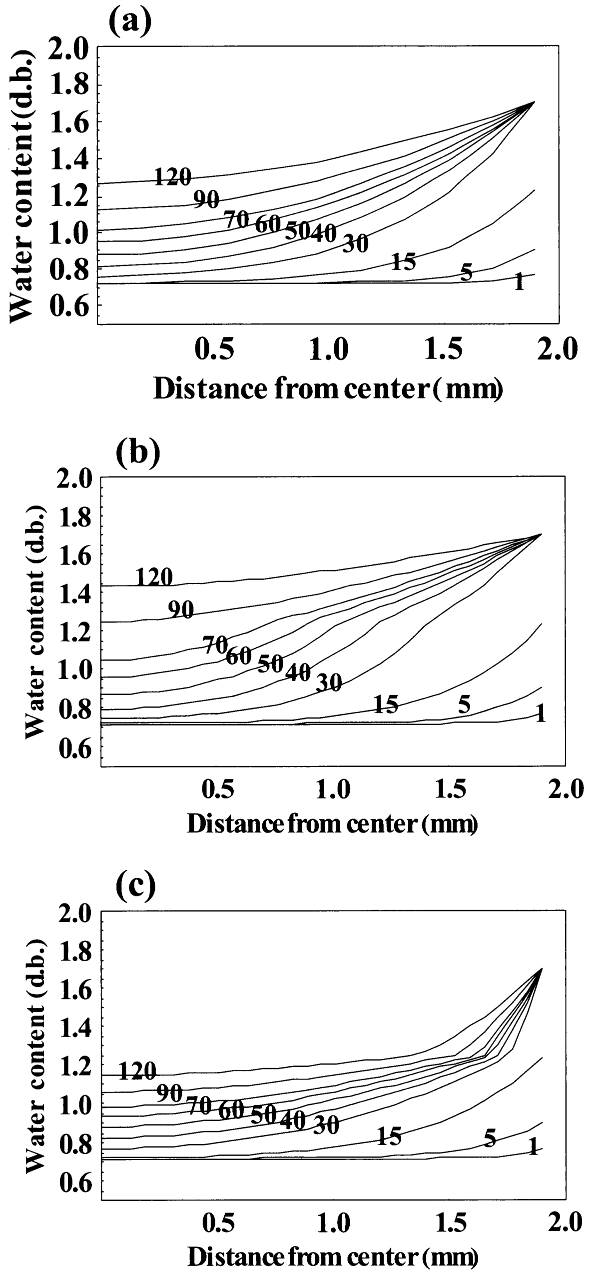

Fig. 3 Water content profile in a slab of wheat flour dough calculated using the WHC profile given in Fig. 2. a: linear WHC profile (line A in Fig. 2), b: bending WHC profile (m=1.25, WHC=1.6) (line B in Fig. 2), c: bending WHC profile (m=1.25, WHC=1.3) (line C in Fig. 2). d.b. means dry basis (kg-water/kg-solid). The numbers indicate boiling time (min).

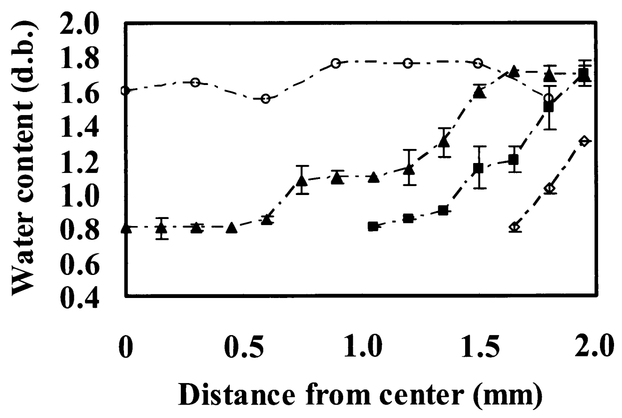

Fig. 4 Water content profile inside a slab of wheat flour dough measured by Fukuoka *et al.* [11]. The numbers indicate boiling time (min). ◇15 min boiling, ■30 min boiling, ▲60 min boiling, ○120 min boiling. d.b. means dry basis (kg-water/kg-solid).

Fukuoka *et al.* [11] measured transient water content profile in a wheat flour dough slab during boiling. In their experiment, wheat flour dough (0.72 kg-water/kg-solid) embedded in an aluminum frame to form a slab (3.8 mm thickness) was put into boiling water for a specified time and was quenched in cold water in order to stop further heating. A piece of rectangular block was cut out from the sample slab. Spin echo images of protons in a vertical slice perpendicular to the boiled surface of the sample piece were observed using an NMR spectrometer. The signal intensity of proton images was converted into water content via proton transverse relaxation time at each pixel in the image. The water content profile across the slab is shown in Fig. 4. The features of the transient water content profile during boiling are summarized as:

(1) The water migration in the wheat flour dough was found to be very slow. Even after 30 min boiling, the water content at the center of the slab remained at the initial level, while water content reached an equilibrium value of 1.7 kg-water/kg-solid at the surface.

(2) At 60 min boiling, a nearly flat water content profile emerged in three regions: at the center, near to the surface and in the intermediate part of these two regions. These flat regions were tied with a sharp gradient curve of water content profile.

(3) When the slab was boiled for 120 min, the water content inside the slab leveled off to equilibrium of 1.7 kg-water/kg-solid.

In an attempt to mimic the feature of measured water content profile after 30 min and 60 min boiling, WHC profile with three bending points at m=0.85, 1.1, and 1.6 kg-water/kg-solid (Fig. 5) was used to calculate water content profiles. The result of calculation is shown in Fig. 6. It was found that the transient water content profile in the dough slab during boiling was well described in its outline by using RWC model with water diffusivity of 5×10^{-10} m^2/s and WHC profile proposed. The breaking points that emerge at three levels of water content (m= 0.85, 1.1, and 1.6 kg-water/kg-solid) in the measured

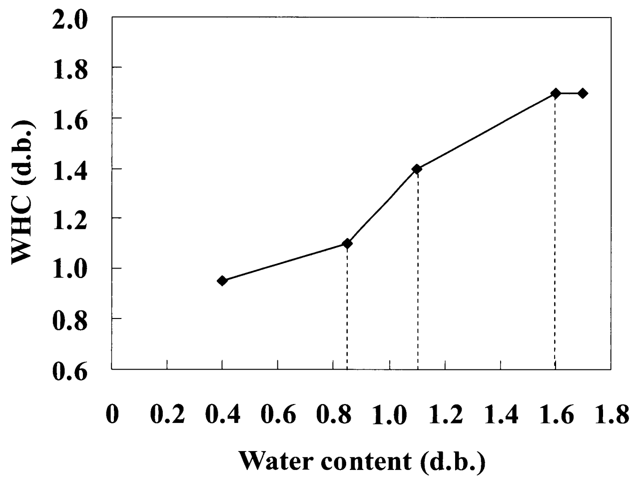

Fig. 5 WHC profile with three bending points (at m=0.85, 1.1, and 1.6 kg-water/kg-solid). d.b. means dry basis (kg-water/kg-solid).

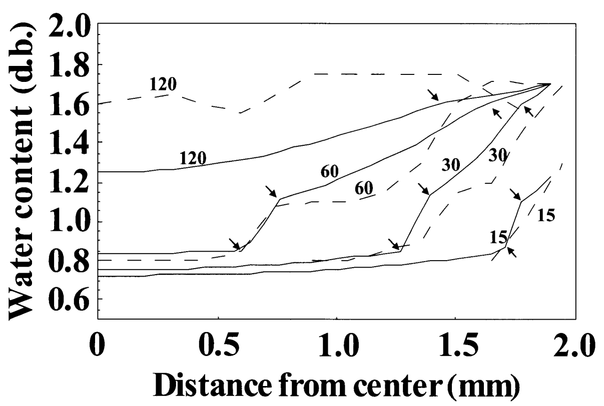

Fig. 6 Water content profile in a slab of wheat flour dough calculated using the WHC profile given in Fig. 5, is compared with the measured profile. The numbers indicate boiling time (min). d.b. means dry basis (kg-water/kg-solid). ——— calculated profile, ------ measured profile. Arrows indicate bending points in transient water content profiles.

water content profile of 30 min boiling and 60 min boiling were successfully depicted. The bending point that appears in WHC profile may be caused by some discontinuous change in the extent of starch gelatinization such as a boundary between considerably gelatinized part and ungelatinized part, and/or change in protein network structure that are responsible for resistive feature of food against expansion due to water sorption [13,14].

For more precise fitting, a detailed consideration of water content depending diffusivity rather than constant diffusivity may work. In particular, the use of higher water diffusivity in high water content region may push up the water content profile after 120 min boiling.

4. Conclusion

Effect of water holding capacity (WHC) profile (WHC plotted against water content with which starchy food is heat-treated) was examined to describe transient water content profile in a wheat flour dough slab during boiling. A WHC profile with bending points was found useful to describe certain characteristic features of transient water content.

NOMENCLATURE

D : diffusivity, m^2/s
j : water diffusion flux , kg-water/ (m^2 s)
m : water content, kg-water/ kg-solid
m^* : water holding capacity, kg-water/ kg-solid
t : time, s
x : position, m
ρ_{solid} : solid density, kg-solid/m^3
TEG : terminal extent of starch gelatinization
θ : heating temperature, ℃

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◇◇◇ **和文要約** ◇◇◇

デンプン食品の茹で加熱過程における水分移動を支配する水分保持容量プロファイル

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米を炊いたり麺を茹でたりするとき，調理前のこれらのデンプン食品は全体が未糊化であり，平衡時に含水率が均一になるという意味で均相系と考えられるが，加熱調理の過程ではデンプンの糊化が不均一に進行し，食品物体の場所（例えば，表面と中心）により平衡含水率が異なるという意味で，不均一系となる．Fickの拡散法則は均一系にのみ適用可能であり，このような不均一系には適用できない．そこで，このような不均一な食品中での水分移動を記述可能なモデルとして著者らにより相対含水率モデル（RWCモデル）が提案されてきた．相対含水率モデルでは水の移動は相対含水率（含水率の水分保持容量（WHC）に対する比）の勾配により駆動されると考える．したがって，相対含水率モデルではWHCが重要な特性（物性）値になる．しかしながら，WHCについて多くは知られていない．

本研究では，WHCプロファイル（WHC値を，デンプン食品が加熱処理受けるときの含水率に対してプロットしたもの）をデンプンの糊化に関する知見に基づいて推定し，このWHCプロファイルをもとにRWCモデルによりモデル食品（小麦粉ドウ平板）をボイルしたときの含水率分布の非定常変化を計算した．WHCプロファイルの折れ曲がりが含水率分布の折れ曲がりにどのように対応するかについての知見が得られ，それを応用して，実測された小麦粉ドウ平板中の含水率分布の特徴を再現させるためのWHCプロファイルを提示した．

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